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Biosorption of Heavy Metals by Low Cost Adsorbents

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***Abstract*—**This paper describes the use of by-products as adsorbents for removing heavy metals from aqueous effluent solutions. Products of almond skin, walnut shell, saw dust, rice bran and egg shell were evaluated as metal ion adsorbents in aqueous solutions. A comparative study was done with commercial adsorbents like ion exchange resins and activated carbon too. Batch experiments were investigated to determine the affinity of all of biomasses for, Cd(II), Cr(III), Ni(II), and Pb(II) metal ions at pH 5. The rate of metal ion removal in the synthetic wastewater by the biomass was evaluated by measuring final concentration of synthetic wastewater. At a concentration of metal ion (50 mg/L), egg shell adsorbed high levels (98.6 – 99.7%) of Pb(II) and Cr(III) and walnut shell adsorbed high levels (35.3 – 65.4%) of Ni(II) and Cd(II). In this study, it has been shown that by-products were excellent adsorbents for removal of toxic ions from wastewater with efficiency comparable to commercially available adsorbents, but at a reduced cost. Also statistical studies using Independent Sample t Test and ANOVA One-way for statistical comparison between various elements adsorption showed that there isn't a significant difference in some elements adsorption percentage by by-products and commercial adsorbents.

***Keywords*—**Adsorbents, heavy metals, commercial adsorbents, wastewater, by-products.

I. Introduction

POLLUTION of the environment with toxic metals has been widespread and often involves large volumes of wastewater. Due to the magnitude of the problem of heavy metal pollution, research into new and cheap methods of metal removal has increased recently [17], [47]. Heavy metals (elements with an atomic density greater than 6 g/cm3) are one of the most persistent pollutants in water. Unlike other pollutants, they are difficult to degrade, but can accumulate throughout the food chain, producing potential human health risks and ecological disturbances. At least 20 metals are classified as toxic which half of them emitted into environment in concentrations that pose great risks to human health. The common heavy metals that have been identified in polluted water include Arsenic, Copper, Cadmium, Lead, Chromium, Nickel, Mercury and Zinc. The danger of heavy metal pollutants in water lies in two aspects of their impact [3].

Firstly, heavy metals have the ability to persist in natural ecosystems for an extended period. Secondly, they have the ability to accumulate in successive levels of the biological chain, thereby causing acute and chronic diseases [3].

Many industries are responsible for polluting the environment with heavy metals contained in their waste-waters. The removal of these metals is of the utmost interest from both environmental and economic viewpoints. The effluents generated by modern industries (petroleum refineries, non-ferrous metal works, aircraft plating and finishing, etc) generally have a complex composition which includes metals (ions or complexes), suspended solids and other components [19], [21]. According to increasingly stringent environmental laws, these effluents must be decontaminated because of their hazard to humans, animals and plants [9].

Several techniques have been proposed for the removal of metals, such as precipitation, flotation, sedimentation, filtration, ion exchange, solvent extraction, membrane processing, electrolytic methods, biological process and chemical reaction [30], [29]. Each method has its merits and limitations in application. The need for economical and effective methods for removing heavy metals from wastewater has therefore resulted in the search for other materials that may be useful in reducing the levels of heavy metals in the environment [39]. Remediation strategies must be designed to support high throughput while keeping costs to a minimum [25]. Since most conventional methods are neither effective nor economical, especially when used for the reduction of heavy metal ions to low concentrations, new separation methods are required to reduce heavy metal concentrations to environmentally acceptable levels at affordable cost. Bio-removal has the potential to contribute to the achievement of this goal [28], [1], [5].

One of the methods employed for removing contaminants, like heavy metals, from wastewater is adsorption [4], [11]. Bio-removal is the accumulation and concentration of heavy metals from aqueous solutions using biological materials [49]. Metals removal has been achieved by adsorption on different materials such as activated carbon, agricultural waste, moss peat, minerals, amongst others [48]. It is advisable that the adsorbent is available in large quantities, abundant in nature, easily regenerable, and economical. Agricultural by-products could be heavy metal adsorbents which could be selective for some metal ions [4], [21]. The agricultural by-products metal ion adsorption may involve metal interactions or coordination to functional groups present in natural proteins, lipids, and carbohydrates positioned on cell walls [44], [13], [25], [16], [27]. The term of biosorption is used to describe the passive non- metabolically mediated process of metal binding to living or dead biomass [43].

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Biosorption of heavy metals from aqueous solutions can be considered as an alternative technology in industrial wastewater treatment. The technique is an emerging technology based on the ability of biological materials to accumulate heavy metals from wastewater by either metabolically mediated or physico – chemical pathways of uptake [7], [23]. Biosorption has been found to be a more rapid mechanism; hence, it has a more significant role in metal sorption from wastewater [40].

Agricultural products such as wool, rice, straw, coconut husks, peat moss, exhausted coffee [12], waste tea [2], walnut skin, coconut fibre, cork biomass (10), seeds of Ocimum basilicum [35], defatted rice bran, rice hulls, soybean hulls and cotton seed hulls [50], wheat bran, hardwood (Dalbergia sissoo) sawdust, pea pod, cotton and mustard seed cakes [46], are also proven as good biomass sources [6], [22].

The use of dead biomass is of particular economic interest, because the biomaterials are used the same way as synthetic adsorbents or ion exchangers and repeated regeneration is possible [28], [31]. The large surface area, micro-porous character and chemical nature of the surface of activated charcoals have made them potential adsorbents for the removal of heavy metals form industrial wastewaters [15].

The adsorption process with activated carbon is attracted by many scientists 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 has been highlighted [32], [34], [9].

The aim for this research is to develop inexpensive and effective metal ion adsorbents from plentiful sources of natural wastes (or by-products) to offer these adsorbents as replacements for existing commercial materials [32]. In this study, by-products of almond skin, walnut shell, saw dust, rice bran, and egg shell were evaluated as metal ion adsorbents in aqueous solutions. A comparative study was done with commercial adsorbents like ion exchange resins and activated carbon. Capabilities were tested for, Pb(II) , Cr(III) , Ni(II), and Cd(II) metal ions at pH 5.

II. Materials and Methods

A. Samples Preparation

Samples include almond skin, walnut shell, saw dust, rice bran, and egg shell, were gathered into clean and separate plastic bags. Samples were washed with DI water and laid flat on clean table to dry. Dry samples were ground using a ball mill. The samples were ready to use after they were sieved and stored in plastic bags [32], [14].

B. Synthetic Wastewater Preparation

The synthetic wastewater samples with 50 mg/L initial concentration were prepared from 1000 ppm analytical standards of $Pb(NO_3)_2$ in HNO_3 0.5mol/l, $Ni(NO_3)_2$ in HNO_3 0.5mol/l, $Cd(NO_3)_2$ in HNO_3 0.5mol/l, $Cr(NO_3)_3$ in HNO_3 0.5mol/l (Merck, Germany). The pH of the wastewater was adjusted to about 5 to prevent hydrolysis.

C. Adsorption Experiment

The experiments were carried out in batch mode for the measurement of adsorption capacities. A mass of 0.5 g of each studied sample was weighed in bottles. Then 50 ml of synthetic wastewater was added to them. The bottles were shaken for 60 minutes (1 h) at room temperature in a reciprocating shaker at the rate of 230 u/min. The separation of the adsorbents and solution was carried out by centrifugation (4000 rpm, 10 min).

D. Analytical Procedure

After being centrifuged, the supernatants were analyzed by Atomic Absorption Spectrophotometer (Varian 240 AAS) [44], [32]. For the quality control purpose, initial synthetic wastewater was processed and analyzed with every sample group. A duplicate analyzed for every sample to track experimental error and show capability of reproducing results [44]. During the analyzing of separated samples by AAS, a QC sample was analyzed with every group of samples. Each of the experiment was carried out in duplicate and the average of two values was used in the calculations.

E. Data Analysis and Statistical Method

Statistical methods were used for the validation and verification analyzes that had been done by atomic absorption. After experiments performed and absorption measured in samples and data obtained by SPSS 22 software and Independent Sample t Test, ANOVA One-way data were analyzed and Excel software was used to depict charts.

III. Results And Discussion

A. Adsorption of Metal Ion from Synthetic Wastewater

Table I shows the experimental results of adsorption of chromium (Cr(III)), cadmium (Cd(II)), lead (Pb(II)) and nickel (Ni(II)) from synthetic wastewater (containing 50 ppm) on seven kinds of different samples. The experimental conditions have been indicated in Table I. When data were analyzed by Atomic Absorption Spectrophotometer, the following equation for removal of heavy metals was used:

$$\%\ \mathrm{Re}\ moval = \frac{(Ci - Cf)}{Ci} \times 100$$

where Ci is the Initial Concentration and Cf is the Secondary Concentration.

B. Adsorption on Biosorbents

Depicted results showed that the same metal ions, different samples had different removal rates. The adsorption capacities for Cr(III) varied from 55.1% to 99.7%. Rice bran and walnut shell had lowest adsorption capacities (55.1%, 60.3 % respectively) however egg shell, saw dust and almond skin showed highest removal rate for Cr(III). The adsorption ratios of Pb(II) were as 74.6, 98.6, 78.5, 87.0 and 91.1% for almond skin, egg shell, rice bran, saw dust and walnut shell, respectively. Egg shell showed highest removal rate for Pb(II) however rice bran and almond skin had lowest adsorption capacities (78.5%, 74.6% respectively). The adsorption ratios of Cd(II) were as 45.2, 41.9, 32.9, 39.5 and 65.4 % for almond skin, egg shell, rice bran, saw dust and walnut shell, respectively. So saw dust and rice bran showed the lowest adsorption capacities (39.5%, 32.9% respectively) where as highest rate was achieved by walnut skin. The adsorption capacities for Ni(II) varied from 14.4 to 35.3 %. So walnut skin has showed highest removal rate where as rice bran and egg shell have lowest (15.0%, 14.4% respectively). For Cr(III), the highest removal rate was 99.7%. However, the highest removal rate for Ni(II) was 35.3% (Fig. 1).

As shown in Table I, different metal ions on the same sample had different removal rates. At the same experimental conditions, Cr(III) had highest removal rate but Ni(II) had lowest removal rate. Egg shell showed highest removal rate for Cd(II), Pb(II) and Cr(III) in metal mixture. Highest removal rates for Ni(II) were achieved by walnut skin [32].

C. Adsorption on Activated Carbon and Ion Exchange Resins

The results of adsorption of metal ions, Pb(II), Cr(III), Ni, Cd(II) on the commercial materials (exchange resins and activated carbon) in single solution and metal mixture have been shown at Table I. This table in comparison presents the adsorption capacity of samples for each metal (Fig. 1).

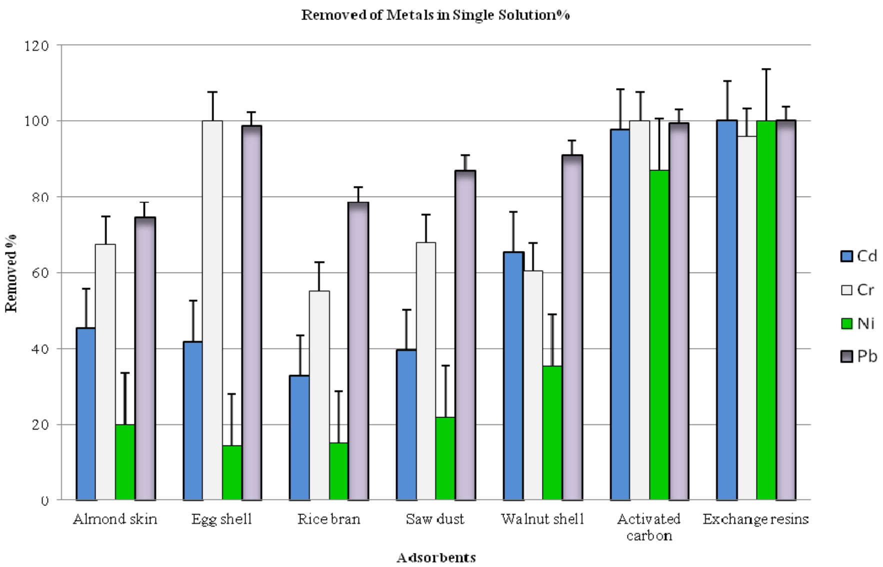

Fig. 1 Removed % of metals by by-products in Single solution (containing 50 ppm)

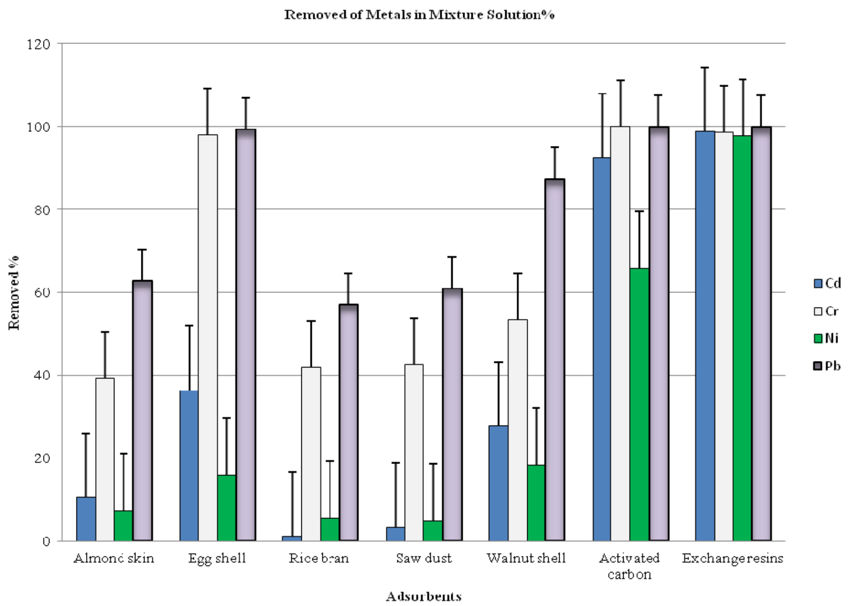

Fig. 2 Removed % of metals by by-products in Mixture solution (containing 50 ppm)

TABLE I
ADSORPTION OF METAL ION FROM SYNTHETIC WASTEWATER

Mixture of Four metals								Single Solutions								Metal solut
Pb		Ni		Cr		Cd		Pb		Ni		Cr		Cd		
50.1		52		47.8		48.8		49.4		48.6		49.2		48.6		Initial conc
4.8		4.8		4.8		4.8		5.0		5.1		5.1		5.3		Initial pH
Remov %	Final conc. mg/l	Remov %	Final conc. mg/l	Remov %	Final conc. mg/l	Remov %	Final conc. mg/l	Remov %	Final conc. mg/l	Remov %	Final conc. mg/l	Remov %	Final conc. mg/l	Remov %	Final conc. mg/l	Samples
62.7	18.7	7.3	48.2	39.3	29.0	10.6	43.6	74.6	12.5	19.9	38.9	67.4	16.0	45.2	26.6	Almond skin
99.4	0.3	15.9	43.7	98.1	0.9	36.4	31.0	98.6	0.7	14.4	41.6	>99.5	0.1	41.9	28.2	Egg shell
57.1	21.5	5.4	49.2	42.1	27.7	1.2	48.2	78.5	10.6	15.0	41.3	55.1	22.1	32.9	32.6	Rice bran
60.9	19.6	4.8	49.5	42.7	27.4	3.3	47.2	87.0	6.4	21.8	38.0	67.8	15.8	39.5	29.4	Saw dust
87.4	6.3	18.3	42.5	53.5	22.2	27.7	35.3	91.1	4.4	35.3	31.4	60.3	19.5	65.4	16.8	Walnut shell
>99.5	<0.1	65.8	17.8	>99.5	<0.1	92.4	3.7	99.4	0.3	87.0	6.3	>99.5	0.1	97.7	1.1	Activated carbon
>99.5	<0.1	97.7	1.18	98.6	6.6	98.8	0.6	>99.5	0.0	>99.5	0.2	95.9	2.0	>99.5	0.1	Exchange resins

Experimental conditions: 0.5 g adsorbent (samples or Activated carbon and Exchange resins) / 50 ml wastewater; shake 1 hours @ 300 rpm (230 u/min); centrifuge 10 minutes @ 4000 rpm; Samples size 40 mash; Activated carbon size 50 – 60 mash

In comparison with the adsorption of metal ions from wastewater by non-commercial samples, the best removal rate for Cr(III) was achieved by egg shell, removing 99.7 % which is the same as activated carbon and more than ion exchange resins under the same test conditions. The best removal rate for Pb(II) was achieved by egg shell, 98.6 % in the tested group of natural samples. This is quite close to results of activated carbon (99.3 %) and ion exchange resins (100 %). Saw dust removed 87.0 % and rice bran removed 78.5 % of Pb(II), which show a good adsorption potential for Pb(II). For Cd(II), the best removal rate was achieved by walnut skin (65.4%). Considering Table I the adsorption capacity of under study plant biosorbents (almond skin, walnut shell, saw dust and rice bran) for all metals in metal mixture was reduced (Fig. 2).

The removal rate of Cd(II) and Ni(II) in metal mixture considerably is lower than single solution. This means that the affinity of these biosorbents to adsorption of Cd(II) and Ni(II) is low. The egg shell shows a relatively stable removal rate in both of single and mixture solutions. This is probably because of the high adsorption capacity of egg shell. The removal rate of Ni(II) by activated carbon in metal mixture declined. The adsorption of other metals on activated carbon didn't show considerable differences in both solutions.

Statistical studies using Independent Sample t Test and ANOVA One-way for statistical comparison between various elements adsorption showed that there isn't a significant difference in some elements adsorption percentage by by-products and commercial adsorbents such as; egg shell, that had the best removal rate for Cr(III), removing >99.5 % which is the same as activated carbon and more than ion exchange resins under the same test conditions and also the best removal rate for Pb(II), 98.6 % in the tested group of natural samples. This is quite close to results of activated carbon (99.4 %) and ion exchange resins (>99.5 %) ($\alpha > 0.05$). The egg shell shows a relatively stable removal rate in both of single and mixture solutions although there is a significant difference between the removal of some metals by by-products and commercial adsorbents in metal mixture and single solution ($\alpha < 0.05$).

The good metal removal properties of by-products in water containing Cd(II), Cr(III), Ni(II) and Pb(II), proved the effectiveness of by-products in the widely used method of remediation of effluents contaminated with metals. With aid of these adsorbents, it is possible to adsorb heavy metal ions from wastewater. In this study egg shell, saw dust and almond skin showed highest removal rate for Cr(III). Egg shell also showed the highest removal rates for Cr(III) and Pb(II) in single solution and metal mixture (99.7 %, 98.6 % at an initial concentration of 50 ppm). This study is in agreement with other researchers who found that various by-products adsorb an ample amount of metal species (Table II).

A variety of low-cost biomass has been developed and commercialized for controlling pollution from diverse sources in different parts of the world [26]. They include anaerobically digested sludge [51], fungi [20], algae [18], and eggshells [24]. Agricultural materials have also been used. These include rice bran, soybean and cottonseed hulls [33], crop milling waste [45], ground nut husk [37], maize cob meal [38], coir, jute and sawdust [48], canola meal [5], and coconut shell [36] amongst others.

Marshall and Champagne evaluated by-products of soybean, cottonseed hulls, rice straw and sugarcane bagasse as metal ion adsorbents in aqueous solutions. At a subsaturating concentration of metal ion (100 ppm), soybean and cottonseed hulls adsorbed high levels (95.6 – 99.7 %) of Cr, Co, Cu, Ni and Zn. Rice straw and sugarcane bagasse had low adsorption capacities (≤ 12 mg/g). (Table II) [32].

Orhan and Buyukgungor 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 adsorbents with 100 ml synthetic wastewater containing Cr(III), Cd(II) and Al metal ions. Batch studies showed that these adsorbents exhibit a good adsorption potential for Al metal ions. The adsorption ratios of Al were as 98, 99, 96, 99.5 and 96 % for waste tea, Turkish coffee, exhausted coffee, nut and walnut shells, respectively [41].

TABLE II
RESULTS OF PAST AND CURRENT RESEARCH REGARDING THE ADSORPTION OF METALS

Removal %	Metals	Adsorbents	Reference	No.
Soybean and cottonseed hulls adsorbed high levels (95.6 – 99.7 %) of Cr, Co, Cu, Ni and Zn. Rice straw and sugarcane bagasse had low adsorption capacities (≤ 12 mg/g).	Cr, Co, Cu, Ni and Zn At an initial concentration of 100 ppm	soybean, cottonseed hulls, rice straw and sugarcane bagasse	32	1
Adsorption ratios of Al were as 98, 99, 96, 99.5 and 96 % for waste tea, Turkish coffee, exhausted coffee, nut and walnut shells, respectively	Cr, Cd and Al	waste tea, Turkish coffee, exhausted coffee, nut and walnut shells	41	2
Egg shell adsorbed high levels (98.6 – 99.7 %) of pb and Cr and walnut shell adsorbed high levels (35.3 – 65.4 %) of Ni and Cd.	Cd, Cr, Ni and Pb At an initial 50 ppm concentration	almond skin, walnut shell, saw dust, rice bran, and egg shell	Present study	3

Ogunsuyi et al. (2006) investigated the potential of oyster shell alongside with maize cob and coconut shell to remove copper ions from solution. Experimental data for the three adsorbents fitted well only to the Freundlich's Isotherm Model. Oyster shell powder showed the greatest potential for copper ion sorption from solution out of the three adsorbents studied. the adsorption potentials of oyster and giant snail shells have been demonstrated by Ajayi et al. (2005). The two adsorbents were effective in adsorbing up to 90% of Pb(II) from solution. The sorption of copper and cadmium ions using activated carbon and other waste materials as adsorbents was reported by Ulmanu et al [52] [40].

Activated carbon prepared from peanut hulls, an agricultural waste by-product has been used for the adsorption of cadmium from synthetic wastewater [42]. Similarly, activated carbons were used for the removal of Cr (VI) effectively from aqueous solutions with a percentage removal of up to 99.99% Cr(VI) at 25°C [15]. One cheap and easily available material having possibilities as suitable sorbent for heavy metal is eggshell. Due to their high calcium content, eggshells usually have no commercial importance. Disposal of eggshells is also a serious problem for egg processing industries due to stricter environmental regulations and high landfill costs [8], [10], [24]**.** In USA annually 120,000 tons of waste eggshells are generated and disposed in landfills [53].

Cellulosic materials and their derivatives have shown good metal ion adsorptive capacity. Although, the efficiency of activated carbon in adsorbing heavy metal ions from wastewater is high enough, because of significant costs involved in preparation of activated carbon and its regeneration, it is only used as a tertiary step in the treatment of wastewater [40].

The by-products were shown to be effective adsorbents for the studied cations in aqueous solutions within the range of working concentrations. Also they could be useful adsorbents in metal removal applications, especially when the low cost and high availability of these materials are considered [32], [34].

IV. CONCLUSION

The adsorption of different metal ions on the same samples had different removal rate**.** Unlike Cr(III) that had highest removal rate, Ni(II) had lowest removal rate (Figs. 1 and 2). For each metal ion, different samples had different removal rate. Egg shell, saw dust and almond skin showed highest removal rate for Cr(III). Egg shell showed the highest removal rates for Cr (III) and Pb(II) in both of single and mixture solution. Considering high adsorption capacity of egg shells, the using of it as an effective adsorbent to remove of Pb(II) and Cr(III) from waste water is proposed.

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