Development of Novel Adsorption Gels for Metal Ions by means of Chemical Modification of Waste Paper

March 2009

Department of Energy and Materials Science
Graduate School of Science and Engineering
Saga University

CHAITANYA RAJ ADHIKARI
DEVELOPMENT OF NOVEL ADSORPTION GELS FOR METAL IONS BY MEANS OF CHEMICAL MODIFICATION OF WASTE PAPER

Chaitanya Raj Adhikari

A thesis submitted in partial fulfillment of the requirements for the degree of

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Approved by

Prof. Katsutoshi INOUE
Supervisor

Prof. Takanori WATARI

Prof. Keisuke OHTO

Assoc. Prof. Hiroyuki Harada

Date: 2009-02-18
ABSTRACT

DEVELOPMENT OF NOVEL ADSORPTION GELS FOR METAL IONS BY MEANS OF CHEMICAL MODIFICATION OF WASTE PAPER

Chairperson of the supervisory Committee: Prof. Katsutoshi INOUE
Department of Applied Chemistry, Saga University

Waste newsprint paper was modified chemically to investigate its adsorption behavior for base and precious metal ions from wastewater and industrial effluents. Iminodiacetic acid, a well known chelating group was introduced into the waste paper by two different approaches i.e. by direct and indirect introduction (through epichlorohydrin spacer). The gels were found to be suitable for adsorption and removal of various toxic metals such as Cd(II), Pb(II), Cu(II), Ni(II), Fe(III) and Co(II). The adsorption capacities of the gels were found to be comparable to that of the various other adsorbents. The gels were applicable in continuous mode of operation and loaded metal ions could be easily recovered by simple acidic treatment. Also, mutual separation of metal ion pairs like Ni(II)-Co(II), Cu(II)-Pb(II), and Cu(II)-Fe(III) was possible by using the spacer type gel. On the other hand, novel waste paper adsorbents for precious metal ions were developed by introducing dimethylamine and p-aminobenzoic acid onto the waste paper matrix. These gels proved to be selective for precious metal ions over other base metal ions. They exhibited high adsorption capacity for Au(III) and moderate capacities for Pd(II) and Pt(IV). Adsorption experiments carried out in column mode by taking multi-component mixture of precious and base metals showed that separation of small concentrations of precious metals from a large excess of base metals is possible by using these gels. These gels also were capable of regeneration because a solution of acidic thiourea (0.1M) was able to elute almost all the metal ion adsorbed on the gel. The special feature of the adsorbents was that Au(III) adsorbed on the gel was reduced to elemental gold particles that appeared on the surface of the test solution and aggregated. Also, these gels confirmed their consistent behavior and stability in an aqua regia leachate solution provided by a renowned metal company. These results have proved that waste paper can be a valuable material in the field of metal separation and recovery.
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Chapter 1

1.1. METALS AND THE ENVIRONMENT

1.1.1. Heavy Metals and Their Impact on the Environment

The toxicity and health hazards associated with heavy metals have been established beyond any doubts. With increasing amounts of metals unearthed, amounts of toxic heavy metals entering the environment increases. As shown in Figure 1.1, the metals 'mobilized' by and partially lost through growing and ever-intensifying human technological activities enter the ecosystem and start to inflict the damages as they move through from one ecological trophic layer into another. They accumulate in living tissues throughout the food chain which has humans at its top. The danger multiplies and humans eventually tend to receive the problems associated with the toxicity of heavy metals pre-concentrated from many different directions. Controlling heavy metal discharges and removing toxic heavy metals from aqueous solutions has become a challenge for the 21st century.¹

![Figure 1.1. Heavy metals pre-concentrating through food chain](image)

'Heavy metal' is a general collective term applying to the group of metals and metalloids with an atomic density greater than 6 g cm⁻³. Although it is only a loosely defined term it is widely recognised and usually applied to the elements such as Cd (cadmium), Cr (chromium), Cu (copper), Hg (mercury), Ni (nickel), Pb (lead) and Zn (zinc) which are commonly associated with pollution and toxicity problems.

Unlike most organic pollutants, heavy metals occur naturally in rock-forming and ore minerals and so a range of normal background concentrations is associated with each of
these elements in soils, sediments, waters and living organisms. On an annual basis, significant quantities of various heavy metals are produced from the mining of their respective ores. In the year 2004, approximately $14,500 \times 10^3$ tons of copper was produced.\(^2\)

Industrial uses of metals and other domestic processes (e.g. burning of fossil fuels, incineration of wastes, automobile exhausts, smelting processes and the use of sewage sludge as landfill material and fertilizer) have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments. Discharged toxic metals typically include Cd, Cu, Ni, Cr, Co, Zn and Pb.\(^3\) Table 1 outlines the industrial sources and potential for pollution for a range of metals discharged.

<table>
<thead>
<tr>
<th>Industry</th>
<th>Metals</th>
<th>Pollution Arising</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metalliferous mining</td>
<td>Cd, Cu, Ni(II) Cr, Co, Zn</td>
<td>Acid mine drainage, tailings, slag heaps</td>
<td>3,4</td>
</tr>
<tr>
<td>Agricultural materials</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fertilizers</td>
<td>Cd, Cr, Mo, Pb, U, V, Zn</td>
<td>Run-off, surface and groundwater contamination, plant bioaccumulation</td>
<td>5,6</td>
</tr>
<tr>
<td>Manures sewage sludge</td>
<td>Zn, Cu, Ni, Pb, Cd, Cr, As, Hg</td>
<td>Landspeeding threat to ground and surface water</td>
<td>5,7,8</td>
</tr>
<tr>
<td>Metallurgical Industries</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specialist alloys and steels</td>
<td>Pb, Mo, Ni, Cu, Cd, As, Te, U, Zn</td>
<td>Manufacture, disposal and recycling of metals. Tailings and slag heaps</td>
<td>9-11</td>
</tr>
<tr>
<td>Waste disposal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Landfill leachate</td>
<td>Zn, Cu, Cd, Pb, Ni, Cr, Hg</td>
<td>Landfill leachate, contamination of ground and surface water</td>
<td>12,13</td>
</tr>
<tr>
<td>Electronics</td>
<td>Pb, Cd, Hg, Pt, Au, Cr, As, Ni, Mn</td>
<td>Aqueous and solid metallic waste from manufacturing and recycling processes</td>
<td>14</td>
</tr>
<tr>
<td>Metal finishing industry</td>
<td>Cr, Ni, Zn, Cu</td>
<td>Liquid effluents from plating processes.</td>
<td>15-17</td>
</tr>
<tr>
<td>Miscellaneous sources</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paints and pigments</td>
<td>Pb, Cr, As, Ti, Ba, Zn</td>
<td>Aqueous waste from manufacture, old paint deterioration and soil pollution.</td>
<td>18</td>
</tr>
<tr>
<td>Batteries</td>
<td>Pb, Sb, Zn, Cd, Ni, Hg</td>
<td>Waste battery fluid, contamination of soil and groundwater.</td>
<td>19-21</td>
</tr>
</tbody>
</table>

While many of the heavy metals are needed by plants at the micronutrient level, higher concentrations are known to produce a range of toxic effects. The "Big Three" metals specially known for their high toxicity and impact are lead, mercury and cadmium which generally occur in simple cationic forms. The big three are closely followed by others,
perhaps not as ubiquitous, such as arsenic that has been a poison of choice for centuries, and chromium, used in large quantities industrially for quite some time. It is important to note that the most toxic forms of these two appear as anionic species in solution (arsenate and chromate).

Although the toxicity of lead has been well known for some time, the toxicology and, correspondingly, the limits to presence in surface waters of copper, zinc, nickel and some others are still being debated in many areas of the world. At high exposure levels, lead causes encephalopathy, cognitive impairment, behavioural disturbances, kidney damage, anaemia and toxicity to the reproductive system.\textsuperscript{22} Chromium is widely recognised to exert toxic effects in its hexavalent form.\textsuperscript{23} Human exposure to Cr(VI) compounds is associated with a higher incidence of respiratory cancers.\textsuperscript{24} Cadmium is associated with nephrotoxic effects particularly at high exposure levels; long-term exposure may cause bone damage as well.\textsuperscript{25} High concentrations of mercury can lead to neurobehavioural disorders and developmental disabilities including dyslexia, attention deficit hyperactivity disorder, intellectual retardation.\textsuperscript{26} Excessive copper concentrations can lead to weakness, lethargy and anorexia, as well as damage to the gastrointestinal tract.\textsuperscript{27} The toxic effects of nickel and other heavy metals are discussed in some detail by.\textsuperscript{28}

Treatment Technologies for the removal of heavy metals

Various methods exist for the removal of heavy metal ions from wastewater which include chemical precipitation/coagulation, membrane technology, electrolytic reduction, ion exchange and adsorption.\textsuperscript{29,30} The advantages and disadvantages associated with each method are listed in Table 1.2.
Table 1.2. Treatment technologies for the removal of heavy metals from wastewaters and associated advantages and disadvantages\(^{31}\)

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Ref.</th>
</tr>
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<tr>
<td>Chemical precipitation</td>
<td>Process simplicity</td>
<td>Large amount of sludge containing metals</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Not metal selective</td>
<td>Sludge disposal cost</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Inexpensive capital cost</td>
<td>High maintenance costs</td>
<td></td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Metal selective</td>
<td>High initial capital cost</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Limited pH tolerance</td>
<td>High maintenance costs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High regeneration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coagulation–floculation</td>
<td>Bacterial inactivation capability</td>
<td>Chemical consumption</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Good sludge settling and dewatering characteristics</td>
<td>Increased sludge volume generation</td>
<td></td>
</tr>
<tr>
<td>Flotation</td>
<td>Metal selective</td>
<td>High initial capital cost</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Low retention times</td>
<td>High maintenance and operation costs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Removal of small particles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane filtration</td>
<td>Low solid waste generation</td>
<td>High initial capital cost</td>
<td>34,35</td>
</tr>
<tr>
<td></td>
<td>Low chemical consumption</td>
<td>High maintenance and operation costs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Small space requirement</td>
<td>Membrane fouling</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Possible to be metal selective</td>
<td>Limited flow-rates</td>
<td></td>
</tr>
<tr>
<td>Electrochemical treatment</td>
<td>No chemical required can be engineered to tolerate suspended solids</td>
<td>High initial capital cost production of H(_2) (with some processes)</td>
<td>36,37</td>
</tr>
<tr>
<td></td>
<td>Moderately metal selective Treat effluent &gt; 2000 mg dm(^3)</td>
<td>Filtration process for flocs</td>
<td></td>
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<tr>
<td>Adsorption</td>
<td>Wide variety of target pollutants</td>
<td>Performance depends on type of adsorbent</td>
<td>38</td>
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<tr>
<td></td>
<td>High capacity</td>
<td>Chemical derivatization to improve its sorption capacity</td>
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<td></td>
<td>Fast kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Possibly selective depending on adsorbent</td>
<td></td>
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The most widely used method of removing heavy metals from solution is to increase the pH of the effluent, thus converting the soluble metal into an insoluble form (i.e. its hydroxide). Ion exchange is the second most widely used method for heavy metal removal from aqueous streams.\(^{39}\) During removal, recovery, or processing of metals, ion exchange acts as a concentrator of metals. The chemistry of the influent stream becomes very important to the success of the ion exchange application. Coagulation–floculation can also be employed to treat wastewater laden with heavy metals wherein the coagulation process destabilises colloidal particles by adding a chemical agent (coagulant) and results in sedimentation.\(^{40}\) Coagulation is followed by floculation of the unstable particles in
order to increase their size and form into bulky flocules which can be settled out. Flotation is employed to separate solids or dispersed liquids from a liquid phase using bubble attachment.\textsuperscript{40} Adsorptive bubble separation employs foaming to separate the metal impurities. Ion flotation, precipitate flotation and sorptive flotation are the main flotation process mechanisms for removal of metal ions from solution. Membrane filtration has received considerable attention for the treatment of inorganic effluent since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals.

Amongst all the treatment processes mentioned, adsorption using sorbents is one of the most popular and effective processes for the removal of heavy metals from wastewater. The adsorption process offers flexibility in design and operation and in many cases produces treated effluent suitable for re-use, free of color and odor. In addition, because adsorption is sometimes reversible, the regeneration of the adsorbent with resultant economy of operation may be possible.\textsuperscript{41} Activated carbon adsorbents are used widely in the removal of organic contaminants and to lesser extent heavy metal contaminants in product purification and pollution control. Carbon is converted to activated carbon by heating in the absence of air. The activation process results in the creation of a network of fine pores in the carbon particles. The vast areas (300–4000 m\textsuperscript{2} g\textsuperscript{−1}) of the walls within these pores account for the most of the total surface area of the carbon.\textsuperscript{42} In spite of its prolific use; activated carbon remains an expensive material and the higher the quality of activated carbon, the higher its cost. Also, in practice activated carbon is employed more frequently for adsorption of organic compounds rather than heavy metal ions.
1.1.2. E-WASTE AND PRECIOUS METALS

1.1.2.1. E-waste

Any appliance using an electric power supply that has reached its end-of-life. (OECD, 2001)\textsuperscript{43}

E-waste for short is a generic term embracing various forms of electric and electronic equipment that have ceased to be of any value to their owners. (Basel Action Network)\textsuperscript{44}

E-waste encompasses a broad and growing range of electronic devices ranging from large household devices such as refrigerators, air conditioners, cell phones, personal stereos, and consumer electronics to computers which have been discarded by their users.\textsuperscript{45}

The use of electronic devices has proliferated in recent decades, and proportionately, the quantity of electronic devices, such as PCs, mobile telephones and entertainment electronics that are disposed of, is growing rapidly throughout the world. In 1994, it was estimated that approximately 20 million PCs (about 7 million tons) became obsolete. By 2004, this figure was to increase to over 100 million PCs. Cumulatively, about 500 million PCs reached the end of their service lives between 1994 and 2003. Five hundred million PCs contain approximately 2,872,000 t of plastics, 718,000 t of lead, 1363 t of cadmium and 287 t of mercury.\textsuperscript{45} This fast growing waste stream is accelerating because the global market for PCs is far from saturation and the average lifespan of a PC is decreasing rapidly - for instance for CPUs from 4–6 years in 1997 to 2 years in 2005.\textsuperscript{46} PCs comprise only a fraction of all e-waste. Other constituents of e-waste are retired mobile phones and all kinds of portable electronic devices such as PDAs, MP3 players, computer games and peripherals.\textsuperscript{47}

When e-waste is disposed of or recycled without any controls, there are predictable negative impacts on the environment and human health. E-waste contains more than 1000 different substances, many of which are toxic, such as lead, mercury, arsenic, cadmium, selenium, hexavalent chromium, and flame retardants that create dioxins emissions when burned. About 70% of the heavy metals (mercury and cadmium) in US landfills come
from electronic waste. Consumer electronics make up 40% of the lead in landfills. These toxins can cause brain damage, allergic reactions and cancer.\textsuperscript{45}

E-waste contains considerable quantities of valuable materials such as precious metals. Early generation PCs used to contain up to 4 g of gold each; however this has decreased to about 1 g today. The value of ordinary metals contained in e-waste is also very high: 1 ton of e-waste contains up to 0.2 tons of copper, which can be sold for about 500 Euros at the current world price.\textsuperscript{48} Recycling e-waste has the potential therefore to be an attractive business.\textsuperscript{49}

1.1.2.2. PRECIOUS METALS

The term precious metal is used for gold, silver and Platinum group metals (PGMs) where Platinum group metals (PGMs) consist of ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt). These metals are extremely scarce compared to other metals due to their low abundance and the complex processes that are required to extract these metals from ores. In the last few years there has been a dramatic increase in the production of these technologically important metals. These metals are separated using the unique chemistry that the precious metals exhibit. The first chemical characteristic exploited is their nobility, which refers to their extremely high inertia toward dissolution in media in which all other base metals dissolve. This is utilised during the selective leaching of base metals from the sulphide ores.\textsuperscript{50} Other chemical characteristics that are exploited include their chloro-complexes, ligand substitution reactions, volatile tetroxides, ion-exchange reactions and oxidation states. All of these chemical characteristics are used not only to refine the PGMs from other metals but also to separate the different PGMs from one another.\textsuperscript{51}

A summary of the most important chlorocomplexes found in the leach solutions is given in the following table from which the mixed aquachloro and polynuclear species have been omitted.
Table 1.3. Common chlorospecies of the precious metal group

<table>
<thead>
<tr>
<th>Metal</th>
<th>Oxidation state</th>
<th>Major chlorospecies</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver (Ag)</td>
<td>I</td>
<td>AgCl</td>
<td>Insoluble</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AgCl₂⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>AuCl₄⁻</td>
<td>Very stable</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>I</td>
<td>AuCl₂⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>AuCl₄⁺</td>
<td></td>
</tr>
<tr>
<td>Platinum (Pt)</td>
<td>II</td>
<td>PtCl₄⁻</td>
<td>Conversion IV to II slow</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>PtCl₆⁺</td>
<td>Most common species, kinetically inert</td>
</tr>
<tr>
<td>Palladium (Pd)</td>
<td>II</td>
<td>PdCl₄⁻</td>
<td>Most common</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>PdCl₆⁻</td>
<td>Conversion II to IV difficult</td>
</tr>
<tr>
<td>Iridium (Ir)</td>
<td>III</td>
<td>IrCl₆⁻</td>
<td>Both species stable and conversion IV to III easy</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>IrCl₆⁺</td>
<td></td>
</tr>
<tr>
<td>Rhodium (Rh)</td>
<td>III</td>
<td>RhCl₆⁻</td>
<td></td>
</tr>
<tr>
<td>Ruthenium (Ru)</td>
<td>III</td>
<td>RuCl₆⁻</td>
<td>Complex equilibria between III and IV, depending on redox potential and chloride concentration</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>RuCl₆⁺</td>
<td></td>
</tr>
<tr>
<td>Osmium (Os)</td>
<td>III</td>
<td>OsCl₆⁻</td>
<td>Os(IV) more stable than Ru(IV)</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>OsCl₆⁺</td>
<td></td>
</tr>
</tbody>
</table>

Steadily increasing demand for precious metals, especially platinum and palladium, has resulted in the scale-up of metal extraction and refining operations worldwide. This, combined with a technology shift towards aqueous/organic-based metal extraction, has resulted in a vast increase in the volumes of aqueous wastewater produced by such operations. In most cases, these wastewaters still contain appreciable amounts of valuable metal. Conventional methods for the removal of low concentrations of dissolved metal ions from wastewaters, such as solvent extraction, chemical precipitation and ion exchange, have significant disadvantages, which include incomplete metal removal, high capital costs, high reagent and/or energy requirements, and generation of toxic sludge or other waste products that require disposal. These disadvantages, together with the need for more
economical and effective methods for the recovery of metals from wastewaters, have resulted in the development of alternative separation technologies.

By the same logic, the rising demand for platinum group metals (PGMs) in industry (e.g., chemical catalysis, automotive catalysts), has prompted the research into new methods for their recovery from spent materials. Pyrometallurgy has been investigated as a possible process. However, this process is usually nonselective and there is a need for the development of alternative processes. The acidic treatment of spent catalysts or scrap materials (usually requiring hot aqua regia) leads to highly acidic solutions containing mixtures of base metals (BMs) and PGMs (including platinum, palladium, gold, rhodium, iridium). Recently, a more benign leaching method, using more dilute aqua regia and microwave-accelerated leaching was described which increases the attractiveness of hydrometallurgical processing. However, the separation of PGMs from BMs in the mixtures is a strategic challenge; and the selective separation of different precious metals is the focus of much research. Most studies focusing on PGMs separation have been dedicated to the design of solvent extraction processes and to the synthesis and testing of conventional ion exchange and chelating resins. However, an increasing interest exists for the use of alternative materials, such as materials of biological origin for the recovery of metals. These materials are abundant and environmentally friendly.
1.2. PAPER AND CELLULOSE

1.2.1. Paper Recycling and Waste Paper

*Paper is a recyclable resource that passes through many hands as it moves through a four-stage lifecycle: production, distribution, consumption, and recovery. Following recovery, the paper can be reused as the raw material for the production of new paper.*

The term **recycled paper** generally refers to used paper recovered for use as raw material in the manufacture of new paper and paperboard. Hence recycled paper is a material that is known or believed to have value in use as an ingredient in the production of paper. Throughout the world, recycled paper is generated from the following four sources:

1. Residential
2. Commercial (shopping malls, stations, local markets, supermarkets, etc.)
3. Industrial (printing and publishing, textile cutters, newspapers, etc.)
4. Office and institutional

Three categories—newsprint, magazines, and corrugated container—account for over 80% of all recycled paper.

Use of recycled paper as raw material for new paper is an important means for reducing waste and effectively using resources, and is therefore of considerable social importance. In 2006, recycled paper (including pulp from recycled paper) accounted for 60.6% of the raw material for creation of new paper, making it the most significant resource for paper production.

Japan's total production of paper and paperboard for 2006 came to 31.106 million tons, making the country the third largest producer after the USA and China. In 2006 Japan recovered about 22.8 million tons of paper, of which it exported about 3.9 million tons. The country also imported about 0.7 million tons. Domestic reuse, therefore, came to about 18.8 million tons, of which 99% was used as raw material for new paper manufacture. The remaining 1% was used as raw material for producing non-paper items such as pulp molds, paper stock board, ground cover for livestock, and solid fuel. Use of recycled paper for such non-paper applications remains relatively low in Japan, but is expected to increase as a result of ongoing efforts to promote effective use of the segment of recycled paper that is not suitable for papermaking.
Hence, the term waste paper refers to the used paper that cannot be further reused as raw material in the manufacture of new paper and paperboard due to its majority content of short fibers that may reduce the strength of paper. Alternatively, waste paper has no value in use as an ingredient in the production of paper.

The waste-cellulose fibers (the so-called “short cellulose fibers”) left from the process of paper production cannot be used for recycling processes and usually have been thrown out in the wastewaters in amounts of several 1000 tons a year; thus presenting a significant environmental pollutant problem. Newspaper and used paper are the principal organic solid wastes. The disposal of solid biomass and waste is becoming an increasingly intricate and costly problem because of the decreasing space availability for landfills and the growing concern about the living environment.

![Waste paper in the landfill site](image_url)

Figure 1.2. Waste paper in the landfill site

**Composition of Waste Paper**

The feedstock composition of newspaper is cellulose 62%, hemicellulose 16%, and lignin 16% (dry basis) whereas the used paper consists of mainly cellulose 85-99% and a negligible portion of lignin.

**1.2.2. Cellulose**

Cellulose constitutes the most abundant and renewable polymer resource available worldwide. It is estimated that by photosynthesis, $10^{11}$-$10^{12}$ tons of cellulose are synthesized annually in a relatively pure form, for example, in the seed hairs of the cotton plant, but more often are combined with lignin and other polysaccharides (so-called hemicelluloses) in the cell wall of woody plants. Cellulose has been used in the form of wood and cotton for thousands of years as an energy source, a building material and for
clothing. The molecular structure of cellulose as a carbohydrate polymer comprises of repeating β-D-glucopyranose units which are covalently linked through acetal functions between the OH group of the C₄ and C₁ carbon atoms (β-1,4-glucan). Cellulose is a large, linear-chain polymer with a large number of hydroxyl groups (three per anhydroglucose (AGU) unit) and present in the preferred "C₁ conformation. To accommodate the preferred bond angles, every second AGU unit is rotated 180 degrees in the plane. The length of the polymeric cellulose chain depends on the number of constituent AGU units (degree of polymerisation, DP) and varies with the origin and treatment of the cellulose raw material. 

Cellulose has a ribbon shape which allows it to twist and bend in the direction out of the plane, so that the molecule is moderately flexible. There is a relatively strong interaction between neighbouring cellulose molecules in dry fibers due to the presence of the hydroxyl (–OH) groups, which stick out from the chain and form intermolecular hydrogen bonds. Regenerated fibres from cellulose contain 250–500 repeating units per chain. 

This molecular structure gives cellulose its characteristic properties of hydrophilicity, chirality and degradability. Chemical reactivity is largely a function of the high donor reactivity of the OH groups. In particular, two main approaches have been tried in the conversion of cellulose into compounds capable of adsorbing heavy metal ions from aqueous solutions. The first of these methods involves a direct modification of the cellulose backbone with the introduction of chelating or metal binding functionalities producing a range of heavy metal adsorbents. Alternative approaches have focused on grafting of selected monomers to the cellulose backbone either directly introducing metal binding capability or with subsequent functionalization of these grafted polymer chains with known chelating moieties.
1.3. LITERATURE SURVEY

1.3.1. Biosorption (Biomass Sorption)

*Biosorption has been defined as the property of certain biomolecules (or types of biomass) to bind and concentrate selected ions or other molecules from aqueous solutions. As opposed to a much more complex phenomenon of bioaccumulation based on active metabolic transport, bio-sorption by dead biomass (or by some molecules and/or their active groups) is passive and based mainly on the "affinity" between the (bio-)sorbent and sorbate.*

Biosorption is the term given to the passive sorption and/or complexation of metal ions by biomass. The mechanism of biosorption is generally based on physico-chemical interactions between metal ions and the functional groups present on the cell surface, such as electrostatic interactions, ion exchange and metal ion chelation or complexation. ⁷⁹

There are biomass types of many various kinds (e.g. leaves, wood or agricultural residues, waste crustacean biomass-anything renewable that grows, including microbes), and while some of them may not sequester metals to any appreciable degree others show a promising potential. It is often the NH₂ group that is active and ubiquitous in fungal cell walls as well as in the chitin/chitosan components of crustacean exoskeletons (e.g. crab shells). ⁸⁰

Functional groups most commonly implicated in such interactions include carboxylate, hydroxyl, amine and phosphoryl groups present within cell wall components such as polysaccharides, lipids and proteins. ⁸¹ Some of the major binding groups for biosorption are as shown in the following table (Table 1.4.). The binding process is independent of metabolism and hence, of a physical nature. It is also usually rapid and reversible and requires minimal energy for activation; in the region of 21 kJ/mol, as opposed to the activation energy required for bioaccumulation (63 kJ/mol). ⁸² This allows for metal ion desorption followed by regeneration and reuse of the biosorbent in successive sorption/desorption cycles. Despite these advantageous process characteristics, few industrial processes make use of biosorption technology for the purpose of recovering metal ions from wastewaters.
### Table 1.4. Major binding groups of biomass

<table>
<thead>
<tr>
<th>Binding Group</th>
<th>pKα</th>
<th>HSAB Type</th>
<th>Ligand Atom</th>
<th>Occurrences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl(-OH)</td>
<td>9.5-13</td>
<td>Hard</td>
<td>O</td>
<td>PS, UA, SPS, AA</td>
</tr>
<tr>
<td>Carbonyl(Ketone)(-COOH)</td>
<td></td>
<td>Hard</td>
<td>O</td>
<td>Peptide bond</td>
</tr>
<tr>
<td>Carboxyl(-CO)</td>
<td>1.7-4.7</td>
<td>Hard</td>
<td>O</td>
<td>UA, AA</td>
</tr>
<tr>
<td>Sulphhydryl(Thiol)(-SH)</td>
<td>8.3-10.8</td>
<td>Soft</td>
<td>S</td>
<td>AA</td>
</tr>
<tr>
<td>Sulphonate(-SO₃)</td>
<td>1.3</td>
<td>Hard</td>
<td>O</td>
<td>SPS</td>
</tr>
<tr>
<td>Thioether(-S)</td>
<td></td>
<td>Soft</td>
<td>S</td>
<td>AA</td>
</tr>
<tr>
<td>Amine(-NH₃)</td>
<td>8-11</td>
<td>Intermediate</td>
<td>N</td>
<td>Ch, AA</td>
</tr>
<tr>
<td>Secondary Amine(-NH)</td>
<td>13</td>
<td>Intermediate</td>
<td>N</td>
<td>PG, Peptide bond</td>
</tr>
<tr>
<td>Amide(-CONH₂)</td>
<td></td>
<td>Intermediate</td>
<td>N</td>
<td>AA</td>
</tr>
<tr>
<td>Imine(=NH)</td>
<td>11.6-12.6</td>
<td>Intermediate</td>
<td>N</td>
<td>AA</td>
</tr>
<tr>
<td>Imidazole</td>
<td>6.0</td>
<td>Soft</td>
<td>N</td>
<td>AA</td>
</tr>
<tr>
<td>Phosphonate[-PO(OH)₂]</td>
<td>0.9-2.1</td>
<td>Hard</td>
<td>O</td>
<td>PL</td>
</tr>
<tr>
<td>Phosphodiester(-POOH)</td>
<td>1.5</td>
<td>Hard</td>
<td>O</td>
<td>TA, LPS</td>
</tr>
</tbody>
</table>

PS: Polysaccharides, UA: Uronic Acid, SPS: Sulphated PS, Ch: Chitosan,

### Table 1.5. Hard, soft and borderline acids and bases

<table>
<thead>
<tr>
<th>Bases</th>
<th>Hard</th>
<th>Soft</th>
<th>Borderline</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂⁻, OH⁻, F⁻, Cl⁻, CO₃²⁻, H⁺, R⁺, CN⁻, Τ, C₂H₄, RNC, C₃H₇⁺, NH₂⁺, NO₃⁻, C₆H₅NH₂, CH₃CO₂⁻, PO₄³⁻, SO₄²⁻, ClO₄⁻, H₂O, ROH, RO⁻, R₂O, NH₃, RNH₂, NH₄⁺</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B(CH₃)₃, GaCl₃, GaI₃, GaBr₃, B(CH₃)₃, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Al(OMe)₃, Mn²⁺, Cr³⁺, Cr(VI), Mn(VII), Mo(VI), W(VI), Sc³⁺, Sc²⁺⁺⁺, La³⁺, Ce³⁺, Lu³⁺, Ti⁴⁺, Zr⁴⁺, Hf⁴⁺, V⁵⁺⁺⁺⁺, UO₂²⁻, Th⁴⁺⁺⁺⁺, Pa⁴⁺⁺⁺⁺, CO₃⁻⁻⁻⁻, SO₃⁻⁻⁻⁻</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

14
1.3.1.1 Biosorption of Heavy Metals: Cellulose Based Sorbents

Unmodified cellulose has a low heavy metal adsorption capacity as well as variable physical stability. Therefore, chemical modification of cellulose can be carried out to achieve adequate structural durability and efficient adsorption capacity for heavy metal ions.\textsuperscript{85} Chemical modification can be used to vary certain properties of cellulose such as its hydrophilic or hydrophobic character, elasticity, water sorbency, adsorptive or ion exchange capability, resistance to microbiological attack and thermal resistance.\textsuperscript{86} The β-D-glucopyranose units which make up the cellulose chain contain one primary hydroxyl group and two secondary hydroxyl groups. Functional groups may be attached to these hydroxyl groups through a variety of chemistries. The principle and main routes of direct cellulose modification in the preparation of adsorbent materials are esterification, etherification, halogenation and oxidation.

Table 1.6. summarises these various methods for direct modification of cellulose leading to heavy metal adsorbent materials. As alternative, valuable properties deficient in native cellulose can be imparted to cellulose by grafting a second polymer as a long branch on the cellulose molecule. High energy radiation, photochemical and chemical initiation techniques are employed to prepare adsorbents by this method.
Table 1.6. Cellulose modification methods with various chemical reagents and associated functional groups\(^7\)

<table>
<thead>
<tr>
<th>Modification reaction</th>
<th>Modifying group</th>
<th>chemicals</th>
<th>(Chelating group)</th>
<th>Adsorption Capacity (mg g(^{-1}))</th>
<th>pH</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Esterification</strong></td>
<td>Wood pulp</td>
<td>Succinic anhydride (Carboxyl)</td>
<td>Cd(II) 169</td>
<td>88</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wood pulp</td>
<td>Citric acid (Carboxyl)</td>
<td>Cu(II) 24, Pb(II) 83</td>
<td>89</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Etherification</strong></td>
<td>Cellulose Carrier (aquacel)</td>
<td>(1) Sodium methylocate</td>
<td>Hg(II) 288</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) Epichlorohydrin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3) Polyethyleneimine (Amino)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood sawdust</td>
<td>Acrylonitrile</td>
<td>Hg(II) 288</td>
<td>Cu(II) 246, Ni(II) 188</td>
<td>6.0, 91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halogenation</td>
<td>Hydroxylamine (Amidoxime)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose powder</td>
<td>6-Bromo-6-deoxycellulose + 2- Mercaptobutanedioic acid (Carboxyl)</td>
<td>Cu(II) 36, Pb(II) 105, Ni(II) 0.93</td>
<td>5.0, 92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cysteine (Amino + Carboxyl)</td>
<td>Cu(II) 22, Pb(II) 28, Ni(II) 8</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>a-Thioglycerol (Hydroxyl)</td>
<td>Cu(II) 2, Pb(II) 6, Ni(II) 10</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3-Mercaptopropionic acid (Carboxyl)</td>
<td>Cu(II) 24, Pb(II) 20, Ni(II) 1</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-aminoethanethiol (Amino)</td>
<td>Cu(II) 6, Pb(II) 81, Ni(II) 5</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Oxidation**

| Cellulose powder      | Sodium metaperiodate (Carboxyl) | Ni(II) 184, Cu(II) 236 | 93 |
|                       | Sodium metaperiodate Hydroxamic acid (Amino) | Cu(II) 246 | 94 |

1.3.1.2. Biosorption of Precious Metals

Since biosorbents are prepared from the naturally abundant and/or waste biomass of agricultural, marine or forest origin, the type of biomass used for biosorption of precious metal ions is varied. The following table (Table 1.7.) gives a list of adsorbents used for precious metal ions recovery. From the table, we can understand that biomass may be used in its "natural state" or modified, e.g. by cross-linking to improve biosorption efficiency and acid conditions generally favor the biosorption of precious metals from solution, especially for the adsorption on bacteria and derivatives of chitosan. The adsorption
capacities for precious metals vary from one to another type of biomass. It is quite tough to select a perfect biomass from the billions of microorganisms and their derivatives. However, few researches have been reported on recovery of precious metals from multielemental solutions and in continuous mode of operation.

Table 1.7. Adsorbents used for precious metal biosorption$^{95}$

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Metal</th>
<th>pH</th>
<th>Qmax (mmol/g)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bacteria</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Streptomyces erythraeus</em></td>
<td>Au$^{3+}$</td>
<td>4.0</td>
<td>0.03</td>
<td>[96]</td>
</tr>
<tr>
<td><em>Spirulina platensis</em></td>
<td></td>
<td>4.0</td>
<td>0.026</td>
<td>[96]</td>
</tr>
<tr>
<td><em>Desulfovibrio desulfuricans</em></td>
<td>Pd$^{2+}$</td>
<td>2.0</td>
<td>1.2</td>
<td>[97]</td>
</tr>
<tr>
<td><em>Desulfovibrio fructosivorans</em></td>
<td>Pd$^{2+}$</td>
<td>2.0</td>
<td>1.2</td>
<td>[97]</td>
</tr>
<tr>
<td><em>Desulfovibrio vulgaris</em></td>
<td>Pd$^{2+}$</td>
<td>2.0</td>
<td>1.0</td>
<td>[97]</td>
</tr>
<tr>
<td><em>Desulfovibrio desulfuricans</em></td>
<td>Pt4+</td>
<td>2.0</td>
<td>0.32</td>
<td>[97]</td>
</tr>
<tr>
<td><em>Desulfovibrio fructosivorans</em></td>
<td>Pt4+</td>
<td>2.0</td>
<td>0.17</td>
<td>[97]</td>
</tr>
<tr>
<td><em>Desulfovibrio vulgaris</em></td>
<td>Pt4+</td>
<td>2.0</td>
<td>0.17</td>
<td>[97]</td>
</tr>
<tr>
<td><em>Penicillium chrysogenum</em></td>
<td>Au(CN)$_2^-$</td>
<td>2.0</td>
<td>0.0072</td>
<td>[98]</td>
</tr>
<tr>
<td><em>Bacillus subtilis</em></td>
<td>Au(CN)$_2^-$</td>
<td>2.0</td>
<td>0.008</td>
<td>[98]</td>
</tr>
<tr>
<td><strong>Fungi</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Saccharomyces cerevisiae</em></td>
<td>Au$^{3+}$</td>
<td>5.0</td>
<td>0.026</td>
<td>[96]</td>
</tr>
<tr>
<td><em>Cladosporium cladosporioides</em></td>
<td>Au$^{3+}$</td>
<td>4.0</td>
<td>0.5</td>
<td>[99]</td>
</tr>
<tr>
<td><em>Cladosporium cladosporioides</em></td>
<td></td>
<td>4.0</td>
<td>0.18</td>
<td>[99]</td>
</tr>
<tr>
<td><em>Cladosporium cladosporioides Strain 1</em></td>
<td>Au$^{3+}$</td>
<td>4.0</td>
<td>0.4</td>
<td>[100]</td>
</tr>
<tr>
<td><em>Cladosporium cladosporioides Strain 2</em></td>
<td>Au$^{3+}$</td>
<td>4.0</td>
<td>0.5</td>
<td>[100]</td>
</tr>
<tr>
<td><em>Cladosporium cladosporioides Strain 1</em></td>
<td>Ag$^+$</td>
<td>4.0</td>
<td>0.4</td>
<td>[100]</td>
</tr>
<tr>
<td><em>Cladosporium cladosporioides Strain 2</em></td>
<td>Ag$^+$</td>
<td>4.0</td>
<td>0.12</td>
<td>[100]</td>
</tr>
<tr>
<td><em>Aspergillus niger</em></td>
<td>Au$^{3+}$</td>
<td>2.5</td>
<td>1.0</td>
<td>[101]</td>
</tr>
<tr>
<td><em>Rhizopus arrhizus</em></td>
<td>Au$^{3+}$</td>
<td>2.5</td>
<td>0.8</td>
<td>[101]</td>
</tr>
<tr>
<td><strong>PVA-immobilized biomass</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>(Fomitopsis carnea)</em></td>
<td>Au$^{3+}$</td>
<td>1–13</td>
<td>0.48</td>
<td>[102]</td>
</tr>
<tr>
<td><em>Aspergillus niger</em></td>
<td>Ag$^+$</td>
<td>5–7</td>
<td>0.9</td>
<td>[103]</td>
</tr>
<tr>
<td><em>Neurospora crassa</em></td>
<td>Ag$^+$</td>
<td>5–7</td>
<td>0.6</td>
<td>[103]</td>
</tr>
<tr>
<td><em>Fusarium oxysporium</em></td>
<td>Ag$^+$</td>
<td>5–7</td>
<td>0.5</td>
<td>[103]</td>
</tr>
<tr>
<td>Adsorbents</td>
<td>Metal</td>
<td>pH</td>
<td>Qmax (mmol/g)</td>
<td>Refs.</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>----------</td>
<td>-----</td>
<td>---------------</td>
<td>-------</td>
</tr>
<tr>
<td>Algae</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Chlorella vulgaris</em></td>
<td>Ag⁺</td>
<td>6.7</td>
<td>0.5</td>
<td>[104]</td>
</tr>
<tr>
<td><em>Chlorella vulgaris</em></td>
<td>Au³⁺</td>
<td>2</td>
<td>0.5</td>
<td>[105]</td>
</tr>
<tr>
<td><em>Sargassum natans</em></td>
<td>Au³⁺</td>
<td>2.5</td>
<td>2.1</td>
<td>[101]</td>
</tr>
<tr>
<td><em>Ascophyllum nodosum</em></td>
<td>Au³⁺</td>
<td>2.5</td>
<td>0.15</td>
<td>[101]</td>
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<tr>
<td><em>Sargassum fluitans</em></td>
<td>Au(CN)²⁻</td>
<td>2.0</td>
<td>0.0032</td>
<td>[98]</td>
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<tr>
<td>Alginate cross-linked with CaCl₂</td>
<td>Au³⁺</td>
<td>2.0</td>
<td>1.47</td>
<td>[106]</td>
</tr>
<tr>
<td>Alginate cross-linked with Ca(OH)₂</td>
<td>Au³⁺</td>
<td>2.0</td>
<td>0.34</td>
<td>[106]</td>
</tr>
<tr>
<td>Dealginated Seaweed Waste</td>
<td>Au³⁺</td>
<td>3</td>
<td>0.4</td>
<td>[107]</td>
</tr>
<tr>
<td>Proteins</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hen eggshell membrane (ESM)</td>
<td>Au(CN)²⁻</td>
<td>3</td>
<td>0.67</td>
<td>[108]</td>
</tr>
<tr>
<td>Hen eggshell membrane (ESM)</td>
<td>AuCl₄⁻</td>
<td>3</td>
<td>3.1c</td>
<td>[108]</td>
</tr>
<tr>
<td>Lysozyme</td>
<td>Au³⁺,Pd²⁺,Pt⁴⁺</td>
<td>–</td>
<td>–</td>
<td>[109]</td>
</tr>
<tr>
<td>Bovine serum albumin (BSA)</td>
<td>Au³⁺, Pd²⁺,Pt⁴⁺</td>
<td>–</td>
<td>–</td>
<td>[109]</td>
</tr>
<tr>
<td>Ovalbumin</td>
<td>Au³⁺, Pd²⁺,Pt⁴⁺</td>
<td>–</td>
<td>–</td>
<td>[109]</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>Au³⁺</td>
<td>5.0</td>
<td>0.18d</td>
<td>[110]</td>
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<tr>
<td>Condensed-tannin gel</td>
<td>Pd²⁺</td>
<td>2.0</td>
<td>1.0e</td>
<td>[111]</td>
</tr>
<tr>
<td>Condensed-tannin gel</td>
<td>Au³⁺</td>
<td>2.0</td>
<td>40e</td>
<td>[112]</td>
</tr>
<tr>
<td>Bayberry tannin immobilized collagen fiber (BTICF) membrane</td>
<td>Pt⁴⁺</td>
<td>3.0</td>
<td>0.23</td>
<td>[113]</td>
</tr>
<tr>
<td>Bayberry tannin immobilized collagen fiber (BTICF) membrane</td>
<td>Pd²⁺</td>
<td>4.0</td>
<td>0.32</td>
<td>[113]</td>
</tr>
<tr>
<td>Acid-washed <em>Ucides cordatus</em> (waste crab shells)</td>
<td>Au(CN)²⁻</td>
<td>3.4</td>
<td>0.17</td>
<td>[114]</td>
</tr>
<tr>
<td>Glutaraldehyde crosslinked chitosan (GCC)</td>
<td>Au³⁺</td>
<td>1.6</td>
<td>2.9</td>
<td>[115]</td>
</tr>
<tr>
<td>Sulfur derivative of chitosan (RADC)</td>
<td>Au³⁺</td>
<td>3.2</td>
<td>3.2</td>
<td>[115]</td>
</tr>
<tr>
<td>Glutaraldehyde crosslinked chitosan (GCC)</td>
<td>Pd²⁺</td>
<td>2.0</td>
<td>2.44</td>
<td>[116]</td>
</tr>
<tr>
<td>Thiourea derivative of chitosan (TGC)</td>
<td>Pd²⁺</td>
<td>2.0</td>
<td>2.54</td>
<td>[116]</td>
</tr>
<tr>
<td>Rubeanic acid derivative of chitosan (RADC)</td>
<td>Pd²⁺</td>
<td>2.0</td>
<td>3.24</td>
<td>[116]</td>
</tr>
<tr>
<td>Thiourea derivative of chitosan (TGC)</td>
<td>Pt⁴⁺</td>
<td>2.0</td>
<td>2.0</td>
<td>[117]</td>
</tr>
<tr>
<td>Glutaraldehyde crosslinked chitosan (GC)</td>
<td>Pt⁴⁺</td>
<td>1.6</td>
<td>2.0</td>
<td>[117]</td>
</tr>
<tr>
<td>Chitosan derivatives</td>
<td>Pd²⁺</td>
<td>2.0</td>
<td>3.5</td>
<td>[118]</td>
</tr>
<tr>
<td>Chitosan derivatives</td>
<td>Pt⁴⁺</td>
<td>2.0</td>
<td>3.2</td>
<td>[118]</td>
</tr>
</tbody>
</table>
Mechanism of biosorption of precious metals

Biosorption of precious metals from solutions can be simplified as chemical sorption mechanisms and physical sorption mechanisms. Chemical sorption mechanisms include complexation, chelation, microprecipitation, and microbial reduction, while physical sorption mechanisms generally involve electrostatic forces and ion exchange. Pethkar et al. used X-ray photoelectron (XPS) and Fourier transform infra-red spectroscopy (FT-IR) for the elucidation of binding mechanisms involved in the adsorption of gold and silver ions to two strains of a fungus, *Cladosporium cladosporioides*. These methods confirmed that no chemical change to the biosorbent took place after metal loading, suggesting that the acidic conditions merely favored electrostatic interaction between gold anions (AuCl₄⁻) and protonated biomass. More recently, more and more studies propose chemical adsorption mechanisms.

Spectroscopic studies of the biosorption of gold(III) by dealginated seaweed waste was carried out by Romero-González et al. It was reported that colloidal Au formed on the surface of dealginated seaweed by reduction of Au(III) to Au(0) was observed using ESEM and four different types of particles were clearly identified. EXAFS measurements showed that colloidal Au is present on the surface of the biosorbent. Evidence of gold reduction from Au(III) to Au(I) and Au(0) was also confirmed by the measured bond distances characteristic of the metal. The coordination number obtained by EXAFS indicated that approximately 75% of the Au on the sample was present in the colloidal form and the remaining Au was bound to S as nearest neighbor. The proposed mechanisms for Au removal from solution are reduction of Au species by components on the surface of the biosorbent to form colloidal metal followed by retention of the ionic Au(I) species at the sulfur containing sites. Similarly, adsorption mechanism of gold and palladium by redox within condensed-tannin gel was reported by Nakano and co-workers. The presence of metallic palladium on the tannin gel particles confirms that the palladium(II) can be reduced to palladium(0), while the hydroxyl groups of tannin gel are oxidized by redox-reaction during the adsorption.
1.4. RESEARCH OBJECTIVES

The short term objectives of the study are:

1. To explore the scope of waste paper as adsorbent
2. To prepare and characterize various waste paper derivatives
3. To test the effectiveness and efficiency of the novel adsorbents in model and real system
4. To suggest ways to separate toxic metals and recover precious metals from e-waste by using novel waste paper gels.
5. To establish waste paper as important adsorption material with competitive capability

The long term objectives of the study are:

1. To contribute to a sustainable society through effective separation and recovery technology
2. To contribute to the protection of environment and improvement in human health.
REFERENCES


Available at http://www.pprc.or.jp accessed on 25 Dec. 2008


Chapter 2

 ADSORPTION OF HEAVY METALS ON IMINODIACETIC ACID TYPE WASTE PAPER

Adsorption gel was prepared from waste recycled paper by immobilizing iminodiacetic acid (IDA) functional group by chemical modification. The gel exhibited good adsorption behavior for a number of metal ions viz. Cu(II), Pb(II), Fe(III), Ni(II), Cd(II) and Co(II) at acidic pH. The order of selectivity was found to be as follows: Cu(II) > Pb(II) > Fe(III) > Ni(II) ~ Cd(II) ~ Co(II). From the adsorption isotherms, the maximum adsorption capacity of the gel for both Cu(II) and Pb(II) was found to be 0.47 mol/kg whereas that for Cd(II) was 0.24 mol/kg. A continuous flow experiment for Cd(II) showed that the gel can be useful for pre-concentration and complete removal of Cd(II) from aqueous solution.

2.1. INTRODUCTION

For a sustainable society in near future, we should gradually reduce our dependence on the limited stock of fossil fuel resources and explore new alternatives based on the renewable biomass resources. That is, various biomass wastes generated in huge amounts in diverse fields like agriculture, forestry and fishery at present should be much more effectively and largely utilized not only for biomass energy, composts and so on but also as feed materials for various advanced functional materials making use of their own original and excellent characteristics.¹

The major proportion of biomass waste consists of polysaccharides such as cellulose and, therefore, it is the most abundant natural resource in the world which is produced by plants through photosynthesis process.² Commercial cellulose supplies an annual world consumption of about 150 million tones of fibrous raw materials. The greatest portion of this amount, derived mostly from pulped wood, is used for the production of papers.³
Waste recycled paper is one of the various cellulosic biomass wastes generated in voluminous amount in various fields. It is an important fact that recycled paper cannot be recycled and reused for infinite times in the form of paper since its fibers are shortened at each stage of recycling and after a few cycles, falling short of the required fiber length, it becomes a waste. Consequently, it is necessary to find alternative applications for recycled paper not only to reduce the amount of waste and cut down the expenses of waste treatment but also, and more importantly, to prepare valuable materials by the effective use of its original good characteristics which have not been utilized yet.

In the present work, we have attempted to use the recycled paper as feed material for preparing adsorption gels for metal ions. To date, only little work has been reported on the adsorption of metal ions by waste recycled paper though a wide range of sorbents based on chemically modified cellulose have been developed for the concentration and selective separation of metal ions. 4-11 Most of these adsorption gels are prepared by chemical modification of pure cellulose. Since waste paper, waste newspaper in particular, contains high amount of lignin, the chemically modified waste paper has a possibility to exhibit different adsorption behavior from the gels prepared from pure cellulose. It is also noteworthy here that since the major component of recycled paper is wood cellulose, typical amorphous cellulose, its chemical modification is easier in comparison to the other forms of cellulose composed mostly of crystalline parts. Although recycled paper itself has no ability to adsorb metal ions, it can be immobilized with a variety of functional groups by simple chemical modification to develop adsorption gels having high selectivity or high affinity to specific metal ions. Hence, in the present work, crushed recycled paper has been immobilized with the functional group of iminodiacetic acid, a typical chelating group, and tested for the adsorption of various heavy and base metals.

2.2. EXPERIMENTAL

Chemicals

The feed material of the gel was fiber material like cotton which was prepared by crushing waste newspaper by using Dalton model P-3S power mill. Analytical grade iminodiacetic acid was purchased from Dojindo, Japan and thionyl chloride from Sigma Aldrich, USA. All other chemicals used for the synthesis and for the adsorption tests were of analytical grade and were used without further purification.
Preparation of the Adsorption Gel

The required amount of crushed waste recycled paper was washed with soap and water many times to remove grease particles and treated with 20% sodium hydroxide solution for 5 hours. It was washed again with water to remove excess NaOH till neutral pH. It was then dried in a convection oven at 50°C for 24 h. Thus pre-treated recycled paper was chemically modified with iminodiacetic acid (IDA) group according to the reaction schemes shown in Scheme 2.1.

At first, 0.5 g of the pretreated paper was chlorinated by mixing together with 25 mL of pyridine in ice bath to which 5 mL of thionyl chloride was added dropwise and the mixture was heated at 70°C for 6 h under N₂-atmosphere. The product obtained (0.5 g) was washed and dried overnight at 70°C in a convection oven. Diethyl iminodiacetate was prepared as follows. Four hundred mL of ethanol saturated with hydrochloric acid gas was prepared and mixed together with 20 g of IDA followed by heating at 80°C for 24 h. The product obtained (28 g) was neutralized with sodium bicarbonate and washed by chloroform.

Finally, 0.5 g chlorinated paper and 1.14 g of diethyl iminodiacetate were mixed together with 50 mL acetonitrile and 1.4 g potassium carbonate and stirred at 50°C for 72 h. The product obtained was filtered and washed with water. It was again dissolved in a mixture of 50 mL ethanol and 10 mL of 1 mol L⁻¹ sodium hydroxide and stirred for 1 day at 60 °C. The pH of the solution was adjusted to 2-3 for giving rise to precipitate. The precipitate was filtered and washed with 0.1 mol L⁻¹ hydrochloric acid followed by distilled water and dried at 60°C in a convection oven to obtain 0.35 g chelating recycled paper gel.
Scheme 2.1. Preparation of IDA-type chelating paper gel

Characterization of the Adsorbent Gel

The quantity of iminodiacetate group immobilized on the cellulose surface was determined by nitrogen elemental analysis. JASCO model 410 Fourier transform infrared (FTIR) spectrometer was also used to record the IR spectra of the gel.

Adsorption Tests

Metal Ion Uptake as a Function of pH

Batchwise adsorption tests were carried out to observe the pH dependence of the adsorption of various metal ions on the IDA-type chelating recycled paper gel. Test solutions containing 0.2 mmol L$^{-1}$ of individual metal ions such as Cu (II), Fe (III), Cd (II), Co (II), and Ni (II) at pH 1-5 were prepared by dissolving corresponding analytical grade individual metal chlorides in 0.1 mol L$^{-1}$ hydrochloric acid solution and in 0.1 mol L$^{-1}$ HEPES (N-[2-Hydroxyethyl] piperazine-N'-[2-ethanesulfonic acid]) solution, a buffer
reagent, followed by mixing these two solutions at an arbitrary volume ratio to adjust pH while dilute sodium hydroxide solution was used to prepare higher pH solution. In case of Pb(II), analytical grade Pb(II) nitrate was used to prepare the test solution. 20 mg of the adsorbent was added to 20 mL of the above mentioned metal solutions at different pH. The pH of the test solution was measured by using a BECKMAN model φ-45 pH meter. The mixtures were shaken for 24 h in thermostated shaker maintained at 30°C. The mixtures were filtered and the filtrate was taken as the sample solution for the metal ion concentration analysis. The concentrations of the corresponding metal ions before and after the adsorption were measured by using Shimadzu model AA-6650 atomic absorption spectrophotometer (AAS).

**Adsorption Isotherm Test**

Different concentration (0.2-2 mmol L⁻¹) of Cu (II), Pb (II) and Cd (II) individual ion solutions were prepared at pH 5, the optimum pH for the adsorption of metal ions. 15 mL of each of these solutions were shaken together with 20 mg of the adsorbent for 24 h in thermostated shaker maintained at 30°C to attain equilibrium. The mixtures were filtered and the concentrations of metal ions were analyzed by AAS as mentioned above.

**Breakthrough Followed by Elution Tests**

About 0.1 g of the dry IDA-paper gel was weighed accurately and packed in a glass column (8 mm diameter, packing height 5.8 mm) and conditioned overnight to pH 5 by washing with water of pH 5 adjusted by 0.1 mol L⁻¹ HEPES solution. Feed solution was prepared by mixing two solutions of 0.1 mol L⁻¹ hydrochloric acid and 0.1 mol L⁻¹ HEPES containing 2 mmol L⁻¹ Cd (II) to adjust the pH to 5, which was fed to the column at 5.0 mL/h by using an Iwaki model PST-100N peristaltic pump. The sample solutions from the outlet were collected using a Bio-Rad model 2110 fraction collector at time intervals of 1 h. After complete breakthrough, the column was washed with distilled water to wash out all unadsorbed Cd (II). Then, elution test was carried out using 1 mol L⁻¹ hydrochloric acid fed at the same flow rate. The eluted solution was collected in a similar way at time intervals of 0.5 h. All the fractions collected were analyzed by using AAS.
2.3. RESULTS AND DISCUSSION

Characterization of the Gel

IR Spectra

Figure 2.1. shows the IR spectra of various forms of recycled paper. As the result of chlorination, a sharp peak appeared at around 620 cm\(^{-1}\) in the spectra of chlorinated paper but it disappeared noticeably in the spectrum of IDA paper. Similarly, an intense but narrower peak corresponding to C=O stretch at 1600-1700 cm\(^{-1}\) region indicates the introduction of carboxyl group of IDA. Similarly, transformations along 3300-3600 cm\(^{-1}\) region from pretreated paper via chlorinated paper to IDA-type paper gel suggest the changes in hydroxyl groups and introduction of amine functionality onto the cellulose matrix.

![IR Spectra of different forms of recycled paper.](image)

Figure 2.1. IR spectra of different forms of recycled paper.

Elemental Analysis

The results of the elemental analysis are shown in Table 2.1. The chemical analysis of nitrogen in the IDA-type chelating adsorption gel shows that 2.17 mol/kg of the functional groups have been immobilized on the cellulose surface. Hence the degree of the immobilization of IDA groups or the extent of the conversion of hydroxyl groups at 6\(^{th}\) position of cellulose unit was evaluated as 60%.
Table 2.1. Elemental Analysis of different forms of the recycled paper

<table>
<thead>
<tr>
<th>Composition</th>
<th>C (%) (observed/calculated)</th>
<th>H (%) (observed/calculated)</th>
<th>N (%) (observed/calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreated Paper</td>
<td>46.29/44.40</td>
<td>5.70/6.17</td>
<td>-</td>
</tr>
<tr>
<td>Chlorinated Paper</td>
<td>35.62 /39.88</td>
<td>3.55 /4.98</td>
<td>-</td>
</tr>
<tr>
<td>IDA-type paper</td>
<td>45.59 / 43.32</td>
<td>4.72 / 5.41%</td>
<td>3.04 / 5.05</td>
</tr>
</tbody>
</table>

Effect of pH on the Adsorption Behavior of IDA-type Recycled Paper Gel

Figure 2.2.(a) shows the results of the batch wise adsorption test of IDA-type recycled paper gel for various metal ions wherein the % adsorption of metal ions are plotted against equilibrium pH. The % adsorption of the metal ion onto the gel was calculated from the following equation:

\[ \% \text{Adsorption} = \left( \frac{C_i - C_e}{C_i} \right) \times 100 \]

where, \( C_i \) represents the initial concentration of the metal ion in the test solution and \( C_e \) represents the equilibrium concentration after adsorption.

From the figure, it can be observed that the percentage adsorption of metal ions on the chelating gel increases with increasing pH in acidic pH range which is a characteristic feature of cation exchange mechanism. The gel shows better adsorption for Cu(II) even at low pH. The % adsorption of Fe (III) is comparable to that of Cu (II). Pb (II) was effectively adsorbed at pH greater than 3. Adsorption behavior to Ni (II), Cd (II), and Co (II) were almost the same. The order of selectivity among the tested metal ions is as follows: Cu(II) > Fe(II) > Pb(II) > Co(II) ≈ Ni(II) ≈ Cd(II). The order of stability constant (log \( K \)) of the corresponding metal-IDA chelates is: Cu(II), 10.63 > Fe(III), 10.42 > Ni(II), 8.19 > Pb(II), 7.45 > Co(II), 6.97 > Cd(II), 5.73 which is nearly the same with the selectivity order mentioned above except for Ni (II).
Figure 2.2. Variation of % adsorption of metal ions on (a) IDA paper gel and (b) original paper as a function of pH. Initial metal concentration = 0.2 mmol L\(^{-1}\). Weight of gel = 20 mg. Shaking time = 24 h. Temperature = 30°C.

Figure 2.2.(b) shows the % adsorption of the metal ions on original recycled paper (i.e. before modification) under the same conditions as IDA-type paper gel. It is clear from the figure that there is negligible adsorption of metal ions at pH lower than 3 except for Fe(III).
Although the % adsorption increases gradually at pH greater than 3, it appears less impressive in comparison to the adsorption behavior of the IDA-type paper gel. However, in the case of Fe(III), precipitation of ferric hydroxide may have occurred at pH greater than 2 since stepwise hydrolysis of Fe$^{3+}$ occurs at pH above 1 in the presence of complexing anions such as Cl$^-$.\textsuperscript{13}

**Adsorption Isotherms**

![Graph](image)

Figure 2.3. (a) Adsorption isotherm of some metal ions on IDA-type chelating paper gel at pH 5. Weight of gel = 20 mg. Shaking time = 24 h. Temperature = 30 °C. (b) Langmuir plot.

Figure 2.3.(a) shows a plot of the adsorption isotherm for Cu(II), Cd(II), and Pb(II) on the IDA-type recycled paper gel i.e. the amount of adsorption against the equilibrium concentration of the metal ions at pH 5. From the figure, it appears that the adsorption of
the metal ions took place according to Langmuir type adsorption in which adsorption increases with increasing metal ion concentration at low concentration region while it tends to approach constant values corresponding to each metal ion at high concentration. From these constant values, the maximum adsorption capacities were evaluated as 0.47 mol/kg – dry gel for both Cu(II) and Pb(II) and 0.24 mol/kg – dry gel for Cd(II).

Figure 2.3(b) shows the linear plot of the adsorption data according to the Langmuir model equation which is expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}}} \times C_e + \frac{1}{Q_{\text{max}}} \times b$$

where, $C_e$ = Equilibrium concentration of metal ion (mol L$^{-1}$)

$Q_e$ = Amount of metal ion adsorbed per unit weight of the adsorbent (mol/kg)

$Q_{\text{max}}$ = Maximum amount of metal ion adsorbed by the gel (mol/kg)

$b$ = Langmuir constant

Table 2.2. shows comparison of the adsorption capacity of the present gel with those exhibited by some IDA immobilized cellulose based adsorbents prepared from cotton fiber, wood powder or commercially available ordinary cellulose filter as starting material. Although direct comparison is difficult in some cases because of the different experimental conditions like pH and method of application, it is apparent from the table that IDA–type recycled paper gel exhibits higher capacity than other types of gels.
Table 2.2. Comparative adsorption capacities of some cellulose based gels and filter containing IDA

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Amount of metal adsorbed in mg /g of gel</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(equilibrium pH)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu(II)</td>
<td>Pb(II)</td>
</tr>
<tr>
<td>Recycled paper gel</td>
<td>29(5)</td>
<td>97.3(5)</td>
</tr>
<tr>
<td>Cotton fiber</td>
<td>27(5)</td>
<td>70(5)</td>
</tr>
<tr>
<td>Wood powder</td>
<td>20.5(4)</td>
<td>45(4)</td>
</tr>
<tr>
<td>Ordinary cellulose filter disc</td>
<td>12.83 (3)</td>
<td>45.17 (5)</td>
</tr>
</tbody>
</table>

Figure 2.4.(a) shows the breakthrough profile of Cd(II) using a column packed with the IDA-type recycled paper gel under the conditions described in the figure legend. From the figure, it is clear that breakthrough occurred after 10 h (1500 bed volume). A total of 150 mL solution was passed to the column for complete saturation of the gel. Considering the amount of the gel packed in the column, the adsorption capacity of the gel (0.16 mol/kg) for Cd (II) looks quite reasonable in comparison to the adsorption capacity obtained from batch wise tests (0.24 mol/kg) because the column experiment differs from batch wise adsorption test in some aspects i.e. less contact time between the metal ion and the gel and lack of agitation (by stirring). Figure 2.4.(b) shows the elution profile of Cd(II) ions with 1 mol L⁻¹ hydrochloric acid solution from the loaded column after complete saturation of the gel. It is clearly seen that Cd(II) is eluted at very high concentration, as high as 25 times compared to the feed concentration within the 2.5 mL fraction collected between 1-1.5 h. Also, nearly equal areas observed in both breakthrough and elution curves of Cd(II) indicated that almost complete recovery (~ 98%) of Cd(II) occurred within a small volume (15 mL) of the eluting solution. The high level of pre-concentration and the fast rate of elution can be very useful for the treatment of Cd (II) in industrial effluents.
Figure 2.4. (a) Breakthrough and (b) elution profile of Cd(II) from the column packed with IDA-type chelating paper gel. [Cd] = 0.2 mmol L\(^{-1}\). pH = 5. Weight of gel = 0.1 g. Eluent = 1 mol L\(^{-1}\) HCl. Feed rate = 5.00 ml/h.

2.4. CONCLUSION

The IDA-type recycled paper gel prepared by immobilization of IDA group onto waste paper exhibited good adsorption behavior for different base and heavy metals in a range of acidic pH. From the adsorption isotherms, the maximum adsorption capacity of the gel for both Cu(II) and Pb(II) was found to be 0.47 mol/kg whereas that for Cd(II) was 0.24 mol/kg. A continuous flow experiment carried out for Cd(II) showed that the gel can be useful for pre-concentration and complete removal of Cd(II) from aqueous solution. This presents a scope of the use of the gel for wastewater treatment and environmental remediation by removal of toxic heavy metal like cadmium.
REFERENCES


PRECONCENTRATION AND SEPARATION OF HEAVY METAL IONS BY CHEMICALLY MODIFIED WASTE PAPER GEL

Iminodiacetic acid was immobilized on waste paper by chemical modification in order to develop a new type of adsorption gel for heavy metal ions. Adsorption behavior of the gel was investigated for a number of metal ions viz. Cu(II), Pb(II), Fe(III), Ni(II), Cd(II) and Co(II) at acidic pH. From batch wise adsorption tests, the order of selectivity was found to be as follows: Cu(II) >> Fe(III) > Pb(II) > Ni(II) >> Co(II) > Cd(II). Column tests were carried out for pairs of metal ions to understand the separation and pre-concentration behavior of the gel. It was found that mutual separation of Ni(II) from Co(II) and that of Pb(II) from Cd(II) can be achieved at pH 3. Similarly, selective separation of Cu(II) from Cu(II)-Fe(III) and Cu(II)-Pb(II) mixtures at pH 1.5 and 2, respectively, was observed by using this new adsorption gel. In all cases, almost complete recovery of the adsorbed metal was confirmed by elution tests. The adsorption mechanism and comparative performance of the gel over other similar adsorbents are discussed.

3.1. INTRODUCTION

In the field of separation and recovery of metal resources, biomass wastes i.e. agricultural and forestry products like rice husks, soybean hulls, sugarcane bagasse, corn stover, peanut hulls, coconut fibers, wood powder as well as marine products such as crustacean shells (particularly chitosan) and algal biomass have been investigated for their capacity and efficiency to extract metal ions.\textsuperscript{1-7} In a number of cases, chitosan and its derivatives have proved to be excellent materials for separation of metal ions. However the production of chitosan generates a horrible smell and a large amount of waste effluent containing protein materials. This consequently raises
the production cost of chitosan and also affects the environment. Thus, from the viewpoint of low cost and green technology, exploring and developing a really competent biomass material that can replace the use of a variety of petroleum based ion exchange resins, chelating resins and extraction solvents is still a big challenge. For this purpose, we have selected and evaluated waste paper as an alternative biomass material, after simple chemical modification. Since waste paper originally possesses an amorphous structure and the breakdown of hydrogen bonds during recycling also increases the amorphous region, it is suitable for easy chemical modification.

To date, there has been very little work on waste paper for the purpose of separation and recovery of metal ions though a wide variety of sorbents based on chemically modified cellulose have been investigated. The presence of larger amorphous regions and a significant proportion of lignin may provide some interesting features in adsorbents based on waste paper. Taking this into consideration, we have immobilized iminodiacetic acid, a well known chelating agent, onto waste paper cellulose to develop an adsorption gel and tested it for the separation and concentration of various metal ions. In the past, some studies have been made by immobilizing iminodiacetic acid on various forms of cellulose as feed material. Chan et al prepared iminodiacetic acid cellulose sorbents using cotton fabric and sawdust respectively, to investigate the mutual separation of Ni(II) and Co(II) though the selectivity for Ni(II) over Co(II) was not marked. Similarly, Gennaro et al prepared iminodiacetic acid cellulose filters from ordinary filter paper disks and Gupta et al utilized pure cellulose as the starting material for an iminodiacetic acid type of chelating cation exchanger. However, these adsorbents were found to be suitable for the simultaneous adsorption of various metal ions only and no scope for mutual separation of coexisting metal ions was found. In this context, we have prepared an iminodiacetic acid modified waste paper gel which is expected to exhibit a distinct ability for selective preconcentration and mutual
separation between coexisting metal ions.

3.2. EXPERIMENTAL

Chemicals

Waste newspaper was crushed by a Dalton model P-3S power mill to obtain a fiber-like material which was used as the feed material. Iminodiacetic acid was purchased from Dojindo Laboratories Co. Ltd., Japan and epichlorohydrin, from Kishida Chemical Co. Ltd., Japan. All other chemicals and reagents were of analytical grade and used without any purification.

Preparation of the adsorption gel

Pretreatment. Pretreatment was necessary to remove greasy materials and ink from the paper and also to activate it for subsequent modification. For this purpose, the fiber-like material was washed many times with Bio-Cleans soap and water and treated with 20% sodium hydroxide solution for 5 hours. It was washed again with water till neutral pH and dried in a convection oven at 60°C for 24 h.

Immobilization of iminodiacetic acid. The pre-treated paper was chemically modified with iminodiacetic acid (IDA) according to a process developed by Sano et al. At first, 2 g NaOH was dissolved in about 15 mL water in a 200 mL flask to which 2 g iminodiacetic acid and 2 mL epichlorohydrin were added with stirring. Reaction between these chemicals was carried out at 60°C for 4 h in an oil bath. Then 4 g NaOH was further added to the mixture and dissolved by stirring. The pretreated waste newsprint paper (2 g) was added subsequently and the reaction mixture was heated in the oil bath at 110°C for 8 h. The product (about 1.84 g in fiber-like form) was filtered, washed with 0.5 mol L⁻¹ HCl followed by distilled water, and dried to obtain the chelating waste paper gel, abbreviated hereafter as waste paper gel. It was characterized by taking its IR spectrum and elemental analysis.
Adsorption tests

Adsorption Kinetics. A test solution containing 0.2 mmol L\(^{-1}\) Cu(II) in 0.1 mol L\(^{-1}\) HCl and 0.1 mol L\(^{-1}\) HEPES, a buffering agent, was prepared and the pH was adjusted to 3 by adding dilute NaOH solution. Ten samples were prepared by weighing 20 mg of the waste paper gel and adding 15 mL of the test solutions into each 50 mL sampling bottle. The mixtures were shaken for different time periods (from 5 min to 25 h) in a thermostated shaker maintained at 30°C after which they were filtered and the filtrate was taken for analysis. The concentrations of the metal ions before and after the adsorption were measured by using a Shimadzu model AA-6650 atomic absorption spectrophotometer (AAS).

Metal ion uptake as a function of pH. To observe the pH dependency of the adsorption of metal ions on the waste paper gel, batch wise adsorption tests were carried out. Test solutions containing 0.2 mmol L\(^{-1}\) of individual metal ions such as Cu (II), Fe(III), Cd (II), Co (II), and Ni (II) at pH 1-6 were prepared by dissolving corresponding metal chlorides in 0.1 mol L\(^{-1}\) hydrochloric acid solution and in 0.1 mol L\(^{-1}\) HEPES solution, followed by mixing these two solutions at an arbitrary volume ratio to adjust the pH. Dilute sodium hydroxide solution was added to prepare higher pH solutions. In the case of Pb(II), however, analytical grade nitrate salt of Pb(II) was used to prepare the test solution. The waste paper gel (20 mg) was added to 15 mL of metal ion solutions at different pH values and the mixtures were shaken for 24 h at 30°C in a thermostatic shaker. The mixtures were filtered and the concentration of the filtrate was measured by AAS.
Adsorption isotherm test. Different concentrations (0.2-2mmol L⁻¹) of Ni (II), and Co (II) ion solutions were prepared individually at pH 3. To 15 mL of each of these solutions, 20 mg of waste paper gel were added and the mixture was shaken for 24 h in a thermostated shaker at 30°C. The mixtures were filtered and the concentrations of metal ions were measured by AAS. Similarly, adsorption isotherms for Cu(II) and Pb(II) were studied at pH 2.

Breakthrough followed by elution tests

The waste paper gel (0.5 g) was packed in a glass column (8 mm diameter) and conditioned to pH 3 by passing acid solution through the column overnight. Feed solution containing 20 ppm each of Ni(II) and Co(II) at the same pH (prepared in 0.1 mol L⁻¹ HCl and 0.1 mol L⁻¹ HEPES) was passed through the column at 6.0 mL h⁻¹ by using an Iwaki model PST-100N peristaltic pump. The solution from the outlet was collected using a Bio-Rad model 2110 fraction collector at time intervals of 1 h. After complete saturation, distilled water was passed through the column to wash out all unabsorbed metal ions. For elution, 0.5 mol L⁻¹ hydrochloric acid was fed at the same flow rate and the solution was collected similarly at time intervals of 0.5 h. All the fractions were measured by using AAS.

Similar tests were carried out for binary solutions of Cu(II) and Fe(III) at pH 1.5 and Cu(II) and Pb(II) at pH 2 both at a rate of 5 mL h⁻¹. Again, column tests for Pb(II) and Cd(II) were carried out at pH 3 at a flow rate of 7.5 mL h⁻¹. In all cases, 0.5 mol L⁻¹ hydrochloric acid was used for elution. In order to confirm the gel stability in repeated use, 10 cycles of adsorption-elution tests for Cu(II) were also performed.

3.3. RESULTS AND DISCUSSION

Characterization of the gel

The waste paper gel was characterized by FT-IR spectrum and elemental analysis. As shown in Figure 3.1., an intense but narrower peak corresponding to C=O stretch in the 1600-1700 cm⁻¹ region indicating the immobilization of the carboxyl groups of IDA onto the cellulose matrices has confirmed the modification. Similarly, transformations along the 3300-3600 cm⁻¹ region from pretreated paper to waste paper gel suggest the changes in the hydroxyl groups and the introduction of amine functionality onto the cellulose. A sharp peak was observed at 1400 cm⁻¹ that indicates the transformations due to the ester bond at the C-6th position of the pyranose unit. Transformations found
at 2900 cm\(^{-1}\) indicate the changes due to the increase in the number of CH\(_2\) groups. All these observations confirm the introduction of IDA to the cellulosic frame of the paper. Also, from elemental analysis, it was found that 0.29 mol kg\(^{-1}\) of iminodiacetate functional groups were immobilized on the cellulose surface. The pKa values of iminodiacetic acid group as determined by the titrimetric method are 3.51 and 8.78 respectively.

![Figure 3.1. FT-IR spectra of the pre-treated waste paper and the iminodiacetic acid group modified waste paper gel.](image)

**Adsorption studies**

Adsorption kinetics were measured for Cu(II), a typical metal ion, at pH 3. Since complete equilibrium was attained within 30 minutes, a period of 24 h was considered to be sufficient for the subsequent batch wise tests.

Figure 3.2 shows the effect of pH on the adsorption behavior of the waste paper gel as observed in batch wise adsorption tests for various metal ions. It is seen from this figure that the % adsorption of metal ions on the gel increases with increasing pH at acidic pH, indicating a cation exchange mechanism. The gel exhibited remarkable adsorption for Cu(II) even at pH values as low as 2. Pb (II) was effectively adsorbed at pH 3. At pH values greater than 4, the gel showed higher adsorption for all metal ions. In comparison to the unmodified paper, the modified paper gel has shown excellent adsorption tendencies for the tested metal ions.\(^{16}\) The selectivity order for the tested metal ions is as follows: Cu(II) >> Fe(III) > Pb(II) > Ni(II) >> Co(II) > Cd(II). However, in the case of Fe(III), the order is different at pH values lower and higher than 2. Since stepwise hydrolysis of Fe\(^{3+}\) occurs at pH values above 1 in the presence of complexing
anions such as Cl\textsuperscript{-}, precipitation of iron may have led to the change in adsorption behavior at pH > 2.\textsuperscript{17} The order of the stability constants (log K) of the corresponding metal-IDA chelates is as follows: Cu(II), 10.63 > Fe(III), 9.42 > Ni(II), 8.19 > Pb(II), 7.45 > Co(II), 6.97 > Cd(II), 5.73; which is nearly the same as the selectivity order reported above.\textsuperscript{18} The selectivity pattern of this gel shows many possibilities for mutual separation of metal ions, one of which is that of Ni (II) from Co(II). Owing to very similar aqueous chemistry, they always coexist in nature. In industrial liquors containing Ni(II) and Co(II), their mutual separation is not easy except from chloride solutions. It can be observed from Figure 3.2. that Ni(II) can be effectively separated from Co(II) at pH 3. Similarly, Cu(II) can be selectively separated from any of the other metal ions at pH 2. At pH 3, mutual separation of Pb(II) from Cd(II) also looks possible.

![Figure 3.2](image)

Fig. 3.2. Variation of % adsorption of metal ions on the waste paper gel as a function of equilibrium pH. Initial metal concentration = 0.2 mM; mass of gel = 20 mg; solution volume = 15ml; shaking time = 24 h; temperature = 30°C.

Since all metal ions employed in this study form stable cations at weakly acidic pH values, the exchange of protons in the carboxylic group of the IDA for such cations present in the test solutions leads to the metal-gel binding. In this process, a five membered chelate ring is considered to be formed by coordination with two carboxylic groups and a nitrogen atom of the IDA group.
Adsorption isotherms

The adsorption of the tested metal ions, Ni(II), Cu(II), Pb(II) and Co(II), increased with increasing metal concentration in the low concentration region while it tended to approach constant values corresponding to each metal ion in the high concentration region, suggesting that the adsorption on the waste paper gel takes place according to the Langmuir adsorption mechanism. On the basis of the Langmuir equation, the Langmuir parameters were evaluated for each of the tested metal ion as listed in Table 3.1.

Table 3.1. Langmuir Parameters for various metal ions.

<table>
<thead>
<tr>
<th></th>
<th>( R^2 )</th>
<th>( q_m (\text{mg g}^{-1}) )</th>
<th>( b (\text{L mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)</td>
<td>0.9983</td>
<td>3.18</td>
<td>4.70</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>0.9999</td>
<td>13.28</td>
<td>37.0</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>0.9961</td>
<td>15.08</td>
<td>1.90</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>0.9984</td>
<td>10.98</td>
<td>22.71</td>
</tr>
</tbody>
</table>

\( R^2 \): Coefficient of correlation, \( q_m \): Maximum adsorption capacity of the gel, \( b \): Langmuir constant

Breakthrough Followed by Elution Tests

Figure 3.3.(a) shows the breakthrough profile of Ni(II) and Co (II) using a column packed with the waste paper gel under the conditions described in the figure legend. More than 350 mL of solution were passed through the column for complete saturation of the gel. The breakthrough of Co (II) occurred after 8 h whereas that of Ni (II) was observed after 31 h. The gel was completely saturated by Co (II) in 14 h and by Ni (II) in 52 h. The adsorption capacity of the gel evaluated from the column adsorption test was 0.167 mol kg\(^{-1}\) (9.8 mg/g of the dry gel) and 0.045 mol kg\(^{-1}\) (2.65mg/g of the dry gel) for Ni(II) and Co(II), respectively, which are lower than those observed in the batch wise tests.
Figure 3.3. (a) Breakthrough (b) Elution profile of Ni(II) and Co(II) from the column packed with waste paper gel. [M] = 20 mg L\(^{-1}\). Weight of gel = 0.5 g. Eluent = 0.5 mol L\(^{-1}\) HCl. Feed rate = 6 mL h\(^{-1}\).

Figure 3.3.(b) shows the elution profiles of these metal ions with 0.5 M hydrochloric acid solution from the loaded column after complete saturation of the gel. It is clearly seen that Ni(II) was eluted at very high concentration, as much as 20 times higher compared to the feed concentration within the 6 mL fraction collected between 1-2 h. From the comparison of the breakthrough and elution curves of Ni(II), it is clear that nearly all of the adsorbed Ni(II) was eluted, revealing almost complete recovery (>95%) of metal ion in a small volume of the eluting solution. The high level of pre-concentration and separation of Ni(II) and its fast rate of elution suggests that the gel can be repeatedly and effectively employed for the mutual separation of Ni(II) and Co(II) in various sample solutions including industrial effluents.

Similarly, Figures 3.4.(a) and (b) show the breakthrough and elution profile for Cu(II) and Pb(II) from the packed column. In the case of Pb(II), breakthrough occurred
before 7 h while, in the case of Cu(II), it occurred only after 55 h. Similarly, saturation of the gel with these metal ions occurred at around 12 h and 97 h, respectively. The adsorption capacity of the gel for Cu(II) evaluated by this method was 0.212 mol kg\(^{-1}\) which is nearly the same as that observed in the batch wise test. The elution profile shows that Cu(II) is eluted at very high concentration, as high as 125 times that of the feed concentration within the 5 mL fraction collected between 1-2 h. Here also, from the comparison of the breakthrough and elution curves of Cu(II), it is obvious that almost complete recovery (>95 %) of metal ions can be achieved within a small volume of the eluting solution. Since Cu(II) exhibited high selectivity over all other metal ions at pH 2 as already observed in the batch wise test, this result ensures that Cu(II) can be separated not only from Pb(II) but also from a number of other coexisting metal ions.

Figure 3.4. (a) Breakthrough (b) Elution profile of Cu(II) and Pb(II) from the column packed with waste paper gel. [M] = 20 mg L\(^{-1}\). Weight of gel = 0.5 g. Eluent = 0.5 mol L\(^{-1}\) HCl. Feed rate = 5 mL h\(^{-1}\).
To reinforce these findings, further breakthrough and elution tests were carried out at pH 1.5 for a binary mixture of Cu(II) and Fe(III). As shown in Figure 3.5., Fe(III) broke through much earlier than Cu(II). When Fe(III) adsorption reached equilibrium, Cu(II) began to break through. Hence, by using the waste paper gel, Cu(II) and Fe(III) can also be easily separated from each other.

![Graph](image)

(a)

Figure 3.5. (a) Breakthrough (b) Elution profile of Cu(II) and Fe(III) from the column packed with waste paper gel. [M] = 20 mg L\(^{-1}\). Weight of gel = 0.3 g. Eluent = 0.5 mol L\(^{-1}\) HCl. Feed rate = 5 mL h\(^{-1}\).

Figures 3.6.(a) and (b) show the breakthrough and elution profiles, respectively, in the case of a Pb(II) - Cd(II) binary mixture. It was found that Pb(II) was selectively adsorbed from Cd(II) at pH 3 and the adsorbed Pb(II) was eluted easily with 0.5 mol L\(^{-1}\) HCl. Comparison of the breakthrough and elution curves shows that almost complete (>98%) elution of the adsorbed Pb(II) was achieved and the low
The results, as shown in Table 3.2, indicate that the gel behaves consistently for elution. The results show that 0.5 M hydrochloric acid solution was passed through the column for a flow rate of 5.5 mL/h. After a definite time interval, the column was washed with a solution maintaining at pH 3, then a 0.5 M solution of gel was passed through the column packed with waste paper gel at a concentration of 0.5 ml. A model solution containing 20 mg/L Cu(II) was used by conducting ten consecutive adsorption-elution cycles. The durability of the waste paper gel for repeated use was tested by conducting ten cycles.

For Figure 3.6, (a) breakthrough (b) elution profile of Pb(II) and Cd(II) from the column.

The eluate of Pb(II) in the feed liquor was converted to a very high concentration in concentration of Pb(II) and Cd(II).
several consecutive cycles. Further, no change in the physical appearance of the gel was observed and the phenomenon of swelling or shrinking was not apparent with repeated use.

<table>
<thead>
<tr>
<th>No. of Cycles</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbed (mg)</td>
<td>1.77</td>
<td>1.79</td>
<td>1.79</td>
<td>1.83</td>
<td>1.884</td>
<td>1.86</td>
<td>1.91</td>
<td>1.82</td>
<td>1.82</td>
<td>1.79</td>
</tr>
<tr>
<td>Eluted (mg)</td>
<td>1.66</td>
<td>1.68</td>
<td>1.68</td>
<td>1.72</td>
<td>1.774</td>
<td>1.75</td>
<td>1.8</td>
<td>1.71</td>
<td>1.71</td>
<td>1.68</td>
</tr>
<tr>
<td>% Recovery</td>
<td>93.78</td>
<td>93.85</td>
<td>93.85</td>
<td>93.99</td>
<td>94.16</td>
<td>94.09</td>
<td>94.24</td>
<td>93.96</td>
<td>93.96</td>
<td>93.85</td>
</tr>
</tbody>
</table>

4. CONCLUSION

Waste paper gel exhibits significant adsorption behavior for a number of heavy metal ions namely Cu(II), Fe(III), Ni(II), Co(II), Pb(II), and Cd(II). Although the extent of immobilization looks small, most of the gel adsorption sites are available for adsorption. Contrary to other cellulose based gels immobilized with the same functional group, this gel shows remarkable selectivity patterns for metal ions. Selective separation of Cu(II) from a number of coexisting metal ions at low pH is feasible by using this novel form of waste paper. Similarly, mutual separation of various metal ion pairs like Ni(II)-Co(II) and Pb(II)-Cd(II) can be achieved at acidic pH. Regeneration of the gel by acid treatment and its remarkable preconcentration behavior has raised its potential for practical application.

REFERENCES


Chapter 4

RECOVERY AND SEPARATION OF PRECIOUS METALS USING IMINODIACETIC ACID MODIFIED WASTE PAPER

Waste paper was developed as functional sorption active material by introducing iminodiacetic acid group. Adsorption tests for a number of metallic species were carried out at a range of hydrochloric acid concentration. In the batch tests distinct selectivity was observed for Au(III) and Pd(II) only and negligible adsorption was observed for Pt(IV) and other metal ions like Cu(II), Fe(III), Ni(II) and Zn(II). Moreover, Au(III) was reduced by the gel giving rise to clearly recognizable beautiful elemental gold particles which was confirmed by means of the XRD-spectrum and SEM-images of the adsorbent after adsorption. The results were compared with that of commercially available ion exchange resin, Diaion CR11, containing iminodiacetic acid group. Adsorption isotherm test showed higher capacity for Au(III) than for Pd(II) owing to the reduction of the former during adsorption. A number of adsorption-elution cycles were generated in column mode which reveals the stability and reusability of the waste paper gel.

4.1. INTRODUCTION

The demand for precious metals like gold, palladium, and platinum is ever increasing due to their newer and broader applications in various sectors such as manufacturing of electronic and electrical devices, automobile catalysts, and biochemical applications, i.e. pharmaceuticals, which have led to the increase of the price of precious metals over the past years. In addition, diminishing quality of the available mined ores and the environmental degradation associated with mining has considerably raised their production cost. Under these circumstances, a world-wide interest in their recovery from secondary resources has emerged. From the viewpoint of sustainable development, this should be taken as a positive note as it will help to reduce the alarming level of electrical and electronic wastes in the developed countries produced as a result of the cutthroat competition in the market of PCs, mobile telephones, and entertainment electronics.
Various processes are in practice currently and many alternatives have been reported in the literature for the effective and efficient recovery of precious metals. Generally precious metals contained in anode slimes generated during electro-refining of nonferrous metals are totally dissolved in hydrochloric acid containing chlorine gas to obtain a concentrated chloride solution, from which each precious metal is separated and recovered by means of solvent extraction and ion exchange. However, various drawbacks such as slow kinetics, high cost, and the release of environmentally unacceptable chemicals in waste streams are associated with the solvent extraction technique. On the other hand, the application of commercially available ion exchange resins and chelating resins is limited due to their non-selective nature and low uptake capacity for precious metals.

In this context, we have investigated the utilization of waste biomasses as sorption active materials for the recovery of valuable metals from waste water. In our previous study, a recovery process for gold from chloride media using an adsorption gel generated from wood, lignophenol, as well as persimmon peel gel has been investigated.

It is evident that tons of wastepaper is being generated in various forms everyday. Unlike pure cellulose, amorphous matrix of paper makes it easier for chemical modification. In our previous work, we have studied the adsorption behavior of modified waste paper for heavy metal ions. In this paper, from the viewpoints of the effective use of wastepaper and the recovery of precious metals from various secondary resources, we have investigated the selective recovery of precious metals using chemically modified wastepaper.

4.2. EXPERIMENTAL

Materials. Waste newspaper was used as the feed material for the adsorption gel. Microcrystalline cellulose was purchased from Merck (Germany). Thionyl chloride was purchased from Sigma Aldrich, USA and Iminodiacetic acid (50%) from Wako Pure Chemical Industries, Japan. Analytical grade chloroauric acid and chloroplatinic acid (both from WAKO, Japan) were used to prepare Au(III) and Pt(IV) test solutions, respectively. All other chemicals used for the synthesis and for adsorption tests were of analytical grade and were used without further purification.

Methodology. Scanning electron microscopy (SEM) analysis of the adsorbent was carried out using a JEOL model JSM 5200 scanning electron microscope under an
acceleration voltage of 15 V. A Rigaku RINT – 8829 X-ray diffractometer was used to record x-ray diffraction spectra (XRD). The amount of adsorption was calculated from the difference in metal concentration before and after adsorption and the weight of the adsorption gel. Metal ion concentrations were measured using a Shimadzu model ICPS-8100 ICP/AES spectrometer. The IR spectra of the adsorption gel were determined with a JASCO model FTIR-410.

Preparation of the Adsorption Gel.

Waste newspaper was crushed by using a Dalton model P-3S power mill, washed with soap and water many times to remove grease particles and then treated with a 20% sodium hydroxide solution for 5 hours. It was washed again with water to remove excess NaOH till neutral pH. It was then dried in a convection oven at 50°C for 24 h.

Subsequently, 0.5 g of the pretreated paper was chlorinated by mixing together with 25 ml of pyridine in an ice bath. Thionyl chloride, (5 mL), was added drop wise and the mixture was heated at 70°C for 6 h under a N₂-atmosphere. The product obtained (0.5 g) was washed and dried overnight at 70°C in a convection oven. Diethyl iminodiacetate was prepared as follows. 400 mL of ethanol saturated with hydrochloric acid gas was prepared and mixed together with 20 g of IDA followed by heating at 80°C for 24 h. The product obtained (28 g) was neutralized with sodium bicarbonate and washed by chloroform.

Finally, 0.5 g chlorinated paper and 1.14 g of diethyl iminodiacetate were mixed together with 50 mL acetonitrile and 1.4 g potassium carbonate and stirred at 50°C for 72 h. The product obtained was filtered and washed with water. It was again dissolved in a mixture of 50 mL ethanol and 10 mL of 1 mol L⁻¹ sodium hydroxide and stirred for 1 day at 60°C. The pH of the solution was adjusted to 2-3 for giving rise to precipitate. The precipitate was filtered and washed with 0.1 mol L⁻¹ hydrochloric acid followed by distilled water and dried at 60°C in a convection oven to obtain 0.35 g chelating recycled paper gel. The iminodiacetic acid modified waste paper gel is named as IDA-paper gel.
Adsorption Tests. A preliminary kinetic study of Au(III), Pd(II) and Pt(IV) uptake on the IDA-paper gel was carried out to determine the optimum time needed to reach equilibrium. The adsorption behavior of the IDA-paper gel for Au (III), Pd(II), Pt(IV), Cu(II), Fe(III), Ni(II), and Zn(II) was individually examined at varying hydrochloric acid concentrations (0.1 M to 4 M) (M = mol/dm$^3$). For each metal ion, the initial metal concentration was 0.2 mM. Fifteen ml of test solutions were mixed together with 20 mg of adsorption gels in stoppered flasks and shaken for 24 h using a thermostated shaker maintained at 30°C to attain equilibrium. Similar batch adsorption tests were carried out for the adsorption of Au(III), Pd(II), and Pt(IV) on Diaion CR11, a commercially available resin produced by Mitsubishi Chemical Company, Japan.
Adsorption isotherms of Au(III), and Pd(II), on IDA-paper gel were also obtained by using test solutions of varying concentrations of these metal ions, i.e. 0.5 - 10 mM in 1 M hydrochloric acid solution. Fifteen ml of each of test solutions were mixed together with 20 mg of adsorption gels and shaken for 60 h at 30°C to attain equilibrium.

Cycle Test for Au(III)/Cu(II) in Column mode. Because of the coexistence of precious metals together with other metal ions in a number of practical applications, a flow experiment for the separation of low concentrations of Au(III) from a high concentration of Cu(II) was carried out. A column packed with 0.1 g of the IDA-paper gel was prepared. Prior to passing the test solution, the column was conditioned with distilled water followed by 1 M hydrochloric acid solution for 24 h. Meanwhile, a test solution containing about 20 mg l⁻¹ of Au(III) and 100 mg l⁻¹ Cu(II) was prepared in 1 M hydrochloric acid. This solution was then pumped at a constant flow rate of 5 ml/h through the column using an Iwaki model PST-100N peristaltic pump for 24 h. To elute the sorbed metal ions, the loaded column was first washed with water and then with a mixture of 0.15 M thiourea and 1 M hydrochloric acid at a flow rate of 5 ml/h. In this way, five consecutive adsorption-elution cycles were run.

4.3. RESULTS AND DISCUSSION

Elemental Analysis. Results of elemental analyses of the IDA-paper gel are shown in Table 4.1. Since paper mainly consists of cellulose units, the % composition of individual elements in the functionalized paper was calculated on the basis of the tentative structure as shown in Scheme 4.1. The degree of modification was calculated by dividing the observed % by calculated % composition of nitrogen and the density of the functional group was calculated from the observed nitrogen value. From Table 4.1., the extent of modification was calculated as 60.2% (2.17 mol/kg functional group density). Paper cellulose is highly amorphous and is easily chemically modified whereas commercial cellulose, in contrast, is crystalline in nature and consequently reagents cannot penetrate easily into the inner parts of the matrix.
Table 4.1. Elemental composition of the IDA-paper gel

<table>
<thead>
<tr>
<th>Composition</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper type</td>
<td>(observed</td>
<td>(observed</td>
<td>(observed</td>
</tr>
<tr>
<td></td>
<td>/calculated)</td>
<td>/calculated)</td>
<td>/calculated)</td>
</tr>
<tr>
<td>Pretreated Paper</td>
<td>46.29/44.40</td>
<td>5.70/6.17</td>
<td>-</td>
</tr>
<tr>
<td>Chlorinated Paper</td>
<td>35.62/39.88</td>
<td>3.55/4.98</td>
<td>-</td>
</tr>
<tr>
<td>IDA-type paper</td>
<td>45.59 / 43.32</td>
<td>4.72 / 5.41%</td>
<td>3.04 / 5.05</td>
</tr>
</tbody>
</table>

**Effect of Shaking Time.** The adsorption kinetics of Au(III) and Pd(II) on the IDA-paper gel was studied at 30°C. Figure 4.1 shows the rate of adsorption of these metals with time. As is evident from the figure, in the case of both Au(III) and Pd(IV), it took nearly 20 h for equilibrium.

![Figure 4.1. Kinetics of adsorption of metal ions on IDA paper gel. Initial concentration of metal ions = 0.2 mM, wt. of gel = 20 mg, temperature = 30°C.](image)

**Batch wise Adsorption Behavior of the IDA-paper Gel.** The adsorption behavior of the IDA-paper gel for various metal ions is shown in Figure 4.2.(a) in which the waste paper gel was found to be selective only for Au(III) and Pd(II), which suggests that the gel not only discriminates against Pt(IV) but is also inert towards base metals such as Fe(III), Cu(II), Zn(II), and Ni(II) which are major contaminants of gold and palladium. Taking account of the fact that most of these metal ions coexist in various industrial waste
solutions and leach liquors, the result is promising for the selective recovery of Au(III) and Pd(II) from any base metal and most interestingly even from Pt(IV).

Figure 4.2.(b) shows that Diaion CR11, a commercially available synthetic ion exchange resin having Iminodiacetic acid functional groups, also exhibited a significant adsorption for all three metals at low concentration of HCl but adsorption for Pt(IV) and Pd(II) decreased gradually at higher concentrations. Thus, it was found to be suitable for selective adsorption of gold from highly acidic solution.

![Graph](attachment:image1.png)

(a)

![Graph](attachment:image2.png)

(b)

Figure 4.2. Adsorption behavior of a) IDA-paper gel b) Diaion CR11 for various metal ions as a function of hydrochloric acid concentration. Initial concentration of metal ions = 0.2 mM, wt. of gel = 20 mg, shaking time 24 h, temperature = 30°C.
Adsorption Isotherms for Precious Metal Ions. Since the gel has exhibited strong adsorption only for Au(III) and Pd(II), the adsorption isotherm study was carried out for these two metal ions. As is evident from Figure 4.3, the gel exhibits a remarkably high adsorption capacity of 3.3 mol/kg (650 mg/g) and 1.42 mol/kg (151 mg/g) dry weight of the gel for Au(III) and Pd(II), respectively in 1 M hydrochloric acid medium. This difference in capacity for Pd(II) and Au(III) is ascribed to the reduction of the Au(III) ion to the elemental form during adsorption as will be described in detail subsequently. It is noteworthy here that Diaion CR 11 showed 1.3 mol/kg capacity (256 mg/g of the resin) for Au(III) under similar experimental conditions.

Figure 4.3. The adsorption isotherms of Au(III) and Pd(II) ions on the waste paper gel. [HCl] = 1 M, weight of adsorbent = 20 mg, volume of the solution = 15 mL, shaking time = 60 h, temperature = 30°C.

In addition, considering the practical importance of the selective adsorption of precious metals in stronger acidic medium, it was preferred to observe the loading capacity of the waste paper gel at higher concentrations of hydrochloric acid. Adsorption isotherm study for Au(III) and Pd(II) was carried out also at 2 M, 3 M, and 4 M hydrochloric acid medium and the respective values are given in Table 4.2. Regardless of the acid concentration, comparable maximum loading capacities were observed for Au(III) and a slightly decreasing order was found for Pd(II). This result can be correlated well with that of Figure 4.2 where the adsorption percentage of Au(III) at higher acidic medium is only slightly lower than at 1 M and the values are in decreasing trend for Pd(II). Nevertheless, the stable
performance of the gel with comparably high adsorption capacities at any concentrations of hydrochloric acid provides strong advantage for the real life application.

Table 4.2. Maximum adsorption capacities of IDA-paper gel for Au(III) and Pd(II)

<table>
<thead>
<tr>
<th>[HCl] (mol.dm⁻³)</th>
<th>Au(III) (mg g⁻¹)</th>
<th>Pd(II) (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>650</td>
<td>151</td>
</tr>
<tr>
<td>2</td>
<td>609</td>
<td>133</td>
</tr>
<tr>
<td>3</td>
<td>603</td>
<td>119</td>
</tr>
<tr>
<td>4</td>
<td>587</td>
<td>101</td>
</tr>
</tbody>
</table>

In order to confirm the reduction of Au(III) to Au(0), the XRD spectrum of the gel was taken after the adsorption of Au(III). Sharp peaks at 2θ values of 38.24, 44.46, 64.6, 77.68 degrees were observed which belong to the metallic gold. The observation suggests the reduction of the Au(III) ion to the elemental form during adsorption. This fact was further reinforced from the SEM image of the gel taken after the adsorption of Au(III) as shown in Figure 4.4.(a) in which very fine aggregated particles of gold (gray complexion) with various shapes are distinct. Also, Figure 4.4.(b) shows a photograph of the sample solution and the gel in a glass vessel after shaking, from which the aggregated gold particles floating on the surface of the HCl solution can be seen. It was also observed that these aggregates became larger and denser with time and fell down to the bottom of the solution in a few hours. These results prove that gold particles formed by the reduction show a tendency to detach from the gel surface and form clean aggregates. This kind of observation was also found in our previous study.³

However, similar experiments for Pd(II) didn’t indicate the presence of elemental palladium which suggests that that the adsorption of palladium is purely an ionic interaction, whereas for gold, the ionic interaction is followed by subsequent reduction to the elemental form. This phenomenon is considered to be responsible for the higher adsorption capacity for gold, even higher than the amount of available functional sites as evaluated from the elemental analysis of the gel. Similarly, the XRD spectrum of Diaion CR11 taken after the adsorption of Au(III) did not exhibit any peaks for gold indicating that reduction of Au(III) does not occur in the case of this commercial resin.
Figure 4.4 (a) SEM image of the waste paper gel after the adsorption of Au\textsuperscript{III} at 100× magnification. Acceleration voltage = 15 kV. (b) Photograph of gold aggregates floating on the surface of HCl solution after adsorption.

**Mechanism of Adsorption.** As chloride media was the experimental condition, Au(III), Pd(II), and Pt(IV) exist mostly as anionic chloro complexes like AuCl\textsubscript{4}⁻, PdCl\textsubscript{4}²⁻, and PtCl\textsubscript{6}²⁻, respectively. Similarly, the tertiary amine group of the IDA-paper gel in hydrochloric acid medium is protonated as described by Equation 1. Hence, the adsorption of metal chloro complexes takes place according to the anion exchange reactions as expressed by Equation (2) for Au(III) and by Equation (3) for Pd(II) and Pt(IV), where the coordination numbers of these metal ions (4 for Au(III) & Pd(II) and 6 for Pt(IV)) are satisfied by coexisting Cl⁻ ions. Other metal ions such as Fe(III) and Zn(II) also give rise to anionic chloro complexes over a wide chloride concentration region and it is well known that these are solvent extracted with high molecular weight amines and adsorbed on anion exchange resins. However, these are not adsorbed to any extent on the present gels, a result which requires clarification in future work.

\[
\begin{align*}
R-N(CH_2COOH)_2 + H⁺.CI⁻ &\leftrightarrow R-N(CH_2COOH)_2H⁺.CI⁻ \quad (1) \\
R-N(CH_2COOH)_2H⁺.CI⁻ + AuCl₄⁻ &\leftrightarrow R-N(CH_2COOH)_2H⁺AuCl₄⁻ + CI⁻ \quad (2) \\
2[R-N(CH_2COOH)_2H⁺.MCI₆⁻^2] &\leftrightarrow [R-N(CH_2COOH)_2H⁺.MCI₆⁻] + 2CI⁻ \quad (3)
\end{align*}
\]

**Recovery of Precious Metals from Industrial Sample.** Before carrying out the adsorption tests, the industrial metal liquor TK was analyzed for its composition, qualitatively by using ICPS-8100, Sequential Plasma Spectrometer. The metal ions present
were as follows (in ppm): Fe(23000), Cu(8200), Ni(5800), Au(130), Pd(10) and Pt(<0.2). It shows that sample TK contains several times excess of copper, iron, and nickel than gold and palladium. The acid concentration of sample TK was found to be 1.5 M and it was expected to contain nitrate ions due to the fact that the solution was an aqua regia leachate.

![Graph](image.png)

Figure 4.5. Solid-liquid ratio for the adsorption of precious metals and copper from sample TK on DMA-paper gel.

A solid-liquid ratio adsorption tests in static mode taking 10 ml of TK with varying mass of the gel showed that almost complete recovery of precious metals takes place at a solid-liquid ratio of 5. The gel adsorbed only Au(III) and Pd(II), retaining the selectivity pattern, and also exhibited stability in strong acidic medium. This result is strongly encouraging in terms of selectivity and consistent adsorption of metal ions even in the presence of nitrate of aqua regia which is a common leaching agent in various metal refineries.

**Cycle Test for Au(III) /Cu(II) in Column mode.** Table 4.3 shows the results of the five consecutive adsorption-elution cycle tests for Au(III) /Cu(II) in continuous mode of operation. It is clear from the table that, more than 90% of the adsorbed Au(III) was eluted and recovered whereas Cu(II) was not adsorbed at all. The recovery % of gold in this study appears quite high and it is probably due to the optimal affinity of the waste paper gel for Au(III) ions.
Table 4.3. Performance of the IDA-paper gel in consecutive adsorption-elution cycles.
Concentration of Metal ions (in ppm): Au(20), Cu(100)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbed (mg)</td>
<td>1.78</td>
<td>1.79</td>
<td>1.75</td>
<td>1.77</td>
<td>1.77</td>
</tr>
<tr>
<td>Eluted (mg)</td>
<td>1.60</td>
<td>1.68</td>
<td>1.68</td>
<td>1.70</td>
<td>1.79</td>
</tr>
<tr>
<td>Recovery %</td>
<td>89.56</td>
<td>93.82</td>
<td>96.03</td>
<td>96.32</td>
<td>101.06</td>
</tr>
</tbody>
</table>

4.4. CONCLUSION

IDA-paper gel has been shown to be an excellent sorbent for the separation and recovery of gold and palladium from coexisting base metal ions in acidic leach liquors. Further, the metal ions loaded onto the gel can be easily recovered by using acidic thiourea. The stability of the gel in this highly acidic medium, its ability to reduce Au(III) to elemental form and more importantly, its high capacity for Au(III) as well as comparably high capacity for Pd(II) are some of the encouraging factors which make it promising for practical application.
REFERENCES


Chapter 5

DIMETHYLAMINE MODIFIED WASTE PAPER FOR THE
RECOVERY OF PRECIOUS METALS

Waste newsprint paper was modified with dimethylamine (DMA) to obtain a tertiary amine type adsorption gel called as DMA-paper gel. This new derivative was investigated for adsorption, from hydrochloric acid medium, of gold, palladium, and platinum as well as some base metals. The gel exhibited selectivity only for precious metals with a remarkably high capacity for Au(III) \textit{i.e.} 4.6 mol/kg-dry gel and comparable capacities \textit{i.e.} 2.1 and 0.9 mol/kg for Pd(II) and Pt(IV) respectively. Also, Au(III) was reduced to the elemental form during adsorption. Furthermore, column adsorption and subsequent elution of the adsorbed metal ions by acidic thiourea revealed encouraging recoveries (approx. 90\%), thus enhancing the scope of the gel for effective preconcentration, separation and recovery of precious metals. The effectiveness of recovery of precious metals from real industrial liquor was also tested and it showed highly encouraging results with respect to the stability of the gel in the harsh medium, and selectivity for the targeted metal ions in the presence of excess of other metal ions.

5.1. INTRODUCTION

Because of our growing concern for environmental pollution, impending metals crises as well as the fuel crisis, methods and processes for materials recycling and recovery have become very urgent for the creation of a sustainable world. Recycling and reuse of metals, in particular, is very important since it expands the supply of feedstock for advanced materials and prevents the practice of excessive mining. The market for electrical and electronic devices has experienced sharp growth recently due to the attractive mini-models and their user friendly features that keep being updated day by day to keep pace with intense competition. Personal computers, mobile phones and entertainment devices have brought unprecedented change to our lifestyle and thus they have become an indispensable
part of our daily life. However these regularly updated amenities have come only at the cost of a growing amount of electrical and electronic waste (e-waste), in municipal dump sites which has created negative impacts on the environment and which have also brought serious problems with regard to the supply of raw materials, especially precious metals which are not only scarce but also very essential for these advanced devices. This new crisis needs to be dealt with cautiously because it has both environmental and economic significance. However we should bear in mind that, in some cases, the precious metals content of the wastes disposed of in this form is unexpectedly higher than that in the ore itself.

The usual practice for the recovery of the metals from such wastes includes dismantling the devices and treating each part separately for metal recovery, after which parts like printed circuit boards (PCBs) are leached with aqua regia or hydrochloric acid containing chlorine gas. The conventional methods for the recovery of precious metals from such leach liquors involve the repeated use of various low capacity and/or low selectivity synthetic reagents. During such operations, large amounts of waste effluents or secondary wastes are generated that require costly treatment.

To try to improve this situation, some research works have been conducted by using adsorbents prepared from various biomass wastes as they are cheap, environmentally benign, biodegradable, and, most importantly, they exhibit special affinity or selectivity towards particular metal species due to the unique natural structure. Fortunately, several biomasses including trees, herbs, agricultural as well as marine byproducts, and also microorganisms have been found to be useful for the separation, preconcentration, and recovery of metals. However, in order to replace the conventional petrochemical based adsorbents by the renewable biomass sorbents in real cases, selectivity, stability, reproducibility and proper disposal schemes need to be verified.

In the present study, the prospective application of chemically modified waste paper for the recovery of Au(III), Pd(II), and Pt(IV) has been tested under acidic conditions.

5.2. EXPERIMENTAL

Materials. Waste newspaper was used as the feed material for the adsorption gel. Microcrystalline cellulose was purchased from Merck (Germany). Thionyl chloride was purchased from Sigma Aldrich, USA and dimethylamine (50%) from Wako Pure Chemical
Industries, Japan. Analytical grade chloroauric acid and chloroplatinic acid (both from WAKO, Japan) were used to prepare Au(III) and Pt(IV) test solutions, respectively. Real industrial leach liquor sample containing several metallic components including precious metals was kindly provided by Tanaka Kikinzoku, Tokyo, Japan. All other chemicals used for the synthesis and for adsorption tests were of analytical grade and were used without further purification.

Methodology. The amount of adsorption was calculated from the difference in metal concentration before and after adsorption and the weight of the adsorption gel. Metal ion concentrations were measured using a Shimadzu model ICPS-8100 ICP/AES spectrometer. Digital micrographs were observed by using a KEYENCE model VHX/VH series micro photographer. The FTIR spectra of the adsorption gel were determined with a JASCO model FTIR-410 using KBr disc base. A Rigaku RINT – 8829 X-ray diffractometer was used to record x-ray diffraction spectra (XRD).

Preparation of the Adsorption Gel. Waste newspaper was crushed by using a Dalton model P-3S power mill, washed with soap and water many times to remove grease particles and then treated with a 20% sodium hydroxide solution for 5 hours. It was washed again with water to remove excess NaOH till neutral pH. It was then dried in a convection oven at 50°C for 24 h.

Subsequently, 0.5 g of the pretreated paper was chlorinated by mixing together with 25 ml of pyridine in an ice bath. Thionyl chloride, (5 ml), was added drop wise and the mixture was heated at 70°C for 6 h under a N₂-atmosphere. The product obtained (0.5 g) was washed and dried overnight at 70°C in a convection oven.

Finally, 0.5 g of chlorinated paper and 5ml of dimethylamine (50%) were mixed together with 1 ml of formaldehyde (35%) and stirred at 90°C for 3 h. The product was washed several times with 0.1 mol/dm³ hydrochloric acid, 0.1 mol/dm³ sodium chloride solution, and finally with distilled water. It was dried at 60°C in a convection oven and crushed to obtain 0.43 g (150 μm mesh size) dimethylamine type adsorption gel in black powder form.

For comparison, commercially available microcrystalline cellulose was also modified by addition of a dimethyl amine group by the same method, and named as DMA-cellulose.
Scheme 5.1. Modification of waste paper with dimethylamine.

**Adsorption Tests.** A preliminary kinetic study of Au(III), Pd(II) and Pt(IV) uptake on the DMA-paper gel was carried out to determine the optimum time needed to reach equilibrium. The adsorption behavior of the DMA-paper gel for Au (III), Pd(II), Pt(IV), Cu(II), Fe(III), Ni(II), and Zn(II) was individually examined at varying hydrochloric acid concentrations (0.1 M to 4 M) (M = mol/dm$^3$). For each metal ion, the initial metal concentration was 0.2 mM. Fifteen ml of test solutions were mixed together with 20 mg of adsorption gels in stoppered flasks and shaken for 24 h using a thermostated shaker maintained at 30°C to attain equilibrium. Similar batch adsorption tests were carried out for the adsorption of Au(III), Pd(II), and Pt(IV) on DMA-cellulose and unmodified waste paper.

Adsorption isotherms of Au(III), Pd(II), and Pt(IV) on DMA-paper gel were also obtained by using test solutions of varying concentrations of these metal ions, i.e. 0.5 - 10 mM in 1 M hydrochloric acid solution. Fifteen ml of each of test solutions were mixed together with 20 mg of adsorption gels and shaken for 60 h at 30°C to attain equilibrium. Similarly, tests to check the effectiveness of DMA-paper gel for the recovery of precious metals from industrial liquors was tested in static mode.

**Column Experiment: Loading and Elution.** Because of their coexistence in a number of practical applications, a flow experiment for the separation of low concentrations of Au(III), Pt(IV) and Pd(II) from a high concentration of Cu(II) was conducted. A column (height = 24.5 cm, inner diameter = 8 mm) packed with 0.1 g DMA-paper gel was prepared. Prior to passing the test solution, the column was conditioned with distilled water followed by 1 M hydrochloric acid solution for 24 h. Meanwhile, a test solution containing about 20 mg l$^{-1}$ of each of Au(III), Pt(IV) and Pd(II) and 100 mg l$^{-1}$ Cu(II) was prepared in 1 M hydrochloric acid. This solution was then pumped at a constant flow rate of 6 ml/h
(Mean residence time = 4.52 min, Superficial flow velocity = 12 cm/h) through the column using an Iwaki model PST-100N peristaltic pump. The effluent solution was collected at 1 h time intervals using a Bio-Rad model 2110 fraction collector prior to measurement of the metal concentrations.

To elute the adsorbed metal ions, the loaded column was first washed with water and then passed a mixture of 0.1 M thiourea and 1 M hydrochloric acid at a rate of 6 ml/h. The eluate solution was collected similarly at 30 minute time intervals prior to determination of the metal concentration. Similarly, for adsorption-elution cycle tests, the column was loaded by passing the test solution containing about 20 mg l⁻¹ each of Au(III), Pd(II) and Pt(IV) in 1 M hydrochloric acid for 24 h and the adsorbed metals were eluted by the same method as described above. The adsorption/elution operation was repeated 3 times.

5.3. RESULTS AND DISCUSSION

Elemental Analysis. Results of elemental analyses of the DMA-paper gel and DMA-cellulose are shown in Table 5.1. Since paper mainly consists of cellulose units, the % composition of individual elements in the functionalized paper and cellulose was calculated on the basis of the tentative structure as shown in Scheme 5.1. The degree of modification was calculated by dividing the observed % by calculated % composition of nitrogen and the density of the functional group was calculated from the observed nitrogen value. From Table 5.1, for the DMA-paper gel, the extent of modification was calculated as 68.5 % (3.6 mol/kg functional group density), whereas, in the case of DMA cellulose, it was only 13.7 % (0.72 mol/kg functional group density). This difference in the extent of the modification under identical experimental conditions is attributable to the difference in the structure of paper and commercial cellulose. Paper cellulose is highly amorphous and is easily chemically modified whereas commercial cellulose is crystalline in nature and consequently reagents cannot penetrate easily into the inner parts of the matrix.

Table 5.1. Elemental composition of the DMA-paper gel and DMA-cellulose.

<table>
<thead>
<tr>
<th>Element</th>
<th>DMA-paper gel</th>
<th>DMA-Cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C %</td>
<td>H %</td>
</tr>
<tr>
<td>Calculated</td>
<td>50.79</td>
<td>7.93</td>
</tr>
<tr>
<td>Observed</td>
<td>45.71</td>
<td>4.45</td>
</tr>
</tbody>
</table>

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**Effect of Shaking Time.** The adsorption kinetics of Au(III), Pt(IV) and Pd(II) on the DMA-paper gel was studied at 30°C. Figure 5.1. shows the rate of adsorption of these metals with time. As is evident from the figure, in the case of Pd(II) and Pt(IV), equilibrium was reached within 5 h, whereas, in the case of Au(III), after a distinct change within 5 h, only slightly increased adsorption takes place after this time, indicating that the adsorption kinetics is fast for all three metal species but some other phenomenon might be occurring in the case of Au(III) resulting in a small but steady increase in adsorption.

![Figure 5.1. Kinetics of adsorption of metal ions on DMA-paper gel. Initial concentration of metal ions = 0.5 mM, [HCl] = 1 M, wt. of gel = 20 mg, temperature = 30 °C.](image)

**Effect of Hydrochloric Acid Concentration on the Adsorption Behavior of the DMA-paper Gel.** The adsorption behavior of the DMA-paper gel for various metal ions is shown in Figure 5.2.(a), from which it is clear that all three precious metal ions i.e. Au(III), Pt(IV) and Pd(II) were quantitatively adsorbed over the whole region of hydrochloric acid concentration, whereas the gel showed no affinity for base metals like Cu(II), Fe(III), Ni(II) and Zn(II). This result indicates that the precious metals can be selectively recovered from any other coexisting base metal ions in hydrochloric acid medium using the DMA-paper gel. According to our previous study, Diaion WA30, a commercially available synthetic anion exchange resin having dimethylamine functional group, showed a sharp decrease in Pd(II) adsorption and a significant increase in Fe(III) adsorption with increasing concentration of hydrochloric acid. Similarly, considerable adsorption of Zn(II) has also been observed at low acid concentration.  

8
The adsorption behavior of the DMA modified cellulose under the same conditions is shown in Figure 5.2.(b). As expected from its poor degree of modification, adsorption of Au(III), Pd(II), and Pt(IV) is quite insignificant. The adsorption behavior of unmodified waste paper also was insignificant (not shown). From this comparison, it can be concluded that the waste paper gel, which can be prepared by a simple modification process, can be utilized as an advanced sorption active material for the recovery of precious metals from complex mixtures with other metals.

Figure 5.2. Adsorption behavior of DMA-paper gel (a), and DMA modified microcrystalline cellulose (b) for various metal ions as a function of hydrochloric acid concentration. Initial concentration of metal ions = 0.2 mM, wt. of gel = 20 mg, shaking time 24 h, temperature = 30°C.
Adsorption Isotherms for Precious Metal Ions. The adsorption isotherm study for Au(III), Pd(II) and Pt(IV) onto the DMA-paper gel was carried out taking individual metal solutions of various concentrations. As shown in Figure 5.3, adsorption increases with increasing metal concentration in the low concentration region while it tends to approach constant values corresponding to each metal species in the high concentration region, i.e. plateau region, suggesting a typical Langmuir type adsorption. From the constant values in the plateau region, maximum adsorption capacity was evaluated as 4.6 mol/kg of the dry gel for gold which means 1 kg of the DMA-paper gel is capable of recovering almost an equivalent amount of gold. Taking account of the selectivity over other metal ions and the simplicity of gel preparation, this result is remarkable. Similarly, the capacities for palladium and platinum were determined to be 2.1 and 0.9 mol/kg respectively, which are also comparatively high compared with those for other adsorbents, as shown in Table 5.2.

Similar to our previous work on a lignophenol gel, the very high capacity for gold is attributed to the reduction of Au(III) to the elemental form during adsorption. In order to confirm the reductive adsorption of gold, the XRD spectrum of the gel before and after adsorption of Au(III), Pd(II), and Pt(IV) was determined. Four peaks at 38°, 44.5°, 64°, and 77° assigning to elemental gold were distinctly observed whereas no such peaks corresponding to elemental palladium and platinum were noticed. From this difference, it is obvious that the adsorption of palladium and platinum is purely an ionic interaction, whereas for gold, the ionic interaction is followed by subsequent reduction to the elemental form. This phenomenon is considered to be responsible for the higher adsorption capacity for gold, even higher than the amount of available functional sites as evaluated from the elemental analysis of the gel. However, the XRD spectrum of Diaion WA30 taken after the adsorption of Au(III) did not exhibit any peaks for gold indicating that reduction of Au(III) does not occur in the case of this commercial resin.
Figure 5.3. The adsorption isotherms for Au(III), Pd(II) and Pt(IV) on DMA-paper gel. \([\text{HCl}]=1 \text{ M}, \text{ vol. of solution}=10 \text{ ml}, \text{ shaking time}=60 \text{ h}, \text{ temperature}=30^\circ \text{C}, \text{ wt. of gel}=20 \text{ mg}.\)

Table 5.2. Comparison of loading capacities for Au(III), Pd(II), and Pt(IV) with other adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Loading capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au(III)</td>
<td>Pd(II)</td>
</tr>
<tr>
<td>Lysine modified crosslinked chitosan</td>
<td>70.3</td>
<td>109</td>
</tr>
<tr>
<td>Glycine modified crosslinked chitosan resin</td>
<td>170</td>
<td>120</td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole-bonded silica gel</td>
<td>4.5</td>
<td>18</td>
</tr>
<tr>
<td>Poly(vinylbenzylchloride–acrylonitrile–divinylbenzene) modified with tris(2-aminoethyl)amine</td>
<td>190</td>
<td>280</td>
</tr>
<tr>
<td>Amberlite IRC 718</td>
<td>136</td>
<td>58.5</td>
</tr>
<tr>
<td>EN-Lignin</td>
<td>607</td>
<td>22.7</td>
</tr>
<tr>
<td>PA-Lignin</td>
<td>384</td>
<td>40.4</td>
</tr>
<tr>
<td>Glutaraldehyde-crosslinked chitosan</td>
<td>565.5</td>
<td>180</td>
</tr>
<tr>
<td>Sulphur derivative of chitosan</td>
<td>624</td>
<td>352</td>
</tr>
<tr>
<td>Glutaraldehyde-crosslinked chitosan flakes</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DMA paper</td>
<td>906</td>
<td>224</td>
</tr>
</tbody>
</table>
Mechanism of Adsorption. As all the adsorption tests were carried out in chloride media, Au(III), Pd(II), and Pt(IV) exist mostly as anionic chloro complexes like AuCl₄⁻, PdCl₂⁻, and PtCl₆²⁻, respectively. Similarly, the tertiary amine group of the DMA-paper gel in hydrochloric acid medium is protonated as described by Equation 1). Hence, the adsorption of metal chloro complexes takes place according to the anion exchange reactions as expressed by Equation 2) for Au(III) and by Equation 3) for Pd(II) and Pt(IV), where the coordination numbers of these metal ions (4 for Au(III) & Pd(II) and 6 for Pt(IV)) are satisfied by coexisting Cl⁻ ions. Other metal ions such as Fe(III) and Zn(II) also give rise to anionic chloro complexes over a wide chloride concentration region and it is well known that these are solvent extracted with high molecular weight amines and adsorbed on anion exchange resins. However, these are not adsorbed to any extent on the present gels, a result which requires clarification in future work.

\[
\begin{align*}
\text{R}-N(CH₃)₂ + H⁺\cdot Cl⁻ & \leftrightarrow \text{R}-N(CH₃)₂H⁺\cdot Cl⁻ \\
\text{R}-N(CH₃)₂H⁺\cdot Cl⁻ + AuCl₄⁻ & \leftrightarrow \text{R}-N(CH₃)₂H⁺\cdot AuCl₄⁻ + Cl⁻ \\
2[R-N(CH₃)₂H⁺\cdot Cl⁻ + MCl₆²⁻] & \leftrightarrow [R-N(CH₃)₂H⁺\cdot MCl₆²⁻ + 2Cl⁻] \quad M = Pt(IV), Pd(II)
\end{align*}
\]

Column Experiment: Loading and Elution. Since the DMA-paper gel has shown high selectivity and adsorption capacity for gold, palladium and platinum, the selectivity over other metal ions was tested by selectively recovering these precious metals from a mixture containing an excess concentration of Cu(II), a representative base metal coexisting in practical waste solutions as mentioned earlier, by means of column operation. Figure 5.4.(a) shows the breakthrough profile of the tested metal ions from the column packed with DMA-paper gel. The breakthrough of Cu(II) took place immediately after the start of flow whereas it took about 250 bed volumes for Pt(IV). Similarly, in the case of Au(III) and Pd(II), breakthrough occurred after more than 300 bed volumes. From the area of the breakthrough curve, the maximum loading capacities of the DMA-paper gel for Au(III), Pt(IV) and Pd(II) were evaluated as 0.26, 0.31 and 0.60 mol/kg of the dry gel respectively. These values are much lower than the values observed in the batch wise adsorption isotherm study, which is possibly attributable to the continuous flow of the solution, competitive adsorption, lower metal concentration compared to that in the
isotherm test (increasing adsorption with increase in metal concentration) and slower reduction kinetics in the case of gold.

![Graph](image)

(a)

![Graph](image)

(b)

Figure 5.4. Breakthrough profiles for Cu(II), Au(III), Pd(II), and Pt(IV). Feed concentration: Cu(II) = 100 ppm, Au(III), Pd(II), Pt(IV) ~ 20 ppm, flow rate = 6 ml/h (a). Elution profiles for loaded metal ions with 0.1 M thiourea in 1 M HCL. Flow rate = 6 ml/h.

Figure 5.4.(b) shows the elution profiles of the loaded precious metal ions with acidic thiourea solution. It reveals that all the metals were eluted with high concentration factors of 35 for Pd (II), 28 for Pt (IV), and nearly 20 for Au (III).

In the same way, a further two more consecutive adsorption-elution cycle tests were conducted. The results are shown in Table 5.3. In the first cycle the test solution was passed until complete saturation was reached (Figure 5.4.) whereas in cycles 2 and 3 the
test solution was passed only for 24 h. For this reason a big difference in the amount loaded in cycle 1 and 2 is observed.

It is clear from the table that, on average, 92.8 % Au(III), 85.2% Pt(IV) and 88.5% Pd(II) were eluted and recovered. The recovery % of precious metals in this study appears quite high and it is probably due to the optimal affinity of the waste paper gel for the metal ions. Almost complete recovery of the loaded metal ions including the reduced gold from the loaded gel verifies the easy regeneration of gel for repeated use. In addition, comparable loading and recovery was achieved in each cycle which means the DMA-paper gel can be effectively used for at least three consecutive cycles adding more economic and environmental benefit to the material.

Table 5.3. Performance of the DMA-paper gel in consecutive adsorption-elution cycles.

<table>
<thead>
<tr>
<th></th>
<th>Cycle 1 (mg)</th>
<th>Cycle 2 (mg)</th>
<th>Cycle 3 (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adsorbed</td>
<td>Eluted</td>
<td>% Recovery</td>
</tr>
<tr>
<td>Au(III)</td>
<td>5.07</td>
<td>4.86</td>
<td>95.9</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>6.09</td>
<td>4.62</td>
<td>75.9</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>6.37</td>
<td>4.32</td>
<td>67.8</td>
</tr>
</tbody>
</table>

The IR spectra of the DMA-paper gel was taken before and after Au(III) loading and elution. In Figure 5.5., the disappearance of a weak band at 1581 cm\(^{-1}\) (corresponding to R\(_2\)-NH) in the gel after adsorption and the appearance of new peaks in 2370-2380 cm\(^{-1}\) region (corresponding to R\(_3\)NH\(^+\), though it may not be strong evidence) indicates the adsorption process. Some new peaks also appear after elution at 958 and 1112 cm\(^{-1}\) in the spectra. However, it is not easy to trace the source of electrons responsible for the reduction of gold to its elemental form by spectroscopic methods as described by Richardson et.al.\(^{20}\)
Recovery of Precious Metals from Industrial Sample. Before carrying out the adsorption tests, the industrial metal liquor TK was analyzed for its composition, qualitatively by using ICPS-8100, Sequential Plasma Spectrometer. Several metal ions and some other elements were found to be present at various proportions of concentration. Metal ions in the order of tentative concentration range in ppm are: in thousands range - Copper, Zinc, Iron, Nickel, Chromium, Aluminum, and Cadmium; in hundreds range - Iridium, Bromine, Calcium, Molybdenum, Gold, Titanium, Erbium, Manganese, and Phosphorus; and in tenths range - Tin, Iodine, Lead, Tungsten, Silver, Palladium, Platinum, and so on. Similarly the concentrations (in ppm) of precious metals and some base metals were measured quantitatively and are found to be Cu(8400), Zn(2600), Fe(1900), Au(250), Pd(16), and Pt(11). It shows that sample TK contains several times excess of copper, iron, and zinc than gold, palladium, and platinum. As the aqueous chemistry of one metal ion may resemble with some other in the mixture, recovering any desired metal from such a complex mixture is a tough task. Also, finding an adsorption material or any solvent extraction agent which is exclusively selective towards a single metal ion is rare. Considering this fact, any sorbent that will be useful to recover precious metals must be especially inert towards the metal ions like copper, iron and zinc and also for other coexisting metal ions.
Figure 5.6. Solid-liquid ratio for the adsorption of precious metals and copper from sample TK on DMA-paper gel.

The acid concentration of sample TK was found to be 2.5 M, hence the adsorption test was carried out without further treatment. Also, as the sample was generated after aqua regia treatment, it is expected to contain some nitrate ions. In order to know the affinity of DMA-paper gel for the precious metals in the TK mixture, solid-liquid ratio adsorption tests in static mode taking 10 ml of TK with varying mass of the gel was carried out. The observed result is summarized in Figure 5.6. It shows that almost complete recovery of precious metals takes place at solid-liquid ratio as less as five. As explained earlier the concentration of copper in sample TK is several folds higher than that of any given metals but its adsorption as observed in Figure 5.6. is nearly zero. Despite the concept that many metal ions including gold, palladium, platinum, and copper form anionic chloro-complexes in acidic chloride medium, the selective adsorption of precious metals in comparatively low concentration over the dominating level of copper ion is very interesting. In addition, the adsorption of other metal ions like iron or zinc, the concentration of which in TK are also several folds of that of the precious metals was found to be negligible. Also, the selectivity pattern over other metal ions present in smaller concentration range was tentatively studied by performing the qualitative measurement of the samples after adsorption and no significant difference in concentration of any such metal ions was detected. These all results confirm the fact that the selectivity pattern of DMA-paper gel
observed in the batch test of individual model solution can be obtained in the real solution too. This result is strongly encouraging in terms of selectivity and consistent adsorption of metal ions even in the presence of nitrate of aqua regia which is a common leaching agent in various metal refineries.

5.4. CONCLUSION

The DMA-paper gel, prepared by simple chemical modification of waste paper, exhibited remarkable capacity and efficiency for the preconcentration and separation of gold, platinum, and palladium from other co-existing metal ions at low to high concentration levels. The high sorption capacity for gold is very interesting because Au(III) is reduced by the gel, after sorption, to the elemental form and gold aggregates are formed. In contrast, Pt(IV) and Pd(II) are sorbed only by pure ionic interaction and their oxidation states remain unchanged. The fact that valuable high demand metals can be recovered by using waste paper looks promising for its practical future application. From an economic viewpoint, this gel raises the prospect for recovering expensive metals at low cost and, from the environmental viewpoint; this gel is quite environmentally benign and acceptable.
REFERENCES


RECOVERY OF PRECIOUS METALS BY \textit{p}-AMINOBENZOIC ACID MODIFIED WASTE PAPER

Waste newsprint paper was chemically modified with \textit{p}-amino benzoic acid to prepare a sorption active gel. This gel proved useful for the selective uptake of gold, palladium, and platinum over other coexisting metal ions such as copper, nickel, zinc, and iron. A remarkably high capacity for Au(III) was observed together with a moderate uptake of Pt(IV) and Pd(IV). Furthermore, Au(III) was reduced to elemental gold which formed aggregates. A high percentage recovery of the precious metal ions (85-95\%) and regeneration of the gel was attained by using a mixture of 0.15 M thiourea and 1 M HCl. Repeated cycles of uptake and elution by using a column packed with this new sorbent indicated that the gel is suitable for industrial application in continuous mode.

6.1. INTRODUCTION

Paper is an important part of our everyday life and also one of the various cellulosic biomass wastes generated in voluminous amounts in various fields. It is not a surprise that paper can be recycled and reused as paper only for a limited number of times due to the shortening of fibre length and lowering of the fibre tensile strength at each successive step of recycling. As a result, it loses most of its value and becomes worthless garbage which occupies 30-40\% of landfill sites in developed countries.\footnote{Also, the fibres left over from the process of paper production, which contain over 70\% of pure cellulose, have been usually discarded with the wastewater in amounts of...}
several thousands tonnes a year, thus presenting a significant environmental pollution problem. Consequently, from the perspectives of both environment and economy, efforts are being made to reclaim value from this cheap biomass in the form of energy and advanced functional materials by the effective use of its unique characteristics.

At the same time, mining of precious metals has been scaled up worldwide owing to the ever increasing demand of these metals in recent decades. During metal refining, large volumes of aqueous by-products are produced, which contain a substantial proportion of high-value metals, along with other metals. These precious metals are discarded, while the discharge of coexisting toxic metals leads to the contamination of the aqueous system.

Conventional methods for the removal or recovery of such low concentrations of dissolved metal ions from wastewaters are solvent extraction, chemical precipitation, and ion exchange (using synthetic ion exchange resins). Such methods suffer from significant disadvantages such as incomplete metal removal, high capital costs, large chemical and/or energy requirements, and generation of toxic sludges or other waste products that require disposal. These drawbacks have given rise to the need for more economical and effective methods for the recovery of metals from wastewaters.

In this context, sorption processes using low cost and widely available biomass materials (living or dead) represent an interesting alternative as they have shown great promise for the treatment of pollutants in industrial effluents. More recently, materials like fungal, algal, and bacterial biomass as well as alginate and chitosan have been extensively studied for their remarkable and high sorption capacities. From an environmental viewpoint, the use of biomass materials is more favourable because it is easier to recover the loaded metal ions from biomass either by elution or by incineration. Sorption by waste paper, in particular, can be a promising alternative since it acquires a special property for binding and accumulating metals even at traces levels,
like other biomasses. In previous work, we have successfully utilized modified waste paper for the preconcentration and separation of heavy metal ions.\textsuperscript{3}

Unlike commercially available cellulose, waste paper cellulose is highly amorphous and hence is more accessible to chemical modification. A high degree of functionalization can therefore be achieved, even under normal laboratory conditions. Generally, amine ligands are known to effectively coordinate to platinum group metals and are applied mainly as anion exchange extractants in hydrometallurgical processes\textsuperscript{7}. Castro et al. have immobilized \( p \)-amino benzoic acid on microcrystalline cellulose to test the sorption of some metal ions viz. Cu(II), Pb(II), Zn(II), Cd(II) and Ni(II) in a pH range of 1-7.\textsuperscript{8} In the present study, we have investigated a waste paper gel modified with the same group for the sorption of precious and other metals from varying concentrations of hydrochloric acid.

6.2. EXPERIMENTAL

Materials. Waste newspaper was used as the feed material for the sorption gel. Thionyl chloride was purchased from Sigma Aldrich, USA, and sodium \( p \)-aminobenzoate from Tokyo Chemical Industries (TCI), Japan. Analytical grade chloroauric acid and chloroplatinic acid (both from WAKO, Japan) were used to prepare the Au(III) and Pt(IV) test solutions, respectively. Ion exchange resins viz. Diaion WA 30, Diaion WA21 and Diaion CR11 were acquired from the Mitsubishi Chemical Corporation, Japan. All other chemicals used for the synthesis and for the sorption tests were of analytical grade and were used without further purification.

Methodology. The amount of sorption was calculated from the difference in metal concentration before and after sorption and the weight of the sorption gel. Metal ion concentrations were measured by using a Shimadzu model ICPS-8100 ICP/AES spectrometer. The IR spectra of the sorption gel were measured with a JASCO model FTIR-410 using KBr pellets. A Shimadzu model XRD-610D (LabX) series X-ray
differential was used to record x-ray diffraction spectra (XRD) using a 2θ range of 10-80 degrees and a scanning rate of 1 degree/min. Scanning electron microscopy (SEM) analysis of the sorbent was carried out using a Hitachi model E1030 Ion Sputter and Hitachi model S-3000, 132-10, EDAX scanning electron microscope under an acceleration voltage of 15 KV (magnification = 100x). An Orion triode electrode, ORION 900011 model (Thermo Electron Corporation) was used for measurement of the Oxidation Reduction Potential (ORP) using a platinum electrode and an Ag/AgCl reference electrode filling solution.

Preparation of the Sorbent. For the preparation of the p-amino benzoic acid modified paper gel, waste newsprint paper was treated with sodium hydroxide and washed several times with water in order to remove any soluble impurities. Chemical modification was performed according to Scheme 6.1. At first, 5 ml of thionyl chloride was dropped onto 0.5 g of pre-treated paper (1), immersed in 25 ml of pyridine for about 1 hour in a N₂ atmosphere and ice bath conditions. After 1 hour, the reaction mixture was heated for 6 h in an oil bath at 70°C. The resultant compound was mixed with water and filtered. It was washed with water many times till neutral pH and then dried in an oven for a day at 50°C. This intermediate product i.e. chlorinated paper (2), was immersed in 25 ml of DMF and 1 g of sodium p-amino benzoate, dissolved in a minimum amount of water, was added. The reaction mixture was stirred with heating at 130 °C in an oil bath for 35 h. The resulting solid was filtered, treated with 0.1 M HCl, washed with water till neutral pH and then dried for a day at 60°C. This p-amino benzoic acid modified paper gel (3) (0.43 g, 86% yield), which is called hereafter PAB-paper gel, was characterised by IR spectra and elemental analysis.
Scheme 6.1. Preparation of the PAB-type waste paper gel

Sorption Tests. A preliminary kinetic study of the uptake for Au(III), Pd(II) and Pt(IV) ions using the PAB-paper gel was carried out to determine the optimum time needed to reach equilibrium. The uptake behaviour of the PAB-paper gel for Au (III), Pd(II), Pt(IV), Cu(II), Fe(III), Ni(II), and Zn(II) was individually examined at varying hydrochloric acid concentrations (0.1 M to 4 M). For each metal ion, the initial metal concentration was 0.2 mM. Fifteen ml of the test solution were mixed together with 20 mg of the gel in stoppered flasks and shaken for 24 h using a thermostated shaker maintained at 30°C. Similar batch tests were carried out for the uptake of Au(III), Pd(II), and Pt(IV) on unmodified waste paper for comparison.

Sorption isotherms of Au(III), Pd(II), and Pt(IV) on the PAB-paper gel were also obtained by using test solutions of varying concentrations of these metal ions, i.e. 0.5-10 mM in 1 M hydrochloric acid solution. Fifteen ml of each of the test solutions were mixed together with 20 mg of the sorption gel and shaken for 60 h at 30°C.

Column Experiment: Sorption and Elution. Because of the coexistence of precious metals together with other metal ions in a number of practical applications, a flow experiment for the separation of low concentrations of Au(III) from a high concentration of Cu(II) was carried out. A column packed with 0.1 g of the PAB-paper gel was prepared. Prior to passing the test solution, the column was conditioned with distilled water followed by 1 M hydrochloric acid solution for 24 h. Meanwhile, a test solution containing about 20 mg l⁻¹ of Au(III) and 100 mg l⁻¹ Cu(II) was prepared in 1
M hydrochloric acid. This solution was then pumped at a constant flow rate of 6.5 ml/h through the column using an Iwaki model PST-100N peristaltic pump. The output solution was collected at 1 h time intervals using a Bio-Rad model 2110 fraction collector prior to the measurement of metal concentrations.

To elute the sorbed metal ions, the loaded column was first washed with water and then with a mixture of 0.15 M thiourea and 1 M hydrochloric acid at a flow rate of 6.5 ml/h. The output solution was collected similarly at 30 minute time intervals prior to the measurement of the metal concentration. Similarly, for sorption-elution cycle tests, the column was loaded by passing the test solution containing 20 mg l⁻¹ Au(III) and 100 mg l⁻¹ Cu(II) in 1 M hydrochloric acid for 15 h and the sorbed metal ion (Au only) was eluted by the same method as described above. The sorption/elution operation was repeated 5 times. The cycle test for Pd(II) and Pt(IV), (both 20 mg l⁻¹ in 1 M hydrochloric acid, passing time = 24 h) was also carried out 4 times under similar conditions.

**ORP Study:** For the ORP measurement, a stock solution containing 2 mM Au(III) in 1 M HCl was prepared. Fifteen ml of the solution was mixed together with 20 mg of the gel in sample bottles and shaken in a thermostated shaker at 30°C for varying time intervals after which the ORP was measured. The residual concentration of Au(III) ion was measured after filtration, as described above.

6.3. RESULTS AND DISCUSSION

**Characterization of the Gel.** The degree of immobilization of the p-amino benzoic acid group onto the waste paper was analyzed by means of FTIR and elemental analysis. FTIR (KBr): Waste paper; ν 3420 (O-H), 2913(C-H), 1164(C-O-C), 899(C=H), 1051 (C-O); and PAB-paper gel; ν 3400 (O-H, N-H broad), 1639(C=O), 1513 (C=C), 1278 (aromatic ring deformation), confirms the introduction of the p-amino benzoic group onto the paper matrix. Elemental analysis: Observed: C, 33.16;
H, 3.35; N, 3.35.; and expected for C₁₃H₁₅NO₆: C, 55.51; H, 5.34; N, 4.98 gives the degree of substitution as 68% which accounts for 2.39 mol of functional group per kg of the paper.

**Sorption Kinetics.** The sorption kinetics of the PAB-paper gel was studied at 30°C. Figure 6.1. shows the rate of sorption of Au(III), Pt(IV) and Pd(II). As is evident from this figure, in the case of Pt(IV), equilibrium was reached within 5 h, whereas, in the case of Au(III) and Pd(II), it took a longer time (about 24 h). The kinetic data in the inset depicts the sorption % in 0-2 h. It is clear from the figure that almost 80% of the Au(III) and Pd(II) ions present in the solution are sorbed within 2 h whereas only about 60% of Pt(IV) was sorbed in the same time. In short, although the total equilibrium time is longer compared to ion exchange resins, the sorption rate at the beginning is quite appreciable. However, for determining the sorption capacity, a longer period (50 h) was adopted, the rationale for which will be justified in a later section.

![Graph](image_url)

**Figure 6.1.** Sorption kinetics of metal ions using the PAB paper gel. Initial concentration of metal ions = 0.5 mM, [HCl] = 1 M, wt. of gel = 20 mg, temperature = 30 °C.
Uptake Experiments at Varying HCl Concentrations. The sorption behaviour of the PAB-paper gel for various metal ions is shown in Figure 6.2.(a), from which it is clear that all three precious metal ions i.e. Au(III), Pt(IV) and Pd(II) were quantitatively sorbed over the whole range of hydrochloric acid concentrations, whereas the gel showed no affinity for metals like Fe(III), Ni(II) and Zn(II). Some Cu(II) was sorbed at low HCl concentrations but sorption was negligible at higher concentrations of HCl. A study on the metal uptake behaviour of unmodified waste paper was also carried out and the degree of sorption was found to be insignificant (result not shown).

In order to compare the results observed for the PAB-paper gel, similar experiments were carried out by using three different types of commercial ion exchange resins containing amine groups. Although an exact analogue of the PAB paper gel was not available, Diaion WA30 (dimethyl amine), Diaion WA21 (polyethylene poly amine), and Diaion CR11 (iminodiacetic acid) were taken as representative amine-containing resins. The selectivity shown by Diaion WA30 was found to be poorer than that of the waste paper gel as reported in our previous study. The results observed for Diaion WA21 and Diaion CR11 are given in Figures 6.2.(b) and (c), respectively. The performance of Diaion WA21 was found to be poorer than that of the paper gel, whereas, in the case of Diaion CR11, only gold selectivity was significant with less sorption affinity for Pt(IV) and Pd(IV). However, besides the difference in selectivity, taking account of the origin of waste paper gel as an easily available biomass waste with little chances for further recycling and the simple steps required for modification, it certainly possesses stronger scope for use as an alternative sorption material.
Figure 6.2. Sorption of various metal ions over a range of hydrochloric acid concentrations. \[ D = \frac{\text{mol} \ M^{n+} / \text{kg of dry gel}}{\text{mol} \ M^{n+} / \text{l of solution}} \]. (a) PAB paper gel, (b) Diaion CR 11, and (c) Diaion WA 21. Initial concentration of metal ions = 0.2 mM, wt. of gel = 20 mg, shaking time 24 h, temperature = 30°C.
Sorption Mechanism. Since all the sorption tests were conducted in hydrochloric acid medium, it is important to note the most stable forms of the metals under discussion in acidic chloride media. The species distribution diagrams for Au(III), Pd(II), and Pt(IV) are shown in Figure 6.3.\textsuperscript{10} It is clear from the figures that Au(III), Pd(II), and Pt(IV) exist mostly as anionic chloro-complexes like $\text{AuCl}_4^-$, $\text{PdCl}_4^{2-}$, and $\text{PtCl}_6^{2-}$, respectively in the strong acidic conditions of the experiment. Because the PAB-paper gel has selectively sorbed only the precious metals, with no distinct sorption affinity for other metal ions, it is important to note the aqueous chemistry of the various other metal ions also in chloride medium. While the anionic chloride species of Au(III), Pd(II), or Pt(IV) exist over a wide range of chloride concentrations, metal ions like Cu(II), Zn(II), Fe(III) and Ni(II) exist mostly as cationic or neutral species and the concentration of anionic chlorides is significant only at higher chloride concentration.\textsuperscript{11} This dominance of the precious metal anions in the 1-4 M HCl concentration range almost certainly accounts for their selective adsorption.

The amine group of the PAB-paper gel in hydrochloric acid medium is protonated as described by Equation (1). Hence, the sorption of metal chloro-complexes takes place according to the anion exchange reactions as expressed by Equation (2) for Au(III) and Equation (3) for Pd(II) and Pt(IV), where the coordination numbers of these metal ions (4 for Au(III) & Pd(II) and 6 for Pt(IV)) are satisfied by coexisting $\text{Cl}^-$ ions.

\[
\begin{align*}
R-\text{NH}_2\text{C}_6\text{H}_4\text{COOH} + \text{H}^+ \cdot \text{Cl}^- & \leftrightarrow R-\text{NH}_2^+(\text{C}_6\text{H}_4\text{COOH})_2.\text{Cl}^- \quad (1) \\
R-\text{NH}_2^+(\text{C}_6\text{H}_4\text{COOH})_2.\text{Cl}^- + \text{AuCl}_4^- & \leftrightarrow R-\text{NH}_2^+(\text{C}_6\text{H}_4\text{COOH})_2.\text{AuCl}_4^- + \text{Cl}^- \quad (2) \\
2R-\text{NH}_2^+(\text{C}_6\text{H}_4\text{COOH})_2.\text{Cl}^- + M\text{Cl}^{2+} & \leftrightarrow R-\text{NH}_2^+(\text{C}_6\text{H}_4\text{COOH})_2.\text{MCl}_2^{2+} + 2\text{Cl}^- \quad M = \text{Pt, Pd} \quad (3)
\end{align*}
\]
Figure 6.3. Chemical speciation diagrams of Au(III), Pd(II), and Pt(IV) ions with respect to chloride concentration.

Sorption Isotherms. Since the PAB-paper gel has shown strong sorption affinity for Au(III), Pd(II) and Pt(IV), its sorption isotherm was examined. As shown in Figure 6.4., sorption increases with increasing metal concentration at low concentration while the isotherms tend to approach constant values corresponding to each metal species at high
concentration, *i.e.* a plateau region, suggesting a typical Langmuir type sorption. From the constant values in the plateau region, the maximum sorption capacity for Au(III) was evaluated as 5.1 mol/kg (1005 gm/kg of dry gel) in 1 M hydrochloric acid medium. Although some studies on sorption on biomasses have reported higher capacities for Au(III) in acidic medium, such a high capacity has been rarely observed. 9,12-16 This high capacity of the PAB-paper gel can be applied for the preconcentration and recovery of gold contained in wastewater generated by metal refineries or other industries. Likewise, the gel has shown about 1.5 mol/kg (160 g/kg of the dry gel) and 0.5 mol/kg (98 g/kg of the dry gel) loading capacity for Pd(II) and for Pt(IV), respectively. Although these values are much lower than that for Au(III), compared to the recovery of Pd(II) and Pt(IV) by other biomass wastes, as shown in Table 1, the capacity is appreciable.

Figure 6.4. The sorption isotherms of Au(III), Pd(II) and Pt(IV) on the PAB-paper gel. Ce = Equilibrium concentration, q = amount of metal uptake, [HCl] = 1 M, wt. of gel = 20 mg, vol. of solution = 15 ml, shaking time = 50 h, temperature = 30°C.
Table 6.1. Comparison of the loading capacities for Au(III), Pd(II), and Pt(IV) on other sorbents.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Loading capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au(III)</td>
<td>Pd(II)</td>
</tr>
<tr>
<td>Ethylenediamine modified crosslinked lignophenol</td>
<td>607</td>
<td>22.7</td>
</tr>
<tr>
<td>gel (EN-Lignin)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary amine modified crosslinked lignophenol</td>
<td>384</td>
<td>40.4</td>
</tr>
<tr>
<td>gel (PA-Lignin)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lysine modified crosslinked chitosan</td>
<td>70.3</td>
<td>109</td>
</tr>
<tr>
<td>Glycine modified crosslinked chitosan resin</td>
<td>170</td>
<td>120</td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole-bonded silica gel</td>
<td>4.5</td>
<td>18</td>
</tr>
<tr>
<td>Poly(vinylbenzylchloride–acrylonitrile–divinylbenzene) modified with tris(2-aminoethyl)amine</td>
<td>190</td>
<td>280</td>
</tr>
<tr>
<td>Amberlite IRC 718</td>
<td>136</td>
<td>58.5</td>
</tr>
<tr>
<td>PAB-paper gel</td>
<td>1004</td>
<td>260</td>
</tr>
</tbody>
</table>

Obviously, the sorption capacity of the gel for Au(III) was much higher than the functional group density of the amino group immobilized on the gel. The high sorption capacity of the gel can be explained in terms of the formation of clearly visible gold particles on the surface of the test solution. During or presumably after sorption, the gel reduced gold ions to elemental gold particles. XRD spectra of the gel were taken before and after the sorption to confirm the presence of elemental gold. Additionally, sorption tests for test solutions containing all three precious metals were carried out to understand the reducing effect of the gel on coexisting metal ions. However, only peaks belonging to elemental gold were observed, as shown in Figure 6.5.(a). This proves that only Au(III) undergoes subsequent reduction after being sorbed on the gel matrix and
the other metal ions do not change their oxidation states. From this difference, it is clear that the sorption of palladium and platinum is purely an ionic interaction, whereas for gold, the ionic interaction is followed by subsequent reduction to the elemental form. In addition, no such peaks for elemental gold were observed in the case of the previously mentioned ion exchange resins under the same test conditions, indicating that the reduction of Au(III) to its elemental form does not occur with the commercial resins (figure not shown). Figure 6.5.(b) shows the SEM image of the PAB-paper gel after gold sorption. The gold clusters of polygonal (mostly hexagonal) shape on the surface of the gel explain the fact that the reduction of gold to the elemental form leads to the separation of adsorbed gold from the gel matrix to form the elemental gold aggregates. The sorption-reduction and aggregation of gold particles allows further sorption of Au(III) ions from the solution resulting in the high loading capacity for gold.

Figure 6.5. (a) XRD spectrum of the PAB-paper gel taken before and after sorption of precious metals. (b) SEM images of the aggregated gold particles on the surface of the gel.
As the high sorption ability of the PAB-paper gel for Au(III) is associated with the reduction of the gold ion to the elemental form, certain changes in the electromotive force (emf) is also expected during the sorption process. A change in solution potential in relation to the sorption kinetics was observed as shown in Figure 6.6. It is clear from the figure that within 5 h almost 90% of the metal ions are sorbed and the oxidation reduction potential (ORP) begins to fall significantly at this point. The reduction process seems to be slow and continuous; lasting for several hours till it reaches a minimum value.

![Graph showing ORP and q vs. Time](image)

Figure 6.6. The oxidation reduction potential (ORP) of the Au(III) solution in contact with the waste paper gel. Initial concentration of metal ions = 2 mM, [HCl] = 1M, wt. of gel = 20 mg, temperature = 30 °C.

**Reduction Mechanism.** It is well known that Au(III) has a higher oxidation reduction potential compared to Pt(IV) and Pd(II) which makes it a powerful oxidising agent with a tendency to reduce to Au(0) in aqueous systems. The oxidation reduction potential (ORP) values for Au(III), Pt(IV) and Pd (II) have been reported as 1.002, 0.744 and 0.62 V, respectively, by Dekker et al.\(^7\) It is not easy to explain the reason why Au(III) is not reduced by amine type commercial anion exchange resins but is reduced in the presence of amine type biomass sorbents like the PAB-paper gel. Obviously the PAB-paper gel is not a unique case; we have already observed a few
precedents for such a phenomenon in the past. In our previous work on cross linked lignophenol as well as its aminated derivatives, we observed similar phenomena and the existence of the large number of phenolic and polyphenolic groups was concluded to be responsible for the reduction of Au(III).\textsuperscript{18} Earlier, the reduction and accumulation of gold by various types of biomass such as alfalfa, natural condensed tannin, calcium alginate, brewery waste, algal biomass and dealginated seaweed waste has been reported in the literature, but unlike in our work, visual observation of fine gold particles on the surface of the solution has not been reported.\textsuperscript{19} Reports of such instances in the case of cellulose and chitosan (original or modified) have not been found.

Although the presence of amine groups containing lone pairs of electrons as well as the electron rich benzene moiety may be responsible for the reduction, the exact mechanism of Au(III) reduction and its accumulation by the biomass is unknown and must be elucidated in future work by taking account of the aqueous chemistry of gold ions and colloids. Park et al. explained the sorption-coupled-reduction of Cr(VI) to Cr(III) in terms of the oxidation of the aldehyde end group of cellulose to the corresponding carboxylic acid.\textsuperscript{20} However, owing to the lack of any evidence of the oxidation of the cellulose matrix, it is difficult to interpret the mechanism in terms of the oxidation of the cellulose aldehyde in waste paper during the reduction of Au(III). Similarly, oxidation of biomass functional groups such as hydroxyl and carboxylic groups cannot be concluded without reliable proof.\textsuperscript{21} In addition, an extensive report on Au(III) reduction by Richardson et.al. using various types of monomeric and polymeric amines has stated that even spectroscopic methods such as NMR were not able to confirm the reduction mechanism.\textsuperscript{22}

**Column Experiment: Sorption and Elution.** Since the PAB-paper gel has shown selectivity for precious metals and a high sorption capacity for gold, a column test was
carried out using a binary mixture of Au(III) and Cu(II) as the latter exists together with precious metals in real waste solutions. Figure 6.7.(a) shows the breakthrough profiles of a model solution containing a low concentration of Au(III) together with 10 times the concentration of Cu(II) after passing through the column packed with 0.1 g of the PAB-paper gel. It is clear from the figure that Cu(II) passes without being sorbed but Au(III) is completely sorbed for up to 40 h. However, saturation was not reached until 130 h due to continuous sorption and reduction.

Figure 6.7. (a) Breakthrough profiles of Au(III) and Cu(II). (b) Elution profile. [Ci is the initial concentration of the metal ions and Ce is the metal ion concentration of the effluent solution.] Feed concentration: Cu(II) = 100 ppm, Au(III) = 20 ppm, flow rate = 6 ml/h, Eluent = 0.1 M thiourea in 1M HCl
Owing to the irreversible strong sorption of the chloro-complexes of Au(III), Pd(II), and Pt(IV) on conventional anion exchange resins, the elution of loaded metal ions is inefficient in many actual cases.\textsuperscript{23} To test the performance of the PAB-paper gel in this regard, the sorbed metal ions were eluted by using a mixture of 0.15 M thiourea in 1 M HCl. Almost complete recovery of Au(III) (~95%) was attained by this method with a preconcentration factor as high as 40 (Figure 6.7.(b)). Interestingly, the dissolution of fine gold particles in the acidic thiourea solution indicates not only the possibility of complete recovery of the loaded gold but also the suitability of the gel for regeneration and its repeated use. For further confirmation, a cycle test was carried out by passing a mixture consisting of 20 mg l\textsuperscript{-1} Au(III) and 100 mg l\textsuperscript{-1} Cu(II) through a column packed with 0.1 g of the gel and eluting the loaded metal ions with acidic thiourea. The results of the experiment are shown in Table 6.2., revealing that more than 90% of the sorbed gold was eluted each time.

In the same way, four consecutive sorption-elution cycle tests were conducted for a mixture containing Pt(IV) and Pd(II). The feed concentration of each metal ion was set at 20 mg l\textsuperscript{-1} for the first cycle. However in order to know the influence of higher concentrations of one metal over the other, in the following cycles, the concentration of Pt(IV) was increased to 100 mg l\textsuperscript{-1}. The results as shown in Table 6.2. are highly significant as not only does the sorption of the two metals take place competitively but also the recovery percentage lies between 80-90% for both of the metal ions.
Table 6.2. Performance of the PAB-paper gel in consecutive adsorption-elution cycles.

a) Recovery of Au(III) in the presence of excess of Cu(II). Feed concentration of metal ions: Au(III)/Cu(II) = 20/100 mg l\(^{-1}\), feed time = 15 h. The sorption of Cu(II) was negligible.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbed (mg)</td>
<td>1.87</td>
<td>1.84</td>
<td>1.95</td>
<td>1.93</td>
<td>1.82</td>
</tr>
<tr>
<td>Eluted (mg)</td>
<td>1.73</td>
<td>1.74</td>
<td>1.77</td>
<td>1.75</td>
<td>1.69</td>
</tr>
<tr>
<td>Recovery %</td>
<td>92.5</td>
<td>94.5</td>
<td>91</td>
<td>91</td>
<td>93</td>
</tr>
</tbody>
</table>

b) Competitive sorption of Pd(II) and Pt(IV). Feed concentration of metal ions: Pt/Pd(II)=20/20 mg l\(^{-1}\) (Cycle 1), Pt/Pd(II)=100/20 mg l\(^{-1}\) (Cycle 2-4), feed time =24 h.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Adsorbed (mg)</th>
<th>Eluted (mg)</th>
<th>Palladium (II) Recovery</th>
<th>Adsorbed</th>
<th>Eluted</th>
<th>Platinum(IV) Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.89</td>
<td>4.16</td>
<td>85</td>
<td>3.79</td>
<td>3.45</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>2.64</td>
<td>2.27</td>
<td>86</td>
<td>4.44</td>
<td>3.75</td>
<td>84.5</td>
</tr>
<tr>
<td>3</td>
<td>3.59</td>
<td>2.98</td>
<td>83</td>
<td>5.33</td>
<td>4.63</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>2.74</td>
<td>2.34</td>
<td>85.5</td>
<td>4.51</td>
<td>4.03</td>
<td>89</td>
</tr>
</tbody>
</table>

6.4. CONCLUSION

The PAB-paper gel, prepared by simple chemical modification of waste paper, exhibited remarkable capacity and efficiency for the preconcentration and separation of gold, platinum, and palladium from other co-existing metal ions at low to high concentration levels. The high sorption capacity for gold is very interesting because Au(III) is reduced by the gel, after sorption, to the elemental form and gold aggregates
are formed. In contrast, Pt(IV) and Pd(II) are sorbed only by pure ionic interaction and their oxidation states remain unchanged. The fact that valuable high demand metals can be recovered by using waste paper looks promising for its practical future application. From an economic viewpoint, this gel raises the prospect for recovering expensive metals at low cost and, from the environmental viewpoint; this gel is quite environmentally benign and acceptable.

REFERENCES


CONCLUSION

The increase in industrial activities has intensified environmental pollution and the deterioration of ecosystems, with the accumulation of pollutants such as heavy metals, synthetic compounds, etc. Mining and metallurgical wastewaters are considered to be the major sources of heavy metal contamination. The pollution of toxic heavy metals is directly related to the increased incidences of various diseases and, hence, their economic and effective removal is very essential.

The use of electronic devices has expanded in recent decades, and proportionately, the quantity of electronic devices, such as PCs, mobile telephones and entertainment electronics that are disposed of, is growing rapidly throughout the world. Recently developed countries are facing the problem of an alarming increase in electronic and electrical wastes, popularly called as e-wastes. Apart from a significant proportion of high valued precious metals, e-waste also contains various other toxic metals and chemicals which may lead to environmental problems, if disposed carelessly.

As metal wastes can be toxic and valuable (as source for secondary raw material), low cost separation and recovery of metal ions by adsorption technique was studied in this work. For this purpose, waste paper, a widely available, low cost biomass was taken as the starting material. It is well known that several tons of paper is wasted in different forms everyday. Utilizing it, various adsorption gels for metal ions were prepared by chemical modification and their performance was investigated. From the results of adsorption tests, the following conclusions have been drawn.

1. Unmodified waste paper doesn’t exhibit any adsorption capability for base and precious metal ions. For this reason, chemical modification is necessary to convert it into an adsorption material for metal ions.

2. Because of its amorphous characteristics, waste paper can be easily and economically modified by using various functional/ chelating groups. This provides waste paper a competitive advantage over microcrystalline cellulose which is commercially available.

3. Iminodiacetic acid modified waste paper gels exhibits significant adsorption for a number of base and heavy metals in a range of acidic pH. Iminodiacetic acid modified waste paper (indirectly modified through a spacer) can be useful for mutual separation of Ni(II) and Co(II), Cu(II) and Fe(III) as well as Cu(II) and Pb(II). The adsorption
capacities of both gels are comparable to those of similar other adsorbents.

4. Dimethylamine modified (DMA-paper) and p-aminobenzoic acid modified (PAB-paper) gels exhibit strong selectivity for Au(III), Pt(IV), and Pd(II), whereas iminodiacetic acid modified (IDA-paper) gel has selectivity only for Au(III) and Pd(II) in strong hydrochloric acid medium. All these gels have no affinity for other contaminating metal ions like Cu(II), Fe(III), Ni(II), Zn(II) etc. This is very important feature from the viewpoint of industrial separation of precious metals from e-waste.

5. The waste paper gels have very high adsorption capacities for gold and comparative capacities for palladium and platinum. In 1 M hydrochloric acid medium, the maximum adsorption capacities of functionalized paper gels are observed as:

<table>
<thead>
<tr>
<th>Adsorption gel</th>
<th>Au(III) (mol/kg)</th>
<th>Pd(II) (mol/kg)</th>
<th>Pt(IV) (mol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IDA-paper</td>
<td>3.3</td>
<td>1.42</td>
<td>-</td>
</tr>
<tr>
<td>DMA-paper</td>
<td>4.6</td>
<td>2.1</td>
<td>0.9</td>
</tr>
<tr>
<td>PAB-paper</td>
<td>5.1</td>
<td>1.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

6. The unique property of the gels (mentioned above in 6) was that they reduced Au(III) to elemental gold particles that appeared on the surface of the test solution and aggregated later. Though the exact mechanism of the selective reduction of gold is unknown, this phenomena is responsible for the high adsorption capacity for Au(III).

7. The adsorption gels are suitable for use in continuous mode of operation and can be regenerated by suitable eluents leading to almost complete recovery of the loaded metal ions. They have consistent adsorption behavior and stability even in very strong acidic medium i.e. aqua regia leachate.
LIST OF PUBLICATIONS


Patent:

CONTRIBUTION TO ACADEMIC CONFERENCES


Curriculum Vitae

CHAITANYA RAJ ADHIKARI

Date of Birth: 1973/11/29, Kaski, Nepal
Permanent Address: Kaski kot-1, Kaski, Nepal
Mailing address: 148, Rastra Bank Marg, Pokhara-8, Kaski, Nepal
Tel: 977-61-525027

Education:
PhD in Chemical Engineering (Oct. 2006-March 2009)
Graduate School of Science and Engineering, Saga University, Japan

M.Sc. in Chemical Engineering (Oct. 2004-Sept. 2006)
Graduate School of Science and Engineering, Saga University, Japan

Distance Learning Course on Public Private Partnerships for Urban Environmental Services (Feb. 2003-Aug. 2003)
UNDP/Yale University Collaborative Program on the Urban Environment

Pokhara University, Nepal

College of Textile Technology, Dhaka University, Bangladesh

Secondary Education: Shree Barahi Secondary School, Pokhara, Nepal
Primary Education: Shree Parashu Primary School, Kashi, Nepal

Current Research Theme: Modeling of sorption active materials using biomass waste (waste paper) and recovery of precious metals from e-waste leachates

Work Experience:
Lecturer (March 2002-May 2004), School of Business, Pokhara University, Nepal
Deputy Production Manager (June 1999- Jan. 2000), Butwal Spinning Mills Ltd., Nepal

Language: Nepali, English, Bengali, Hindi, Japanese, Sanskrit etc.
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平井・筒井国際特許事務所
福岡県福岡市博多区博多駅前2丁目20-1
〒812-0011 大博多ビル9階
☎092-414-3157 ☘pat-.hirai@nifty.ne.jp
基体に含まれるセルロースに、貴金属を吸着する官能基としてイミノジ酢酸又はジアルキルアミンを結合させたもの
前記セルロースの結合化度は略70％以下であり
前記基体は適宜量のヘミセルロース及び/又はリグニンを含有している
ことを特徴とする吸着剤。

【請求項４】
前記官能基としてジェチルアミンを結合させた場合、基体の乾燥重量当たりに結合された官能基の量は1.0mol/1から5.0mol/1である請求項1記載の吸着剤。

【請求項５】
前記吸着剤に貴金属を吸着させた後、当該吸着剤にチオ尿素及び塩酸の混合溶液を接触させ、当該吸着剤から貴金属を脱離させる請求項4記載の貴金属の回収方法。
【発明者】
【住所又は居所】佐賀県佐賀市本庄町1番地 国立大学法人佐賀大学内
【氏名】川喜田 英孝

【発明者】
【住所又は居所】佐賀県佐賀市本庄町1番地 国立大学法人佐賀大学内
【氏名】アディカリ，チャイタニャ ラジ

【発明者】
【住所又は居所】佐賀県佐賀市本庄町1番地 国立大学法人佐賀大学内
【氏名】バラシュリ，ドゥルガ

【発明者】
【住所又は居所】佐賀県佐賀市本庄町1番地 国立大学法人佐賀大学内
【氏名】井上 勝利

【発明者】
【住所又は居所】佐賀県佐賀市本庄町1番地 国立大学法人佐賀大学内
【氏名】大渡 啓介

【特許出願人】
【識別番号】504209655
【氏名又は名称】国立大学法人佐賀大学

【代理人】
【識別番号】100099634
【弁理士】
【氏名又は名称】平井 安雄
【電話番号】092-414-3157

【手数料の表示】
【予納台帳番号】030719
【納付金額】16,000円

【提出物件の目録】
【物件名】特許請求の範囲 1
【物件名】明細書 1
【物件名】図面 1
【物件名】要約書 1
【包括委任状番号】0416464
【課題】 植物材を原料として基体を構成した場合であっても、貴金属の回収効率が高い吸着剤及び貴金属を回収する方法を提供する。
【解決手段】 貴金属を吸着する本吸着剤は、基体に含まれるセルロースに、貴金属を吸着する官能基としてイミノジ酢酸又はジアルキルアミンを結合させており、セルロースの結晶化度は約70%以下であり、基体は適宜量のヘミセルロース及び／又はリグニンを含んでいる。
【選択図】 なし
発明の名称：吸着剤及び貴金属の回収方法
【技術分野】
0001
本発明は、金、パラジウム及び白金等の貴金属を吸着する吸着剤、及び該吸着剤を用いて貴金属を回収する方法に関する。
【背景技術】
0002
金、パラジウム及び白金等の貴金属は、電気・電子部品の材料又は触媒材料等として需要が増大しているため、廃棄物又は廃液から貴金属を効率的に回収する技術の開発が要求されている。
0003
廃棄物又は廃液から貴金属を効率的に回収するには、廃棄物にあっては強酸溶液によって廃棄物中の金属を溶解させた金属溶液を調製し、廃液にあっては貴金属を含む種々の金属が溶解した金属溶液であるので、そのまま又はpHを調整し、かかる金属溶液に吸着剤を接触させて、金属溶液中の貴金属を吸着剤に吸着させる方法が知られている。
0004
貴金属を吸着させる吸着剤として、例えばダイヤイオン（登録商標）WA30（三菱化学株式会社）というような市販のイオン交換樹脂を用いることができるが、かかるイオン交換樹脂にあっては、当該イオン交換樹脂からこれに吸着させた貴金属を脱離させる工程において貴金属の回収率が低いという問題があった。
0005
そのため、貴金属を吸着させたイオン交換樹脂を燃焼させて貴金属を回収する方法が考えられるが、高価なイオン交換樹脂を回分的に使用しなければならず、貴金属の回収コストが嵩む。更に、例えば前記市販樹脂にあっては、ポリスチレンをジビニルペンゼンで架橋させた3次元構造の粒状ポリマーが基体であるため、容易に燃焼させることが出来ないのに加え、排気問題というような新たな問題を招来する。
0006
そこで、後記する特許文献1には、セルロース、ポリエチレン、又はポリプロピレンといった高分子基体に、イミノジ酢酸基、アミン基、アミドキシム基、又はリン酸基等のキレート形成基をグラフト重合により導入した吸着剤が開示されている。
0007
かかる吸着剤にあっては、貴金属を吸着させた吸着剤に無機酸、有機酸又は有機溶媒を接触させることによって吸着剤から貴金属を容易に脱離させることができる。
【特許文献1】特開2006−26588号公報
【発明の開示】
【発明が解決しようとする課題】
0008
しかしながら、このような従来の吸着剤にあっては次のような問題があった。
すなわち、高分子基体としてポリエチレン及びポリプロピレンといった合成樹脂を用いた場合、使用不能となった吸着剤を処分するに当たって、前同様、排気問題等の新たな問題を招来する。
これを回避するために高分子基体としてセルロースを用いることが考えられるが、この場合、高分子基体にキレート形成基を導入し得る量に限界があるため、吸着剤単位重量当たりの貴金属の吸着量が少なく、貴金属の回収効率が低いういう問題があった。
0009
本発明は、斯かる事情に鑑みてなされたものであって、植物材を原料として基体を構成した場合であっても、貴金属の回収効率が高い吸着剤、及び該吸着剤を用いて貴金属を回収する方法を提供する。
【課題を解決するための手段】
植物材を原料として基体を構成した吸着剤において、当該基体に官能基を結合させ得る量化限界があるのは、基体に含まれるセルロースの結晶化された領域の内部に官能基が進入することができないためであると考えられた。

そこで、本発明者らが観察したところ、結晶化度が基準値以下のセルロースを含む基体を用い、そのセルロースに官能基を結合させる操作を行った場合、セルロースの官能基の結合反応を契機として、セルロースの結晶化された領域が雪崩的に非晶質化し、これによってその内部まで官能基を導入させることができるという知見を得て、本発明を完成させた。

すなわち、(1) 本発明に係る吸着剤は、基体に含まれるセルロースに、貴金属を吸着する官能基としてイミノジ酢酸又はジアルキルアミンを結合させており、前記セルロースの結晶化度は70%以下であり、前記基体は、適量のヘミセルロース及び／又はリグニンを含有していることを特徴とする。

前述した結晶化度の基準値は70%程度である。従って、結晶化度が70%を超える場合、当該セルロースの基体の内部に貴金属と結合する官能基を導入させることができず、セルロースへの官能基の結合量が著しく低いので、貴金属の回収効率が低くなる。

一方、結晶化度が70%以下のセルロースを含む基体を用い、前述したようにセルロースへの官能基の結合反応を契機として、当該セルロースの結晶化された領域が雪崩的に非晶質化するため、その内部まで官能基が導入され、セルロースへの官能基の結合量が飛躍的に増大する。これによって、吸着剤単位質量当たりの貴金属の吸着量が増大するので、貴金属の回収効率が飛躍的に向上する。

ところで、セルロースの結晶化度が低くなるにつれてセルロース繊維間の結合力も低下するので、セルロース纖維が流出し易くなり、吸着剤としての形態を維持し難くなる。

しかしながら、本発明に係る吸着剤の基体には、形態維持成分としてヘミセルロース及び／又はリグニンが含有されており、セルロースの結晶化度が低くなった場合であっても、前記形態維持成分によって複数のセルロース纖維間が架橋された状態になっているため、吸着剤の3次元形態が維持される。従って、吸着剤を容易に取り扱うことができ、また吸着剤の一部が流出して貴金属の回収率が低下する、ということが防止される。

なお、前述したジアルキルアミンのアルキル基は、メチル基、エチル基、プロピル基を含む群から選択される1種であり、メチル基が好適である。

(2) また、本発明に係る吸着剤は必要に応じて、前記官能基としてイミノジ酢酸を結合させた場合、基体の乾燥重量当たりに結合された官能基の量は1.0 mol/1から4.0 mol/1であることを特徴とする。

結合されたイミノジ酢酸の量が基体の乾燥重量当たり1.0 mol/kg未満の場合は貴金属の吸着量が十分でなく、4.0 mol/kgを超えた場合はセルロースへの化学修飾が困難である。

(3) また、本発明に係る吸着剤は必要に応じて、前記官能基としてジアルキルアミンを結合させた場合、基体の乾燥重量当たりに結合された官能基の量は1.0 mol/1から5.0 mol/1であることを特徴とする。

結合されたジアルキルアミンの量が、1.0 mol/kg未満の場合は貴金属の吸着量が十分でなく、5.0 mol/kgを超えた場合はセルロースへの化学修飾が困難である。
（4）一方、本発明に係る鉄金属の回収方法は、基体に含まれるセルロースに鉄金属を
吸着する官能基を結合させることによって吸着剤に溶於を接触させ、該溶液に含まれる鉄金属を前
記吸着剤に吸着させることによって前記鉄金属を回収する方法において、前記セルロース
に前記官能基としてイミノ化酸又はジアミルアミンを結合させることにより、前記セルロ
ースの結晶化度は約70％以下であり、前記基体は適宜量のヘミセルロース及び/又はリ
グニンを含有している吸着剤を用いることを特徴とする。

【0019】
かかる吸着剤にあっては、前述したように吸着剤単位質量当たりの貴金属の吸着量が多
いので、貴金属の回収効率が高いため。
一方、かかる吸着剤は、形態維持成分としてヘミセルロース及び/又はリグニンが含有
されているので、3次元形態が維持され、その取り扱いが容易である。また、吸着剤の一
部が流出して貴金属の回収率が低下する、ということが防止される。
なお、吸着剤と前記溶液との接触は、前記溶液に吸着剤を添加して攪拌するパッチ法に
ってもよいし、吸着剤を充填させたカラムに溶液を通流させるカラム法によってもよい。

【0020】
（5）本発明に係る貴金属の回収方法は必要に応じて、前記吸着剤に貴金属を吸着させ
た後、当該吸着剤にチオ尿素及び塩酸の混合溶液を接触させ、当該吸着剤から貴金属を脱
離させることを特徴とする。

【0021】
貴金属を吸着させた吸着剤にチオ尿素及び塩酸の混合溶液を接触させることにより、吸
着剤から貴金属を効率的に脱離させることができる。また、貴金属の脱離と共に、吸着剤
の再生もなされるため、吸着剤の再生操作を行うことなく、再度の回収作業を実施するこ
とができるため、回収作業の効率化が図れる。
【発明を実施するための最良の形態】

【0022】
（本発明の実施形態）
以下に本発明に係る実施の形態について説明する。
（吸着剤の基体の原料）
本発明に係る吸着剤の基体の原料としては、吸着用成分としてセルロースを含む、形態
維持成分としてヘミセルロース及び/又はリグニンを含む、紙を用いた。かかる紙として
は、新聞紙を用いることができるが、これ以外にもクラフト紙、オフィス用紙等、種々の
紙を用いることができる。

【0023】
基体に含まれるセルロースは、結晶化度が70％程度以下であることが好ましい。結晶
化度が70％程度を超える場合、当該セルロコースの結晶の内部に貴金属と結合する官能基
を殆ど導入することができず、セルロースへの官能基の導入率が著しく低いので、貴金属
の回収効率が低い。

【0024】
一方、結晶化度が70％程度以下のセルロースを含む基体を用いた場合、後述するセル
ロースへの官能基の導入操作中に、結晶質部分が懸濁的に非晶質化するため、その内部ま
で官能基が導入され、セルロースへの官能基の導入率が飛躍的に増大する。これによって
、吸着剤単位質量当たりの貴金属の吸着量が増大するので、貴金属の回収効率が飛躍的に
向上する。

【0025】
セルロースの結晶化度を低下させるには、水酸化ナトリウム溶液で処理する方法、セル
ロース及び/又はヘミセルロースの酵素で処理する方法、紫外線を照射する方法等を単
独で、又は組み合わせて適用することができる。

【0026】
したがって、結晶化度が70％程度を超えるセルロースを主成分として含む紙であって
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も、上記した方法を適用することによって、当該セルロースの結晶化度を70%程度以下にすることによって本発明に係る吸着剤の基体の原料とすることができる。

一方、古紙、及び紡紙を再生した再生紙にあっては、当初よりセルロースの結晶化度が70%程度以下であるため、かかる低結晶化操作を省略することができる。

【0027】


【0028】

ところで、セルロースの結晶化度が低くなるにつれてセルロース繊維間の結合力も低下するので、セルロース繊維が流出し易くなり、吸着剤としての形態を維持し難くなる。

しかしながら、本発明に係る吸着剤の基体の原料には、形態維持成分としてヘミセルロース及び/又はリグニンが含有されており、セルロースの結晶化度が低くなった場合であっても、前記形態維持成分によって複数のセルロース繊維間が架橋された状態になっているため、吸着剤の3次元形態が維持される。従って、吸着剤を容易に取り扱うことができ、また吸着剤の一一部が流出して貴金属の回収率が低下する、ということが防止される。

【0029】

ここで、形態維持成分を含有するヘミセルロース及び/又はリグニンは、乾燥基体単位質量当たり約10%以上含まれることが好ましい。乾燥基体単位質量当たりヘミセルロース及び/又はリグニンが約10%程度未満の場合、吸着剤の形状維持効果が不十分な場合があり、吸着剤の取り扱いが困難となり、また吸着剤の一部又は全部が流出して貴金属の回収率が低下する場合が生じる。

【0030】

なお、基体に含まれるヘミセルロース及び/又はリグニンの量の上限は、基体の原料に含有されるヘミセルロース及び/又はリグニンの量の上限のため特に制限されないが、ヘミセルロース及び/又はリグニンの含有量が多い場合、相対的にセルロースの含有量が少なくなり、吸着剤の単位質量当たりの官能基の量も少なくなるので、少なくともセルロースの含有量より少ないことが好ましい。

より好ましくは、ヘミセルロース及び/又はリグニンの含有量の上限は、乾燥基体単位質量当たり約40%である。これによって、クラフト紙、ダンボール紙等、幅広い紙を原料としてそのまま使用することができる。

【0031】

更に好ましくは、ヘミセルロース及び/又はリグニンの含有量の上限は、乾燥基体単位質量当たり約20%である。これによって、基体に含まれるセルロースの結晶化度をより低下させた場合であっても、吸着剤の3次元構造を確実に維持することが出来る一方、セルロースの結晶化度をより低下させることによって、官能基の結合量をより多くすることができ、貴金属の回収効率をより高くすることができる。

【0032】

（吸着剤の基体の前処理）

次に、前述した基体に官能基を導入すべく基体を前処理する方法について説明する。

前処理は、紙を物理的・機械的に処理して処理後繊維状をなす工程を含んでいる。具体的には、基体となる紙を粉碎機により繊維状になるまで粉碎する。

【0033】

古紙を用いる場合にあっては、粉碎物を炭酸水素ナトリウム溶液で処理することによって、古紙に含有しているインク成分を洗浄して洗う処理を行った後、水洗する。なお、必要に応じて、再度の粉碎処理を実施する。

また、新聞紙等、印刷された古紙を用いる場合、インクを洗浄除去する洗浄液によって粉碎物処理する操作を所要回数実施して、インク成分を除去しておくとよい。

【0034】
このように前処理して得られた粉末物を用いて、次のようにして吸着剤を調製する。
すなわち、粉末物に含まれるセルロースにイミノジ酢酸又はアルキルジアミンといった
貴金属を選択的に吸着する官能基を結合させて吸着剤を得るのであるが、そのために、前
記粉末物に含まれるセルロースの構成単位であるグルコースの第6位の水酸基を塩酸基で
置換してセルロース誘導体を生成する。
(0035)
このような塩素化処理は、グルコースの第6位の水酸基を塩化チオニルの塩酸基で置換
する次の反応スキームによって実施することができる。
(0036)
[化1]

![化学式]

(0037)
このようにして生成したセルロース誘導体にジアルキルアミンを直接的に反応させて、
前記グルコースの第6位の塩酸基をジアルキルアミンで置換し、ジアルキルアミンをセル
ロースに結合・固定させる。
(0038)
一方、イミノジ酢酸にあってはこのように直接的に固定させることができ困難であるため、
ジエチルイミノ酢酸をセルロース誘導体に反応させて、前記グルコースの第6位の塩酸基
をジエチルイミノ酢酸で置換することによって、ジエチルイミノ酢酸をセルロースに固定
させた後、ジエチルイミノ酢酸を加水分解してイミノジ酢酸になる。
これらの反応スキームをまとめると次のように示すことができる。
(0039)
この反応スキーマにおいて、R1は、メチル基、エチル基、プロピル基を含む群から選択される1種であり、R2は、メチル基、エチル基、プロピル基を含む群から選択される1種であるが、R1及びR2ともメチル基が好適である。このようにして吸着剤が得られる。

ここでは、吸着剤へのセルロースに固定されるイミノジ酢酸の量は、基体の乾燥質量に換算した場合、1.0 mol/kgから4.0 mol/kgであり、好ましくは2.0 mol/kgから3.0 mol/kgである。1.0 mol/kg未満の場合は金屬の吸着量が十分でなく、4.0 mol/kgを超えた場合はセルロースへの化学修飾が困難である。

また、吸着剤へのセルロースに固定されるジアルキルアミンの量は、基体の乾燥質量に換算した場合、5.0 mol/kgから5.0 mol/kgであり、好ましくは2.0 mol/kgから4.0 mol/kgである。1.0 mol/kg未満の場合は金屬の吸着量が十分でなく、5.0 mol/kgを超えた場合はセルロースへの化学修飾が困難である。

（金属の回収方法）
このようにして得られた吸着剤と貴金属を含む金属溶液を接触させて、吸着剤に貴金属を吸着させる。かかる吸着操作としては、吸着剤と金属溶液を撹拌・混合、その後、両者を分離する、所謂バッチ法によっても良いが、吸着剤を添加した塔に金属溶液を通流させる連続法によっても良い。

ここで貴金属を含む金属溶液としては、貴金属を含む廃液を塩酸等の酸で溶解させた溶液を用いることができる。また、廃液を塩素化して塩化物（固体）とし、これを水、酸等の溶媒で溶解させた溶液を用いることもできる。一方、排メッキ液等の廃液からそれに含まれる貴金属を回収する場合は、当該廃液に塩酸溶液を加えて、廃液中の塩化物イオンの濃度を適当な値に調整しておくとよい。
そして、貴金属を吸着させた吸着剤から当該貴金属を脱離させる。
吸着剤から貴金属を脱離させるには、チオ尿素及び塩酸の混合液と吸着剤を接触させることにより吸着剤から貴金属を溶離させる。これにより、貴金属の溶離と同時に吸着剤の再生を行うことができる。また、吸着剤に吸着させた貴金属のほとんどを当該吸着剤から溶離させることができる。

[0046] チオ尿素及び塩酸の混合液は、チオ尿素の配合量が0.5mol/1から5mol/1であり、塩酸の配合量が1.0mol/1から10mol/1である。チオ尿素の配合量が0.5mol/1未満である場合、貴金属の溶離が不十分であり、チオ尿素の配合量が5mol/1を超えた場合、硫黄が析出することができる。また、塩酸の配合量が1mol/1未満である場合、溶離効率が低下し、塩酸の配合量が10mol/1を超えると、吸着剤の基体の劣化が顕著に生じる一方、当該溶液の取り扱いに危険を伴う。

また、吸着剤から貴金属を脱離させる方法として、吸着剤を焼却させることによって当該吸着剤に吸着されていた貴金属を残留させる方法を適用することもできる。

[0047] この場合、吸着剤の基体は紙であるため、吸着剤を迅速・容易に焼却することができる。また、吸着剤を焼却する際に有害なガスが発生することもなく、比較的簡単な設備で焼却操作を実施することができるため、焼却操作に要するコストが少ないと考えられる。

【実施例1】

【0048】

A. 吸着剤の調製

（a）前処理及び塩素化

新聞紙を、粉碎機（ダルトン製P－35型パワーミル）を用いて細裂になるまで粉碎した後に、粉碎物を洗剤溶液中で摺拌・ろ過する操作を数回繰り返した。得られた洗浄物を20質量％の炭酸水素ナトリウム水溶液中で5時間摺拌した後に、水洗操作を中性になるまで繰り返した後にろ過して処理物を得た。この処理物を再度粉碎した後に、対流乾燥機を用いて50℃で24時間乾燥した。

【0049】

このようにして得られた基体0.5gと25mlのピリジンを添加し、水浴中で摺拌しつつ5mlの塩化チオニールを滴下して加えた。次いで、摺拌油を70℃に昇温し、窒素雰囲気下で6時間摺拌することによって、前述したセルロース誘導体を生成した。得られた生成物を水洗し、対流乾燥機を用いて70℃で乾燥した。

【0050】

（b）ジェチルイミノニョ酢酸の官能基の固定

塩酸で酸化したエタノール400mlと20gのイミノニョ酢酸とを混合し、80℃で24時間摺拌した後に、炭酸水素ナトリウム水溶液で中和し、さらにクロロホルムで洗浄してジェチルイミノニョ酢酸を得た。

【0051】

次に、前述した如く乾燥した生成物0.5g及び1.14gのジェチルイミノニョ酢酸を50mlのアセトニトリル及び1.4gの炭酸カリウムと共に50℃で72時間摺拌した後にろ過し、ろ過物を50mlのエタノールと10mlの0.1mol/1の炭酸水素ナトリウム水溶液との混合液に投入し、60℃で1日間摺拌して溶離させた。この溶液のpHを2～3に保つと沈殿が生成する。この沈殿をろ過した後、0.1mol/1の塩酸を次いで水で洗浄し、最後に蒸留乾燥を用いて60℃で乾燥することによりイミノニョ酢酸の官能基を固定化した吸着剤0.35gを得た。

【0052】

この吸着剤について分析を行い、基体の含有量を測定することにより、イミノニョ酢酸の官能基の含量を求めたところ、吸着剤の乾燥重量に対して2.17mol/kgであった。これは基体に含まれるセルロースを構成するグルコースの6位の水酸基の60％に官能基の固定化が起こったことに相当する。
0.5gの乾燥乾燥生成物に5mLのジメチルアミン及び1mLの35％のホルマリンを加え、90℃で3時間沸騰し、0.1mol/Lの塩酸、0.1mol/Lの塩化ナトリウム水溶液で洗浄し、次いで水洗した後、対流乾燥機を用いて60℃で12時間乾燥させる
ことによって、吸着剤を得た。

この吸着剤についても元素分析を行い、窒素の含有量を測定することにより、ジメチルアミンの官能基の量を求めたところ、吸着剤の乾燥重量に対して3.60mol/kgであった。これは測定数を含むせるセルロースを構成するグルコースの6位の水酸基の69%
に官能基の固定化が起こったことに相当する。

B. 吸着剤の吸着特性の検討
（a）イミノソレア酸の官能基を固定化した吸着剤の選択性の検討

溶液として塩化亜（III）酸、塩化水素（IV）酸、ならびに塩化バリウム（II）を、また金属として銅（II）、鉄（III）、ニッケル（II）及び亜鉛（II）の塩酸塩を用いた。

イミノソレア酸の官能基を固定化した本発明において吸着剤を乾燥質量で20mg分取して
検出法をアミノコに高濃度にして、これらの0.2mol/Lの前記各金属イオンを含む0.5～4
mol/L dm³の塩酸溶液15mLを注入して、30℃で保たれた恒温槽中に2
4時間振盪させて吸着処理を行った。

吸着処理後の塩酸溶液中の各金属イオンの濃度をICP分析装置（島津製作所製IC
P88100型ICP発光分析装置）により測定し、吸着剤に吸着された各金属イオンの
吸着百分率を次式により求めた。
吸着百分率＝（吸着処理前の塩酸溶液中の金属濃度ー吸着処理後の塩酸溶液中の金属濃度
）／吸着処理前の塩酸溶液中の金属濃度×100

図1は、イミノソレア酸の官能基を固定化した吸着剤を用いた金属イオンの吸着百分率と
塩酸濃度との関係を示したグラフであり、縦軸は吸着百分率を、横軸は塩酸濃度をそれぞれ
示している。なお、図中、黒塗り菱形印はAu（III）、白抜き丸印はCu（II）、
白抜き菱形印はFe（III）、白抜き四角印はNi（II）、白抜き三角印はPd（I
I）を、黒塗り四角印はPt（IV）、白抜き三角印はZn（II）をそれぞれ示している。

図1より明らかのように、金及びバリウムは吸着剤に、塩酸濃度が0.5～4mol/
Lの範囲において70％以上吸着されていたが、当該塩酸濃度範囲において、白金の吸
着百分率は20％以下であった。一方、当該塩酸濃度範囲において、卑金属イオンは吸着
剤に全く吸着されていなかった。
以上の結果は、本吸着剤により、金及びバリウムを卑金属イオンから選択性に分離・
回収することができるということを示している。

（b）ジメチルアミンの官能基を固定化した吸着剤の選択性の検討

図2は、ジメチルアミンの官能基を固定化した吸着剤を用いた金属イオンの吸着百分率と
塩酸濃度との関係を示したグラフであり、縦軸は吸着百分率を、横軸は塩酸濃度をそれぞれ
示している。なお、吸着試験はイミノソレア酸の官能基を固定化した吸着剤に単に前述
した方法と同様に行った。また、図中、黒塗り菱形印はAu（III）、白抜き丸印はCu
（II）を、黒塗り三角印はFe（III）、黒塗り丸印はNi（II）、白抜き四角印
はPd（II）を、白抜き三角印はPt（IV）、白抜き菱形印はZn（II）をそれぞれ示し
ている。
図2から明らかのように、金、パラジウム、及び白金は、塩酸濃度が0.5-4mol/lの範囲において60%吸着されていた。

【0061】
一方、鈷金属イオンにあては、鈷が、塩酸濃度2mol/l以下の濃度において20%程度、本吸着剤に吸着していたが、それ以外の濃度範囲では殆ど吸着されなかった。また、鈷以外の鈷金属にあては、いずれの塩酸濃度範囲にあっても、本吸着剤に殆ど吸着されていなかった。
以上の結果は、本吸着剤は、金、パラジウム、白金を鈷金属から選択的に吸着することが示示している。

【0062】
（c. イミノジ酢酸の官能基を固定した吸着剤の飽和吸着量の検討）
イミノジ酢酸の官能基を固定化した吸着剤を乾燥重量で20mg分取して検討フラスコに投入し、異なる濃度の金（III）イオン、又はパラジウム（II）イオンを含む1mol/lの塩酸溶液15mlを注注入、30℃で60時間振盪した後、金（III）イオン又はパラジウム（II）イオンの吸着量を測定し、両イオンの飽和吸着量を求めた。

【0063】
図3は、イミノジ酢酸の官能基を固定化した吸着剤に対する金（III）イオン及びパラジウム（II）イオンの飽和吸着量を検討した結果を示すグラフである。図中、縦軸は、乾燥重量1kg当たりの吸着剤に対して吸着した金属イオンのモル数を、横軸は、吸着操作を行った後の塩酸溶液の金属濃度をそれぞれ示している。
なお、図中、黒塗り菱形印は金（III）を、黒塗り三角印はパラジウム（II）をそれぞれ示している。

【0064】
図3より明らかのように、いずれの金属の場合もいわゆるランクミュラ型の吸着曲線を示しており、吸着量が飽和によらず一定になった領域の吸着量の値から、本吸着剤の飽和吸着量は、金イオンについては3.30mol/kgであり、パラジウムイオンについては1.42mol/kgであると求められた。
従って、本吸着剤にあっては、吸着剤1kg当たり660kgの金を吸着することができる。

【0065】
（d. ジメチルアミンの官能基を固定化した吸着剤の飽和吸着量の検討）
ジメチルアミンの官能基を固定化した吸着剤を用い、金イオン、白金イオン、パラジウムイオンについて、前同様の試験を行って、各イオンの飽和吸着量を求めた。

【0066】
図4は、ジメチルアミンの官能基を固定化した吸着剤に対する金（III）イオン、白金（IV）イオン及びパラジウム（II）イオンの飽和吸着量を検討した結果を示すグラフである。図中、縦軸は、乾燥重量1kg当たりの吸着剤に対して吸着した金属イオンのモル数を、横軸は、吸着操作を行った後の塩酸溶液の金属濃度をそれぞれ示している。
なお、図中、黒塗り菱形印は金（III）を、黒塗り四角印は白金（IV）を、黒塗り三角印はパラジウム（II）をそれぞれ示している。

【0067】
図4より明らかのように、この吸着剤でも各金属イオンはランクミュラ型の吸着曲線を示していた。そして、各グラフより、この吸着剤の飽和吸着量は、金イオンについては4.6mol/kgであり、白金イオンについては2.1mol/kgであり、パラジウムイオンについては0.9mol/kgであると求められた。
従って、本吸着剤にあっては、吸着剤1kg当たり906kgの金イオンを吸着することができる。

【0068】
C. カラム法による貴金属の回収の検討
（a. 吸着試験）
図5は、カラム法による吸着試験に使用した装置構成を示す模式図であり、図中、1は吸着剤を充填するカラムである。また、図6は、図5に示したカラム1の拡大図である。
図5及び図6に示したように、カラム1は2重筒になっており、外筒11には第2ポンプ3によって恒温水が供給されるようになっている。また、カラム1の内筒12内の装置中央には、吸着剤を充填してなる吸着剤層22が配設されており、該吸着剤層22はその両端側に配置されたガラスビーズ層21、21によって挟持されている。内筒12の底部にはガラスフィルタ25が配設しており、このガラスフィルタ25によって内筒12内の充填物が固定されている。

0069
内筒12には供給液のまわり4からそこに貯留されている供給液が、第1ポンプ2によって内筒12の底部から供給されるようになっている。内筒12内を通流した供給液は内筒12の頭部から流出され、一定量ずつ分取する分取器5によって分取されるようになっている。

0070
このような装置のカラム1に、ジェチルアミンの官能基を固定化した吸着剤を充填して吸着剤層22を形成した。なお、内筒12には内径8mmであり、長さは30cmのものを用い、この内筒12に吸着剤を乾燥重量で1000mgとなるように充填した。

0071
1mol/lの塩酸溶液に、銅（II）、金（III）、白金（IV）、バラジウム（II）をそれぞれ20mg/l、24mg/l、21mg/l、19mg/lになるように溶解させた金属溶液を前述した供給液のまわり4に貯留しておき、カラム1の内筒12内に、前記金属溶液を6ml/時の流量で通流させた。
そして、カラム1から流出された溶液中の各金属の濃度を経時的に検出した。

0072
図7は、金属溶液を通流したカラムから流出された溶液中の各金属の濃度を経時的に検出した結果を示すグラフであり、縦軸は各金属の濃度を、横軸は通流を開始してからの時間をそれぞれ示している。なお、流出された溶液中の各金属の濃度は、前記金属溶液における各金属の濃度に対する比で示している。
また、図中、白抜き菱型印はバラジウムを、白抜き四角印は白金を、白抜き三角印は金を、白抜き丸印は銅をそれぞれ示している。

0073
図7から明らかのように、銅にあっては通流開始直後から検出され始め、通流を開始してから数時間後には、通流させた金属溶液中の濃度と同じ濃度であった。
一方、金、白金、及びバラジウムにあっては、通流を開始してから約30時間後から検出始め、約70時間～80時間経過後に通流させた金属溶液中の濃度と同じ濃度が検出された。

0074
（b. 脱離試験）
次に、このような貴金属を吸着させた吸着剤から当該貴金属を脱離させた。
図8は、図7に示したように貴金属を吸着させた吸着剤から脱離される貴金属の濃度を経時的に検出した結果を示すグラフであり、縦軸は各金属の濃度を、横軸は脱離を開始してからの時間をそれぞれ示している。なお、流出された溶液中の各金属の濃度は、吸着剤に通流させた金属溶液における各金属の濃度に対する比で示している。

0075
また、図中、白抜き菱型印はバラジウムを、白抜き四角印は白金を、白抜き三角印は金を、白抜き丸印は銅をそれぞれ示している。
脱離用溶液は、0.1mol/lのチオ尿素と1mol/lの塩酸との混合溶液を用い、該混合溶液を、流速6ml/hで通流した。

0076
図8から明らかのように、いずれの時点にあっても、脱離操作によって流出された溶液
に金は検出されなかった。かかる結果及び図8に示した結果より、本吸着剤に金は吸着されないことが分かる。[0077]

一方、金、白金、及びパラジウムにあっては、脱離開始から約1時間半経過後から脱離開始から4時間経過するまでの間に、比較的低いピークが存在しており、各貴金属とも、吸着剤に通過させた金属溶液の濃度より高い濃度に濃縮されていた。ここでは、前述した混合溶液におけるチオ尿素の濃度は、0.1mol/1以上5mol/1以下であることが好ましい。チオ尿素の濃度が0.1mol/1未満である場合、貴金属の脱離率が低下し、5mol/1を超えた場合、硫黄が析出する。

[0078]
また、混合溶液における塩酸の濃度は、1.0mol/1以上10.0mol/1以下であることが好ましい。塩酸の濃度が1.0mol/1未満である場合、貴金属の脱離率が低下し、10mol/1を超えた場合、混合液の取り扱い及び脱離操作後の混合液の処理が困難である。

[0079]
（c. 繰り返し試験）
次に、前記吸着試験と脱離試験を繰り返す試験を行った。

金属溶液が銅を含まない場合以外は前述した吸着試験及び脱離試験の条件と同じ条件に
し、吸着剤に貴金属を吸着させる操作と当該吸着剤から貴金属を脱離させる操作を3回
繰り返して、各回における貴金属吸着量、脱離量、及びこれからの求められる回収率を求
めた。その結果を次の表1に示す。

[0080]

<table>
<thead>
<tr>
<th></th>
<th>1回目</th>
<th>2回目</th>
<th>3回目</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>吸着量 (mg)</td>
<td>吸着量 (mg)</td>
<td>吸着量 (mg)</td>
</tr>
<tr>
<td>金</td>
<td>5.1</td>
<td>3.6</td>
<td>3.5</td>
</tr>
<tr>
<td>白金</td>
<td>6.1</td>
<td>2.8</td>
<td>2.6</td>
</tr>
<tr>
<td>パラジウム</td>
<td>6.4</td>
<td>2.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>

[0081]
表1から明らかのように、いずれの貴金属にあっても1回目の吸着量より2回目の吸着量が少なくなっていたが、2回目と3回目の吸着量に差異は認められなかった。

回収率については、いずれの貴金属にあっても2回目以降において85％以上であった。

以上の結果より、脱離用溶液としてチオ尿素と塩酸との混合溶液を用いることにより、吸着剤から貴金属を脱離させると共に、吸着剤の再生も可能であることが確認された。

[0082]
（d. X線回折及び顕微鏡観察）
以上説明した貴金属の吸着試験を行った吸着剤、貴金属脱離試験を行った吸着剤についてX線回折分析及び電子顕微鏡観察を行っている。

図9は、ジメチルアミノの官能基を固定化した吸着剤に金を吸着させた後にX線回折を行った結果を示すグラフである。

[0083]
図9から明らかのように、吸着後の回折パターンにおいて、元素状の金に特有の4本の鋭いピークが観察された。なお、金を吸着させる前の吸着剤についてもX線回折を実施したが、かかるピークは観察されなかった。

従って、吸着させた金は、元素状の金として吸着剤表面に付着しているものと考えられ
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なお、イミノジ酢酸の官能基を固定化した吸着剤の場合も、図9と同様なパターンであった。

【0084】
一方、図10は、ジメチルアミンの官能基を固定化した吸着剤に金を吸着させた試料の
電子顕微鏡写真である。
図10に示した電子顕微鏡写真中、白い部分が析出した元素状の金である。
かかる結果は、前述した図9に示した結果と一致していた。

【0085】
図11及び図12は、ジメチルアミンの官能基を固定化した吸着剤の顕微鏡写真であり
、図11は金を吸着させたものあり、図12はテオ尿素と塩酸とを混合させた脱離用溶液
を用いて金を脱離させた後のものである。
図11から明らかのように、脱離操作を行う前にあっては元素状の金の粒子が観察され
たが、図12から明らかのように、脱離操作後であってはそのような粒子は観察されず、
前記脱離用溶液によって吸着剤から金が脱離されていた。

【実施例2】

【0086】
吸着剤の基体に含まれるセルロースの結晶化度と官能基の導入量との関係を求めた結果
について説明する。
基体として古紙及び微結晶セルロース（メルク社製）を用いた。
これらの基体について、実施例1で説明した方法により、前処理及び塩素化した後、ジ
メチルアミンを官能基として固定化し、そして、官能基の固定前後の基体に含まれるセル
ロースの結晶化度を前記したX線測定法を用いて測定した。
次の表2は、その結果を示すものである。

【0087】
【表2】

<table>
<thead>
<tr>
<th></th>
<th>古紙</th>
<th>本吸着剤</th>
<th>微結晶セルロース</th>
<th>比較用吸着剤</th>
</tr>
</thead>
<tbody>
<tr>
<td>I_051</td>
<td>270</td>
<td>82</td>
<td>794</td>
<td>204</td>
</tr>
<tr>
<td>I_20</td>
<td>94</td>
<td>76</td>
<td>142</td>
<td>84</td>
</tr>
<tr>
<td>結晶化度 (%)</td>
<td>65.2</td>
<td>7.3</td>
<td>82.1</td>
<td>58.82</td>
</tr>
</tbody>
</table>

【0088】
表2から明らかのように、古紙を用いた基体の結晶化度は70%より低い65.2%であり
、古紙を基体としてジメチルアミンを固定した本吸着剤の結晶化度は7.3%であっ
た。そして、かかる基体に固定された官能基の量を求めたところ、基体の乾燥質量1g当
たり3.6mol/1の官能基が固定されていた。

【0089】
一方、微結晶セルロースを用いた基体の結晶化度は70%より高い82.1%であり、
微結晶セルロースを基体としてジメチルアミンを固定した比較用吸着剤の結晶化度は58
.8%であった。そして、かかる基体に固定された官能基の量を求めたところ、基体の乾
燥質量1g当たり0.7mol/1の官能基が固定されていた。

後者の比較用吸着剤、即ち微結晶セルロースを基体としてジメチルアミンを固定した吸
着剤について、貴金属の吸着特性を検討した。

【0090】
図13はその結果を示すグラフである。
なお、図中、白抜き丸印は金（III）を、白抜き三角印はパラジウム（II）を、白抜き
四角印は白金（IV）を示しており、本試験の詳細な条件は図2について説明したことに
なじである。

図3から明らかのように、微結晶セルロースを基体としてジェメチルアミンを固定した
吸着剤には、金及び白金は強く吸着し得ることがなかった。

【0091】

一方、前述した図2に示したように、古紙を基体としてジェメチルアミンを固定した吸着
剤には、金、白金は、及びパラジウムのいずれの貴金属も、略100%吸着されてい
た。

以上の結果より、基体に含まれるセルロースの結合度が70%程度を超える場合、セ
ルロースの結晶の内部に貴金属と結合する官能基を殆ど導入することができず、セルロー
スへの官能基の導入率が著しく低いので、貴金属の回収効率が低い。

【0092】

一方、結晶度が70%程度以下のセルロースを含む基体を用いた場合、セルロースへ
の官能基の導入操作中に、結晶質部分が露銅的に非晶質化するため、その内部まで官能基
が導入され、セルロースへの官能基の導入率が飛躍的に増大する。これによって、吸着剤
単位質量当たりの貴金属の吸着量が増大するので、貴金属の回収効率が飛躍的に向上する

【0093】

ところで、基体に含まれるセルロースの結晶度が低い場合、吸着剤の取り扱いが困難
となり、セルロースの一部が吸着剤から流出する腐があるが、前述した古紙を用いた吸着
剤にあっては、ペミセルロース及びリグニンを含有しているため、結晶化度が7.3%と低
い値であっても、吸着剤の全体として縮まっているので、吸着剤の取り扱いが容易であり
、セルロースの一部が吸着剤から流出する腐がない。

【図面の簡単な説明】

【0094】

【図1】イミノジ醇酸の官能基を固定化した吸着剤を用いた金属イオンの吸着百分率
と塩酸濃度との関係を示したグラフである。
【図2】ジェメチルアミンの官能基を固定化した吸着剤を用いた金属イオンの吸着百分
率と塩酸濃度との関係を示したグラフである。
【図3】イミノジ醇酸の官能基を固定化した吸着剤に対する金（III）イオン及びパ
ラジウム（II）イオンの飽和吸着量を検討した結果を示すグラフである。
【図4】ジェメチルアミンの官能基を固定化した吸着剤に対する金（III）イオン、白
金（IV）イオン及びパラジウム（II）イオンの飽和吸着量を検討した結果を示すグラ
フである。
【図5】カラム法による吸着試験に使用した装置構成を示す模式図である。
【図6】図5に示したカラムの拡大図である。
【図7】金属溶液を通過したカラムから流出された溶液中の各金属の濃度を経時的に
検出した結果を示すグラフである。
【図8】貴金属を吸着させた吸着剤から脱離される貴金属の濃度を経時的に検出した
結果を示すグラフである。
【図9】ジェメチルアミンの官能基を固定化した吸着剤に金を吸着させた後にX線回折
を行った結果を示すグラフである。
【図10】ジェメチルアミンの官能基を固定化した吸着剤に金を吸着させた試料の電子
顕微鏡写真である。
【図11】ジェメチルアミンの官能基を固定化した吸着剤の顕微鏡写真である。
【図12】ジェメチルアミンの官能基を固定化した吸着剤の顕微鏡写真である。
【図13】微結晶セルロースを基体としてジェメチルアミンを固定した吸着剤について
、貴金属の吸着特性を検討した結果を示すグラフである。

【符号の説明】
1 カラム
2 第1ボンプ
3 第2ボンプ
5 分取器
1 1 外筒
1 2 内筒
2 1 ガラスビーズ領域
2 2 吸着剤領域
Old newspaper could be worth its weight in gold
17:12 07 July 2008
NewScientist.com news service
Colin Barras

Hold onto that old newspaper, it could be worth its weight in gold. That’s the message from Japanese scientists who say that newsprint is a vital ingredient in a new process for recovering gold and other precious metals from industrial waste metal solutions. The treated paper can hold its weight in gold, they say.

Old electronic consumer devices such as computers, televisions and mobile phones are an important source of precious metals, which are used in their manufacture. But recovering the metals isn’t easy and usually requires large quantities of chemicals that are known to damage the environment.

Now a team of Japanese chemists says it can do a similar job using inexpensive and renewable materials.

Katsutoshi Inoue and colleagues at Saga University in Japan, crushed and washed old newspapers and then combined the pulp with a chlorine compound. The chlorinated paper was then treated with dimethylamine (DMA) and formaldehyde to form what they call a DMA-paper gel. Finally, this is dried to powder form.

Strong liquor

Inoue’s team tested the DMA-paper gel’s ability to bind to, or adsorb, metal using a standard industrial sample consisting of a liquor produced by dissolving old metallic components in hydrochloric acid.

The liquor contains the common metals copper, zinc and iron, each in concentrations ranging from 190 to 840 parts per thousand. However, it also contains 250 parts per million of gold and 11 to 16 parts per million of platinum and palladium.

The gel turned out to be highly selective in the metals it adsorbed. It took up over 90% of the gold, platinum and palladium, but almost negligible quantities of copper, zinc and iron.

The waste paper is a crucial part of the gel’s structure: the amorphous nature of the cellulose within the paper allows chemicals to penetrate easily into its matrix and leads to a high carrying capacity — one kilogram of gel can hold 908 grams of gold.

Slow but sure

“And you can use the gel again after the metal [is removed],” says Chaitanya Raj Adhikari, a member of Inoue’s team. Adhikari says it is as yet unclear exactly why the DMA-paper gel is so selective for precious metals. “Although amine groups in DMA are known to favour precious metals,” he says.

“Our gel is prepared from inexpensive, renewable resources and it has high selectivity and capacity for precious metals,” says Adhikari. “Those properties make it a wonderful adsorbent.”

Jiunnin Yu at Kunming University of Science and Technology in Yunnan province, China, agrees that the DMA-paper gel gives impressive yields, but says it takes at least five hours to adsorb the precious metals, a significant disadvantage that may limit its industrial use. “The adsorbing kinetics are very slow,” he says.

Journal reference: Environmental Science & Technology (DOI: 10.1021/es80155x)

Related Articles

Instant gold, and where to find it
http://technology.newscientist.com/article/mg19325871.500
Research highlights

Inorganic polymer-based microchips are resistant to solvent attack

Prices of microreactors stamped down

Polymer-based microreactors turn inorganic to best organic solvent attacks and reduce prices.

Dong-Pyo Kim from the Chungnam National University, Daejeon, Korea, and colleagues used inorganic polymers to make microreactors that are resistant to attack by organic solvents and should be cheap to manufacture.

Microreactors are miniaturized devices where reactions take place within a confined space typically in the form of microchannels on a chip. They have a number of advantages over conventional reaction systems including yield, energy efficiency, reaction control and safety.

A variety of materials have been used to make microreactors, including metal, silicon, glass and polymers. However, while metallic and silicon-based devices are durable they are expensive to make. Conversely, polymer reactors are cheap to manufacture but prone to attack by organic solvents limiting their use. Now Kim’s team has developed inorganic polymer microreactors which offer the best of both worlds.

The team made microreactors using two commercially available inorganic polymers—polyvinylsilazane and allyldipropargylcarboxylate—and a well-established microimprinting lithography technique. Kim believes this low cost method could be used for mass production. Tests showed the microreactors are resistant to attack by a variety of organic solvents.

To create the microreactor, Kim dropped liquid inorganic polymer onto a glass slide under a nitrogen atmosphere. He then placed a stamp—with the microchannel in relief on its surface—into the polymer and cured it using UV light. The polymer solidified, and the stamp was removed leaving the impression of the microchannel. The polymer was then heated before a second glass slide coated with the polymer was placed on top, enclosing the channel.

To demonstrate the performance of their new microreactors the team showed that they could be used to carry out three synthetic organic reactions—synthesis of 3,5-dimethoxybenzaldehyde, a Diels–Alder cycladdition and a Knoevenagel condensation. Kim is currently exploring ways to improve the fabrication process as well as looking at applying these microreactors in other fields such as biotechnology and biomedical engineering.

Nicola Burton

Reference

Selective recovery of valuable metals from industrial wastewater

Newspaper filters out gold

Ordinary newspaper can be used to recover precious metals from industrial wastewater, say researchers in Japan.

Kazutoshi Inoue, and co-workers from Saga University, formed an active gel by treating newspaper with p-aminobenzoic acid—a readily available compound used in sunscreen. Inoue shows that when water is passed through a column packed with this modified paper, gold, palladium and platinum are filtered out in preference to other metals.

Recycling valuable precious metals from industrial effluent is highly desirable, but not easy. Current methods suffer from incomplete metal removal, are expensive and have toxic waste products. Inoue’s method overcomes these problems, whilst also providing a use for old newspapers. Jarek Drelich an expert in materials science at Michigan Technological University, Houghton, US, agrees saying that the route opens the prospect of mass producing waste-biomass-based sorbents that could benefit not only the hydrometallurgical industry but also the paper recycling industry.

Inoue showed that a column packed with the gel could be used repeatedly, a good sign for industrial applications. Future challenges for the Japanese workers include separation and purification of the recovered metals.

Rananne Owen

References

Old newspapers prove to be useful absorbents

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CNS Chem. Sci., 2008, 8, C65–C72
Vana ajaleht võib olla kulda väär

Jaapani teadlased teatavad uue meetod, kuidas metallitiibustest väärismetalle eraldada. Elistatud tõidelud ajalehepaber suudab nende sõnul siduda oma kasutaja võrdse koguse kudla.

Vanad elektroonikatoodud, arvutid, telefoned ja mobiiltelefonid sisaldavad väärismetalle, kuid nende eraldamine pole sugugi õhne ülesanne, sest aseleks kunagi palju keskkonnale ohtlikke kemikale, vahendas Tartu Olkkooli tehnioloogiaportaal Novator.

Nüüd on Jaapani keemikud võtnud jookumid lahenduse, kuidas saada metalitid käite näite, et protsess oleks odav ning kasutada sahko taastuvald materjala.

Sagi olukord teadlane Katsuosi Inoue laali puunudest hügie vanu ajaleht ning töötes nissutatud paberisegu looõhendiga. Seejärel tõlgendab paberist dünamiidiriiiga ja formaldehüüdiga, mille tulemusena tekkis geel, mis kuldistati publikiks.

Publi võimet metaalite siduda testil lahuses, kus vanu metallijaakide kõik tõidelud soolihappega.

Publi korjas metaalite üses vägaagi valikulisest: üles 50 protsendi kulla, plaatinast ja palladiumist, kuid peaaegu tasuoseta koguses vaske, tanini ja rauda.

Teadlaste sõnul suudab kilogramm ajalehepaberist valmistatud geeli endaga siduda 900 grammil kudla.

«Lisa on võimalik seda geeli kasutada uuesti, kui metall on eemaldatud,» üles lahenduse väljastamises osalenud Chattanya Raj Adhikari.

Hilma Kunmingi olukooli teadlane Jiamin Yu sõnul on geeli sisald võimu puudus. Nimelt võtab väärismetalid sidamise aega võhemalt viis tundi ja nii pikk aeg võib olla takistuseks meetodi rakendamises töötuses. 

Toimetas Stiri Erata, Tarblja24.ee
Old newspapers can literally land you a gold mine!

ANI
Tue, Jul 8 02:35 PM

London, July 8 (ANI): Japanese scientists have suggested that newsprint is a vital ingredient in a new process for recovering gold and other precious metals from industrial waste metal solutions.

Though old electronic consumer devices such as computers, televisions and mobile phones are an important source of precious metals, recovering them isn't easy and usually requires large quantities of chemicals that are known to damage the environment.

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Katsutoshi Inoue and colleagues at Saga University in Japan, crushed and washed old newspapers and then combined the pulp with a chlorine compound.

The chlorinated paper was then treated with dimethylamine (DMA) and formaldehyde to form what they call a DMA-paper gel. Finally, this is dried to powder form.

Inoue's team tested the DMA-paper gel's ability to bind to, or adsorb, metal using a standard industrial sample consisting of a liquor produced by dissolving old metallic components in hydrochloric acid.

The liquor contains the common metals copper, zinc and iron, each in concentrations ranging from 190 to 840 parts per thousand.

However, it also contains 250 parts per million of gold and 11 to 16 parts per million of platinum and palladium.

The gel turned out to be highly selective in the metals it adsorbed. It took up over 90% of the gold, platinum and palladium, but almost negligible quantities of copper, zinc and iron.

The waste paper is a crucial part of the gel's structure: the amorphous nature of the cellulose within the paper allows chemicals to penetrate easily into its matrix and leads to a high carrying capacity - one kilogram of gel can hold 906 grams of gold.

"And you can use the gel again after the metal is removed," said Chaitanya Raj Adhikari, a member of Inoue's team.

"Our gel is prepared from inexpensive, renewable resources and it has high selectivity and capacity for precious metals," according to Adhikari. "Those properties make it a wonderful adsorbent," he added. (ANI)
Makulatura na wagę złota
08-07-2008 11:00

Makulatura, gazeta, stara dimetylosamina, formaldehyd, tel DMA-papierowy, metale szlachetne, chlor

Od dzisiaj stare gazety mogą być nie tylko ponownie przetwarzane na papier. Dzięki nim będzie można odszukać metale szlachetne z elektroniką, np. zutych części komputerów, telefonów komórkowych czy telewizorów (Environmental Science & Technology).

Do tej pory nie było to łatwe i wymagało używania duchowych i szkodliwych dla środowiska związków chemicznych. Zespół Kaizutoshi Iwone z Saga University w Japonii opracował jednak dużo tańsze i przyrodnie technologie. Na praktykownej stacji papieru zmoczyli go i dodali do pulpę chlornu. Następnie potraktowali całość dimetylosaminą (DMA) oraz formaldehydem, by w ten sposób powstał tel DMA-papierowy. Na końcu został on wysuszony i przetworzony na proszek.

Japończycy przetestowali zdolność adsorpacyjną żelu, wprowadzając do niego standardową próbą przemysłową. Jest to rozwój uzyskany przez rozpuszczanie metalowych części w kwasie solnym. Znajdują się w nim różne metale: półmetal, np. miedź, cynk i żelazo (w stężeńach wahaących się od 19 do 84% części na wysad), ale również szlachetne i przejściowe, m.in. zło (25% części na milion) oraz platyna i palladium (11-16 części na milion).

Okazało się, że żel był bardzo selektywny w odniesieniu do różnych rodzajów metali. Wyląpił 90% złota, platyny i palladiu, lecz zaledwie 1% ilości miedzi, cynku i żelaza. Zalety papieru stanowi ważny element opisywanej technologii. Amorficzna natura celulozy pozwala na łatwiejszą penetrację metalu przez metale i zwiększa możliwość w zakresie ich włączania - jeden kilogram żelu jest w stanie utrzymać do 906 gramów złota. Po usunięciu metale żel można wykorzystać ponownie - wyjaśnia Chaitanya Raj Adhikari, członek japońskiej ekspertyzy. Dodaje też, że nie wiadomo, czemu tak wybiórczo działa on na metale szlachetne, choć nie da się ukryć, że grupy aminowe w DMA wykazują do nich powodowanie.

Inni eksperci doceniają prace Japończyków, podkreślając jednak, że adsorpcja przebiega bardzo wolno i trwa co najmniej 5 godzin. Wygodnie, stanowi to poważny minus i ogranicza możliwości zastosowania wynalazku w przemyśle.

Autor: Anna Błonia
Źródło: New Scientist

Inni eksperci doceniają prace Japończyków, podkreślając jednak, że adsorpcja przebiega bardzo wolno i trwa co najmniej 5 godzin. Wygodnie, stanowi to poważny minus i ogranicza możliwości zastosowania wynalazku w przemyśle.

Świeca to jest ich wynalazek to tylko oni są ekspertami. Produkcja piwa czy wina wcale nie trwa krócej.
Panen Emas dari Koran Bekas

SELASA, 8 JULI 2008 | 21:00 WIB

JAKARTA, SELASA - Jangan buang koran bekas Anda karena siapa tahu bisa bermanfaat untuk memanen emas.

Menurut ilmuwan Jepang, koran bekas merupakan salah satu bahan ramuan gel ramah lingkungan untuk memisahkan emas dari sampah elektronika.

Selama ini kita tahu bahwa komputer bekas, televisi, dan ponsel mengandung logam mulia pada sebagian komponennya. Namun, sampah dibuang begitu saja karena memisahkan logam yang diinginkan termasuk sulit. Seringkali membutuhkan zat kimia beracun yang dapat merusak lingkungan.

Dengan koran bekas, para ilmuwan dari Universitas Saga, Jepang tidak hanya membuat proses tersebut menjadi lebih mudah, namun juga murah dan ramah lingkungan. Tim ilmuwan yang dipimpin Katsutoshi Inoue menghancurkan koran bekas menjadi bubur dan membersihkannya dengan mencampurkan ke dalam cairan korin. Bubur kertas tersebut kemudian dicampur dimethylamine (DMA) dan formaldehid sehingga membentuk senyawa dalam bentuk gel.

Kemudian, gel dikeringkan dan ditumbuk menjadi bubuk. Bubuk tersebut diuji untuk mengikat atau menyerap logam dari sampah elektronika yang biasanya telah dicairkan dengan asam hidroklorik.

Cairan beracun tersebut mengandung logam berat seperti tembaga, seng, dan besi yang masing-masing berkonsentrasi antara 190-840 bagian per mil. Namun, sekitar 250 bagian per mil adalah emas dan antara 11-16 bagian per mil adalah platina dan palladium.

Bubuk gel tersebut ternyata efektif memenan logam mulia. Senyawa gel mengikat sekitar 90 persen emas, platina, dan palladium, namun tembaga, seng, dan besi tidak terikat.

Kertas bekas menjadi komponen utama gel tersebut karena berasal dari kayu sehingga memilki kandungan selulosa yang sangat tinggi. Sifat alami selulosa yang fleksibel memudahkan zat kimia menembus matrik larutan logam dan mengikatnya. Satu kilogram gel dapat mengikat 805 gram emas.


Hal tersebut mungkin kurang efektif jika dipakai pada skala industri. Namun, sambilanya temuan ini telah menjajikan senyawa yang murah dan lebih ramah lingkungan untuk memanen logam-logam mulia dari sampah elektronika.
Old newspapers can literally land you a gold mine!

Malaysia News.Net
Tuesday 8th July, 2008 (ANI)

London, July 8: Japanese scientists have suggested that newsprint is a vital ingredient in a new process for recovering gold and other precious metals from industrial waste metal solutions.

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The chlorinated paper was then treated with dimethylamine (DMA) and formaldehyde to form what they call a DMA-paper gel. Finally, this is dried to powder form.

Inoue's team tested the DMA-paper gel's ability to bind to, or adsorb, metal using a standard industrial sample consisting of a liquor produced by dissolving old metallic components in hydrochloric acid.

The liquor contains the common metals copper, zinc and iron, each in concentrations ranging from 160 to 840 parts per thousand.

However, it also contains 250 parts per million of gold and 11 to 16 parts per million of platinum and palladium.

The gel turned out to be highly selective in the metals it adsorbed. It took up over 90% of the gold, platinum and palladium, but almost negligible quantities of copper, zinc and iron.

The waste paper is a crucial part of the gel's structure: the amorphous nature of the cellulose within the paper allows chemicals to penetrate easily into its matrix and leads to a high carrying capacity - one kilogram of gel can hold 906 grams of gold.

"And you can use the gel again after the metal is removed," said Chaitanya Raj Adhikari, a member of Inoue's team.

"Our gel is prepared from inexpensive, renewable resources and it has high selectivity and capacity for precious metals," according to Adhikari. "Those properties make it a wonderful adsorbent," he added.
Newspapers Offer Solution for Precious Metal Recycling
Treated paper extracts precious metals, ignores regular ones

A massive amount of gold and other precious metals is used every year to fabricate electronic consumer devices such as computers, television sets and mobile phones. It might not seem so obvious at first, but the landfill may literally be a gold mine. The real problem with recycling these metals is that the process is usually very complicated and expensive, requiring large amounts of chemical compounds that have damaging effects on the environment.

Japanese researchers now claim that they have developed a gold and other precious metal extraction method involving the use of treated paper, able to hold an amount of gold equivalent to its own weight. Old newsprint is first crushed and washed, then mixed with chlorine. Afterwards, the chlorine paper is treated with dimethylamine and formaldehyde, thus creating dimethylamine-paper gel which can then be turned into powder.

While testing the newly developed compound for its metal binding capabilities in a standard industrial liquid containing old metallic components in hydrochloric acid, the research team of the Saga University, Japan realized that it could absorb up to 90 percent of the gold, palladium and platinum concentrations, while more common metals such as copper, zinc or iron bonded to the paper in insignificant quantities.

Because of its amorphous nature, cellulose plays a crucial role in the structure of the gel as it allows chemicals to penetrate it easily, thus enabling it to absorb and hold roughly the same amount of metal as its own weight.

"And you can use the gel again after the metal is removed," said Chaitanya Raj Adhikari, a member of the team of researchers assisting the leader of the study Katsutoshi Inoue of the Saga University.

Although the results are rather impressive, other researchers point out a downside to the process: It takes about five hours for the paper to absorb the metals. "The adsorbing kinetics are very slow," said Jianmin Yu of the Kunming University of Science and Technology, China.
Kopalnia Wiedzy

Komentarze do wiadomości => Ciekawostki => Wątek zaczytany przez: kopalniawiedzy Lipiec 08, 2008, 10:07:15 am

Od dziś stare gazety mogą być nie tylko ponownie przetwarzane na papier. Dzięki nim będzie można odzyskać metale szlachetne z elektroniki, np. zużytych części komputerów, telefonów komórkowych czy telewizorów (Environmental Science & Technology).

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Tytuł: Odp: Makulatura na wagę złota
Wiadomość wysłana przez: waldi888231200 Lipiec 08, 2008, 11:00:49 am

Czytaj

Inni eksperci doceniają prace Japończyków, podkreślają jednak, że adsorpcja przebiega bardzo wolno i trwa co najmniej 5 godzin. Wg nich, stanowi to poważny minus i ogranicza możliwość zastosowania wynalazku w przemyśle.

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Tytuł: Odp: Makulatura na wagę złota
Wiadomość wysłana przez: mikroos Lipiec 08, 2008, 01:41:05 pm

Czytaj: waldi888231200 Lipiec 08, 2008, 11:00:49 am

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Panen Emas dari Koran Bekas

by nchiha clan on Thu Jul 24, 2008 4:49 pm

Jangan buang koran bekas Anda karena siapa tahu bisa bermanfaat untuk memenan emas. Menurut ilmuwan Jepang, koran bekas merupakan salah satu bahan ramuan gel ramah lingkungan untuk memisahkan emas dari sampah elektronika.

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