REMOVAL OF METAL IONS FROM WASTEWATER WITH NATURAL WASTES

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ABSTRACT

This paper reported the research of the removal of priority metal ions, such as, lead, nickel, zinc from wastewater by using tree leaves. Twelve different kinds of tree leaves were tested at the room temperature. The experiments were carried out with 2 g of 40 - 50 mash leaves in 200 ml synthetic wastewater containing about 50 ml/l metal ions. The initial pH of the synthetic wastewater was about 5. The experiments showed that highest removal rate was 96 % for lead (Pb^{++}), 61.7 % for Nickel (Ni^{++}), and 71.3 % for Zinc (Zn^{++}). The goal for this research is to develop inexpensive, highly available, effective metal ion adsorbents from natural wastes as alternative to existing commercial adsorbents.

INTRODUCTION

Industrial and municipal waste water frequently contain metal ions. These metal ions, when present in sufficient quantity, can be harmful to aquatic life and human health. Current methods for such wastewater treatment include precipitation, coagulation/flotation, sedimentation, flotation, filtration, membrane process, electrochemical techniques, ion exchange, biological process, and chemical reaction. Each method has its merits and limitations in application. The adsorption process with activated carbon is attracted by many scientist because of the effectiveness for the removal of heavy metal ion at trace quantities. But the process has not been used extensively for its high cost. For that reason, the use of low cost materials as sorbent for metal removal from wastewater have been highlighted. More recently, great effort has been contributed to develop new adsorbents and improve existing adsorbents like granular activated carbon, other adsorbents such as iron oxide coated sand [1], porous cellulose carrier modified with polyethyleneimine [2], iron coat granular activated carbon [3], modified chitosan [4] etc. One of the exploitation is the use of natural wastes. Materials investigated are Cotton [28]; walnut waste [22]; peanut skins[24,27]; sugar cane waste and onion skin [19]; coffee grounds [20]; tea leaves [32]; apple waste [21]; wool fibre [16]; green algae and rice hull [29]; bark and other cellulosic material [17,18,23,25,26,30,31], Cottonseed hulls, Rice straw, soybean hulls [5], linseed flax straw [10]. Because of the low cost, high availability of these materials, and no need for complicated regeneration process. This method is attracting more and more Scientists and Engineers.

Marshall and Champagne [5] evaluated byproducts of soybean and cottonseed hulls, rice straw and sugarcane bagasse as metal ion adsorbents in aqueous solutions. The adsorption capacities for Zn(II) varied from 0.52 to 0.06 meq/g dry weight of byproduct. Rice straw and sugarcane bagasse had low adsorption capacities($\leq$ 0.12 meq/g). At a subsaturating concentration of metal ion (100mg/L), soybean and cottonseed hulls adsorbed high levels (95.6-99.7%) of Cr(III), Co(III), Cu(II), Ni(II), and Zn(II). In the test of wastewaters with environmentally unacceptable concentrations of Zn(II), Cu(II) and Ni(II), the percentage of metal ion adsorbed ranged from 53.4 to 99.8% depending on the particular wastewater and metal ion. Although not as effective as a commercial chelating resin in removing metals from wastewaters, soybean and cottonseed hulls could be useful adsorbents in metal removal applications, especially when the low cost and high availability of these materials are considered.

Vazquez, Antorrena, Gonzalez, and Doval [6] reported the ambient temperature adsorption of the metal cations Zn^{2+}, Cu^{2+} and Pb^{2+} on Pinus pinaster bark pretreated with acidified formaldehyde solution. They investigated the influences of the pretreatment conditions and of the pH of the cation solution on the adsorption capacity of the bark. They found that the bark was an excellent adsorbent for removal of toxic ions from wastewater with efficiency comparable to commercially available adsorbents, but at a reduced cost. Under favorable conditions, the fractions of dissolved ion adsorbed 85-95% for Pb^{2+}, 55-85% for Cu^{2+} and 51-57% for Zn^{2+}.

Periasamy and Namasivayam [7] studied to use activated carbon prepared from peanut hulls (PHC) for the adsorption of Cd (II) from synthetic wastewater. An almost quantitative removal of 20 mg/L

Cd (II) by 0.7 g of PHC/L of aqueous solution was observed in the pH range 3.5-9.5. A comparative study with commercial granular activated carbon (CAC) showed that the adsorption capacity of PHC was 31 times larger than that of CAC.

de Vasconcelos and Beca [8] investigated the feasibility of using pine bark for the decontamination of waste waters from heavy metal ions, Pb (II), Cd (II) and Cr (III). It was concluded that the adsorbent's fraction size and 'concentration' as well as the solution's pH and metal ion concentration, reached significant levels that should be considered. They believed that with optimal operating conditions, pine bark may be successfully used to solve the pollution problems of industrial waste waters.

Orhan and Buyukgungor [9] used adsorbents such as waste tea, Turkish coffee, exhausted coffee, nut and walnut shells to remove heavy metals from wastewater. Batch studies were conducted at room temperature and adsorption experiments were carried out by shaking 0.3 g of adsorbent with 100 ml synthetic wastewater containing Cr (VI), Cd (II) and Al (III) metal ions. The remaining concentration of heavy metals in each samples after adsorption at various time intervals was determined spectrophotometrically. Batch studies showed that these adsorbents exhibit a good adsorption potential for Al (III) metal ions. The adsorption ratios of Al (III) were as 98, 99, 96, 99.5 and 96% for waste tea, Turkish coffee, exhausted coffee, nut and walnut shells, respectively.

The aim for this research is to develop inexpensive and effective metal ion adsorbents from plentiful sources of natural wastes (or byproducts), such as tree leaves to offer these adsorbents as replacements for existing commercial materials. Tree leaves has been proven for its effectiveness for the cleaning of air pollution and balance environment. However, to our knowledge, few such studies have been performed previously to use the tree leaves to clean the wastewater. As we mentioned earlier, tea leaves, a kind of tree leaves, has been proven for its ability to remove the metal ions from wastewater. But the availability of tea leaves is much less than tree leaves.

EXPERIMENT:

Tree leaf preparation: The leaves were gathered from twigs into clean plastic bags. Washed with DI water and laid flat on clean table to dry. Dry leaves were grounded with CUISINART MINI-MATE PLUS CHOPPER/GRINDER. After grounded, the leaf particles were sieved and stored into plastic bag by size, and ready for use.

Synthetic wastewater preparation: The synthetic wastewater samples, Pb^{++}, Ni^{++}, and Zn^{++}, were prepared from $Pb(NO_3)_2$, $ZnSO_4 \cdot 7H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$. All chemicals were supplied by Fisher Chemical, ACS Certified.. The pH of the wastewater was adjusted to about 5 to prevent hydrolysis.

Analysis of the concentration of wastewater and quality control: The concentration of metal ion in wastewater was analyzed by Atomic Absorption Spectrophotometer. For the quality control purpose, DI water digested and analyzed with every sample group to track any possible contamination source. A duplicate analyzed for every sample to track experimental error and show capability of reproducing results. A QC sample analyzed with every group of samples. Concentration of the QC sample is within the same curve range as the samples and digested the same as the samples to verify the accurate recovery of the unknown samples with a sample of known concentration.

Adsorption experiment: The experiments were carried out in the batch mode for the measurement of adsorption capacities. The bottles with 250 ml capacity was filled with wastewater and adsorbent. The bottles were shaken for a predetermined period at room temperature in a reciprocating shaker. The separation of the adsorbents and solution was carried out by centrifugation. The solution was analyzed by Atomic Absorption Spectrophotometer. The adsorption of metal ions by the adsorbents is subsequently calculated by mass balance.

RESULTS AND DISCUSSION

Adsorption on tree leaves: Table 1 listed the adsorption of three kinds of metal ions on twelve kinds of tree leaves. As shown in table 1, different metal ion on the same tree leaf had different removal rate. At the same experimental conditions, lead (Pb^{++}) had highest removal rate, nickel (Ni^{++}) had lowest removal rate. For lead, the highest removal rate in the tested leaves reached 96 %. however, the highest removal rate for nickel was 61.7 %.

For the same metal ion, different tree leaves had different removal rates. In the tested leaf group, Common Persimmon (CP) and Mountain-Laurel (ML) showed highest removal rate for lead (Pb^{++}). Common Persimmon (CP) also showed higher removal rate for nickel ion (Ni^{++}) and Zinc ion (Zn^{++}). The highest removal rates for Nickel ion (Ni^{++}) and Zinc ion (Zn^{++}) were Sugar Maple leaves. They were 61.7 % for Nickel ion (Ni^{++}) and 71.3 % for Zinc ion (Zn^{++}).

Influence of contact time on adsorption:

Preliminary experiments showed that the adsorption of metal ions by leaves reached equilibrium in less than 30 minutes. Figure 1 showed the experimental results of adsorption of Zinc ion (Zn^{++}) and lead ion (Pb^{++})from synthetic wastewater containing 50 ppm Zn^{++} with Common Persimmon and Mountain Laurel leaves. The experiments were carried out under the conditions of room temperature, with 1 g of 40 - 50 mash leaf size in 100 ml of synthetic wastewater. The initial pH for the synthetic wastewater was 5. The contact time used from 30 minutes to 3 hours for Zinc adsorption and from 2 to 60 minutes for Lead adsorption. A reciprocating shaker, shacked samples at the rate of 300 rpm. The separation of the leaves with solution was carried out by centrifugation. The experiments showed that the removal rate occurs quickly, seemly reaching equilibrium within the first thirty minutes of adsorption.

Adsorption on activated carbon: Table 1 also showed the results of adsorption of metal ion, Pb^{++}, Ni^{++} and Zn^{++} on the commercial material, activated carbon. The experiments were conducted under the same conditions as in the adsorption by tree leaves. The experimental conditions has been indicated in Table 1.

In comparison with the adsorption of metal ions from wastewater by tree leaves, the activated carbon did not showed supreme results. The best removal rate for Pb^{++} was by Common Persimmon & Mountain Laurel, both removing 95.9 %, which is higher than activated carbon under the same test conditions. Magnolia removed 92.9 % and Eastern Redbud removed 91.8 % of Pb^{++}, which is quite close results as activated carbon. The best removal rate for Ni^{++} was by Sugar Maple, 61.7 %, in the tested group of tree leaves, which is lower than activated carbon, 68.5 %. For Zn^{++}, the best removal rate was by Sugar Maple, 71.3 %, not much difference from activated carbon, 72.1 %.

CONCLUSION:

(1) Tree leaves can be used in the wastewater treatment process for the removal of metal ions.
(2) The adsorption of the metal ion on tree leaves reached equilibrium in 30 minutes.
(3) The adsorption of different metal ions on the same tree leaf had different removal rate, lead (Pb^{++}) had the highest removal rate, nickel(Ni^{++}) had lowest removal rate.
(4) For the same metal ion, different tree leaves had different removal rate Common Persimmon and Mountain-Laurel showed highest removal rate for lead (Pb^{++}). Sugar Maple leaf showed the highest removal rates for Nickel ion (Ni^{++}) and Zinc ion (Zn^{++}).

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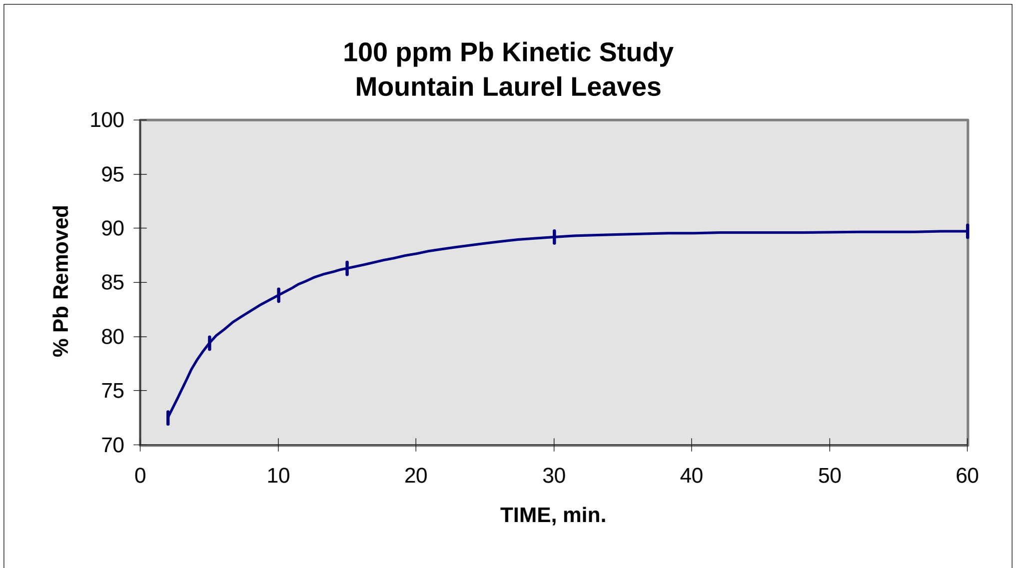
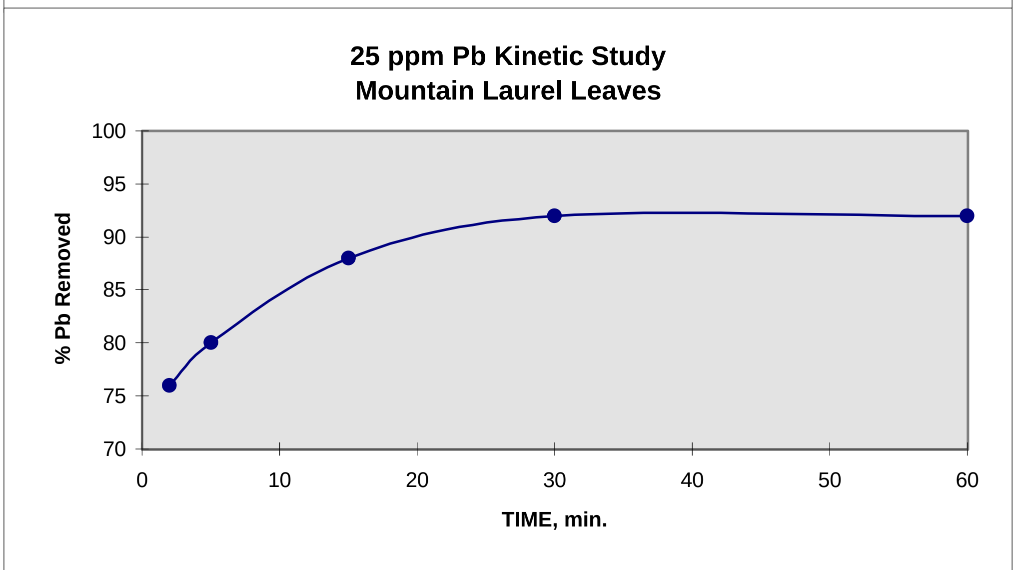
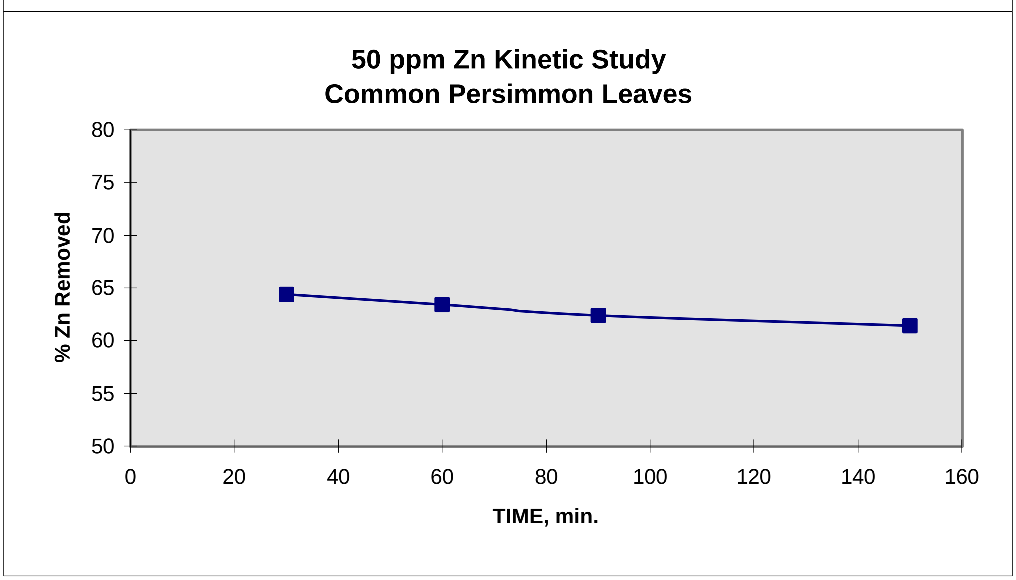
Table 1. Adsorption of metal ion from synthetic wastewater

Metal solution	**Pb^{++}**		**Ni^{++}**		**Zn^{++}**	
Initial concentration	49.00 mg/L		48.25 mg/L		50.50 mg/L	
Initial pH	5.42		5.46		5.56	
Leaf	**Final conc.**	**Removed%**	**Final conc.**	**Removed%**	**Final conc.**	**Removed%**
Bayberry Wax-Myrtle	7.0	85.7	34.5	28.5	36.0	28.7
Common Persimmon	2.0	95.9	21.5	55.4	18.5	63.4
Common Sassafras	8.0	83.7	35.5	26.4	33.0	34.7
Eastern Redbud	4.0	91.8	29.5	38.9	28.5	43.6
Flowering Dogwood	6.0	87.8	26.0	46.1	18.0	64.4
Glossy Privet	6.0	87.8	31.0	35.8	30.5	39.6
Southern Magnolia	3.5	92.9	35.5	26.4	31.5	37.6
Mountain-Laurel	2.0	95.9	22.0	54.4	20.5	59.4
Sugar Maple	11.0	77.6	18.5	61.7	14.5	71.3
Pecan	10.5	78.6	24.5	49.2	22.0	56.4
Pin Oak	8.0	83.7	33.5	30.6	34.5	31.7
Willow Oak	8.0	83.7	34.5	28.5	35.5	29.7
Activated carbon	3.0	93.9	15.2	68.5	14.1	72.1

Experimental conditions:
1. 2 g adsorbent (leaves or activated carbon) / 200 ml wastewater
2. Shake 2 hours @ 300 rpm
3. Centrifuge 10 minutes @ 4000 rpm
4. Leaf size 40 - 50 mash; Activated carbon size 50 - 60 mash.


100 ppm Pb Kinetic Study
Mountain Laurel Leaves
% Pb Removed
100
95
90
85
80
75
70
0
10
20
30
40
50
60
TIME, min.


25 ppm Pb Kinetic Study
Mountain Laurel Leaves
% Pb Removed
100
95
90
85
80
75
70
0
10
20
30
40
50
60
TIME, min.


50 ppm Zn Kinetic Study
Common Persimmon Leaves
% Zn Removed
80
75
70
65
60
55
50
0
20
40
60
80
100
120
140
160
TIME, min.