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REMOVAL OF SOME HEAVY METALS FROM AQUEOUS SOLUTIONS USING SAWDUST

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Sorption of lead and copper on sawdust (SD) has been studied by using batch techniques. The equilibrium sorption levels for lead and copper were a function of the solution pH, contact time, sorbent and sorbate concentration. Maximum removal of lead and copper is at pH about 5.0 and 7.0, respectively. The study showed that sawdust was effective in heavy metals removal, and the sawdust can be regenerated using acidic solution. Data indicated that the generated sawdust may adsorb heavy metals higher than the untreated one.

Keywords: Sawdust, lead, copper, adsorption

The presence of heavy metals in wastewater and surface water is becoming a sever environmental and public health problem. Chemical precipitation has been traditionally proposed to remove heavy metals from aqueous solutions. However, metal removal in the precipitation – coagulation system is, in many cases, insufficient to meet strict regulatory requirements. Adsorption has been shown to be an economically feasible alternative method for removing trace metals from water (Huang and Ostovic, 1978; Matsumoto *et al.* 1989; Lai *et al.*, 1994 and Allen and Brown, 1995).

Natural materials that are available in large quantities, or certain water products from agricultural operations, may have potential as inexpensive adsorbents. Due to their low cost, after these materials have been expended, they can be disposed of without regeneration. Generally, adsorbents can be assumed as low cost if they require little processing which are abundant in nature, or are a by-product or waste material from industry (Bailey *et al.*, 1998).

Number of investigations have shown that heavy metals will bind to sawdust and other agricultural products (Dean *et al.*, 1972; Randall *et al.*, 1974; Randall and Hantala, 1975; Raji and Anirudhan, 1997 and Ajmal *et al.*, 1998).

The focus of this study was centered on gaining more information to understanding the chemical and physical phenomena associated with the binding of heavy metals to untreated sawdust. Another concerns to obtain significant data for the application of this technique in agricultural and industrial scales.

MATERIALS AND METHODS

Sawdust (SD) for these experiments was obtained from furniture factories in the fraction of <0.5 mm. Sawdust is composed mainly of cellulose (30%) and lignin (19%), both with the capacity to bind metal cations due to carboxylic and phenolic groups.

Synthetic waste solutions' containing lead and copper with varying pH and concentrations was prepared using analytical reagent grade lead sulphate and copper sulphate, respectively. Sulphuric acid and sodium hydroxide were used to prepare the different metal solutions.

The effects of several parameters such as pH, initial concentration, contact time and quantity of sawdust on the adsorption were studied.

Desorption and sawdust regeneration experiments were performed using acidic stripping solution (0.1 M nitric acid). Initial concentrations of metals used in these investigations were kept at concentrations of 10, 25, 50 and 100 mg/l Pb and 2, 3, 5, 10 and 20 mg/l Cu. The mixture of the solutions and sawdust were stirred in a shaker at 150 rpm continuously for 1 h. Separate samples each for lead and copper were drawn after 5, 15, 30 and 60 min, intervals and analysed using Unicam model 929 atomic absorption spectrometer (AAS).

RESULTS AND DISCUSSION

Effect of Initial Concentration

Amount of 10, 20 and 40 g sawdust were added, respectively, in three different flask each containing 100 ml of the test solution without any pH adjustment. The observations were shown in figs. (1 a and b). From this experiment, lead and copper show a similar behaviour for adsorption to sawdust. Data also show that the rate of metal removal is higher at the beginning of all cases. That is probably due to larger surface area of the sawdust being available at beginning for the adsorption of metals. As the surface adsorption sites became exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles.

It is also found that the higher removal of lead and copper was related to the lower concentration of the metals, where ranged from 92 to 96% Pb and from 74 to 85% Cu, while in the higher initial concentration the percent removal ranged from 79 to 84% Pb and from 70 to 78% Cu. The availability of adsorptive sites of the sawdust is a possible explanation for this phenomenon.

Fig. (2) show an example for this comparison indicating that lead has more affinity for adsorption on the sawdust than copper.

It is important to mention that these testes done condition without any pH adjustment. However, it is supported that the metal solution may affect metal affinity for adsorption on sawdust and that the processes for metal adsorption may change the pH of an unbuffered solution.

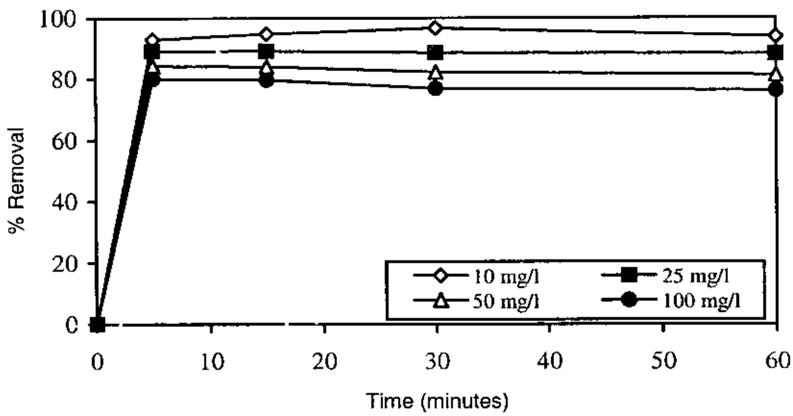

Fig. (1a). The effect of initial concentration of lead on adsorption. Sawdust 40 g/l.

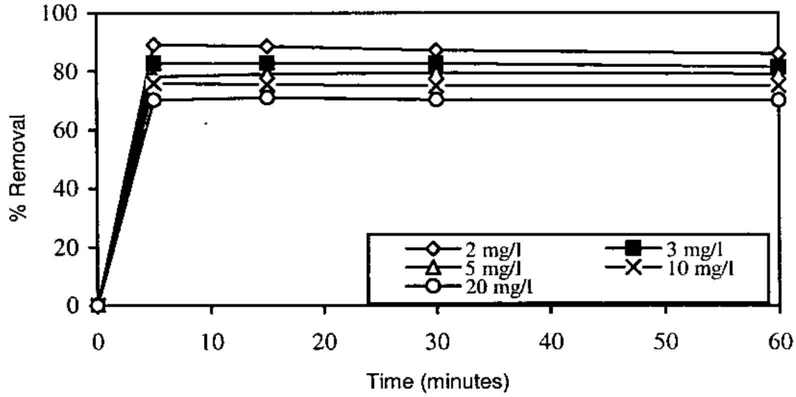

Fig. (1b). The effect of initial concentration of copper on adsorption. Sawdust 40 g/l.

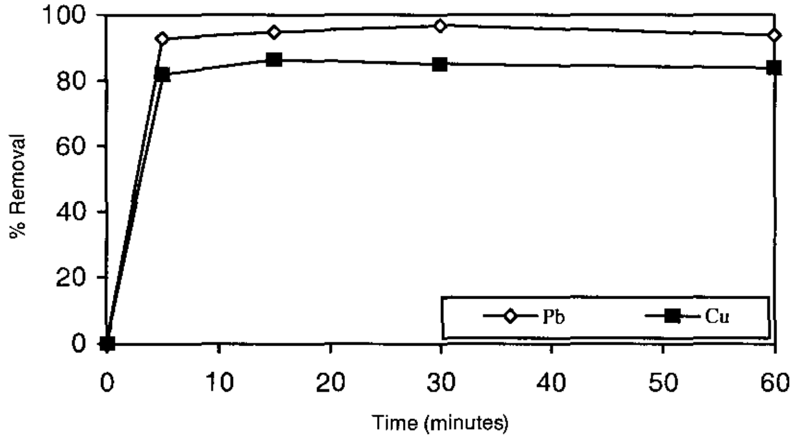

Fig. (2a). Comparison of the adsorption of lead and copper. Sawdust: 40g/l; lead, initial concentration: 10.0g/l; copper, initial concentration 10.0 mg/l.

Effect of Adsorbent Concentration

The effect of sawdust concentration on lead and copper adsorption was studied in room temperature with different amounts of sawdust varying from 10 to 40 g/l, while the other parameters, such as pH, metal solution volume (100 ml), are kept constant.

Fig. (3) show that the removal percentage of lead increases rapidly with increasing the concentration of sawdust. Similar trend was observed with copper (Table 1). The cation exchange properties of sawdust can be attributed to the presence of carboxylic and phenolic functional groups, which exist in either the cellulosic matrix or in the materials associated with cellulose, for example, hemi cellulose and lignin (Lee, 1996).

Fig. (4) presents a comparison of metals removal as a result to varying sawdust concentration. From the results, it is revealed that within a certain range of initial metal concentration, the percentage of metal adsorption on sawdust is determined by the sorption capacity of the sawdust and the selectivity of the sawdust to different metal ions. It is appear that lead has more preference than copper for adsorption on the sawdust.

Effect of pH

Metal removal is strongly dependent on pH. The effect of pH on sorption of lead and copper on sawdust was studied at room temperature by varying the pH of metal solution from 2.0 to 10.0. The results are shown in Fig. (5).

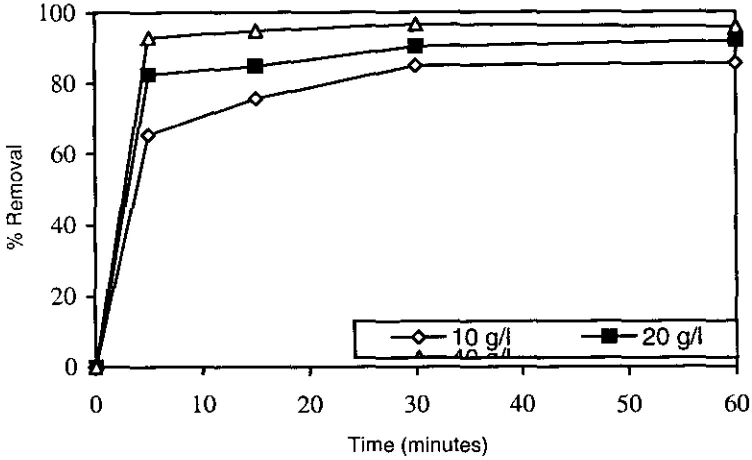

Fig. (3). Effect of adsorbent concentration on the removal of lead. Temperature: 25°C; initial concentration: 10mg/l; pH: 5.

Table (1). Removal of copper (%) and pH of final solution after 60 min of agitation.[a]

Sample	Adsorbent Concentration g/l	Cu initial 2.0 ppm		Cu initial 3.0 ppm		Cu initial 5.0 ppm		Cu initial 10.0 ppm		Cu initial 20.0 ppm	
		%	pH	%	pH	%	pH	%	pH	%	pH
S D	10	61.30 ±.08	4.60	81.83 ± .05	4.55	78.34 ± .07	4.41	80.33 ± .11	4.25	78.87 ± .08	3.93
	20	63.80 ± .09	4.56	82.33 ± .06	4.56	81.06 ± .09	4.32	81.20 ± .08	4.44	78.79 ± .06	4.12
	40	74.90 ±.06	4.71	81.33 ± .09	4.42	82.60 ± .04	4.32	83.73 ± .10	4.30	81.93 ± .07	4.10

a = Temperature: 25 °C; pH: 5.

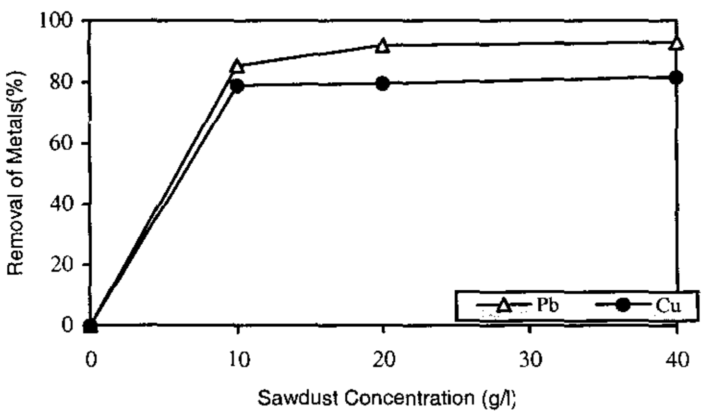

Fig. (4). Effect of sawdust concentration on the removal of lead (II) and Cu (II). Initial concentration of lead and copper: 10 mg/l; temperature: 25°C; pH: 5; contact time: 1 h.

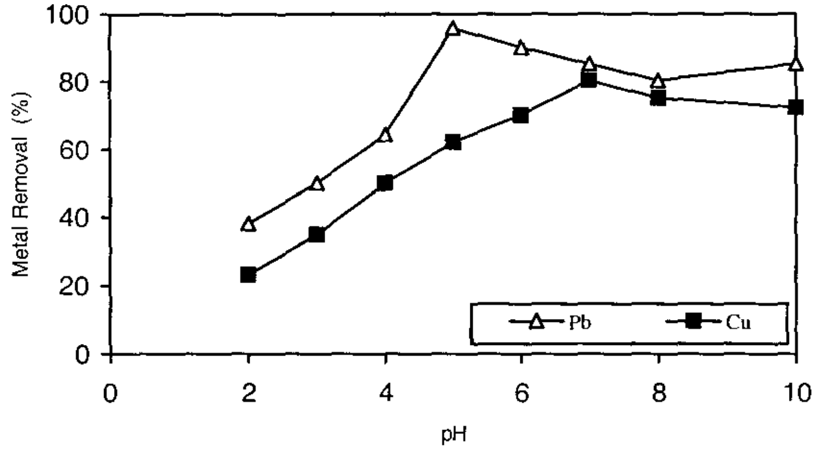

Fig. (5). The effect of pH on metal removal through sawdust adsorption. Temperature 25°C; equilibrium time 3 h; sawdust: 20g/l; initial concentration: 5.0 mg/l.

It can be observed from pH experiments that the maximum removal of Pb II (96 %) by sawdust sorption occurs at a pH of about 5.0, while that of Cu (II), 80 %, dose at a pH of about 7.0. In the pH range 5 –7, maximum adsorption was observed due to the partial hydrolysis of metal ions resulting in the formation of $M(OH)^+$ and $M(OH)_2$. $M(OH)_2$ would have adsorbed to a great extent on the non – polar surface than would $M(OH)^+$. In the acidic pH range, 2 –3, there would be a competition between H^+ and M^{2+} ions for adsorption on the ion exchangeable sites, leading to low removal of metal ions.

The equilibrium was quite dependent upon pH. In most cases, removal of Pb (II) or Cu (II) from solutions ceased as pH of the solutions in contact with the adsorbent dropped to 3.0 – 3.5. When the pH was further lower by any case, for instance the introduction of acid, the equilibrium might be reversed. That is the metal ions were stripped from the solid into the acid.

Regeneration of Sawdust

The ion exchange, M^{2+}- H^+, is easily reversible, depending upon pH. Sawdust samples which used in heavy metals adsorption and adsorbed up to 80 %lead and copper were stripped with 0.1M NO_3 (pH ~ 1.2). The heavy metals were almost completely removed from the sawdust after 5h. These concentrations represent almost a complete exchange of H^+ ions from the acid to the sawdust. The generated sawdust samples were washed several times with redistilled water until its pH reached the regular range. After dried in an oven at 105°C, the regenerated sawdust used to adsorb heavy metals again (Ya *et al.*, 2001). Data shown in table (2) indicate that the regenerated sawdust may adsorb heavy metals higher than the untreated one. This could be attributed to the impurities of sawdust, which could be removed after regeneration and more exchangeable surface area becoming available.

TABLE (2). Removal of Pb (II) and Cu (II) (%) from untreated and regenerated sawdust.

Initial Concentration mg/l	Lead removal %		Initial Concentration mg/l	Copper removal %	
	Untreated SD	Regenerated SD		Untreated SD	Regenerated SD
10.00	92.87	95.11	3.00	83.50	85.07
25.00	89.06	91.70	5.00	82.80	83.11
50.00	83.80	85.14	10.00	79.88	81.17
100.00	80.01	83.05	20.00	81.77	81.99

SD = Saw dust

Desorption of heavy metals

Desorption experiments were performed on the various lead and copper concentrations. These experiments were carried out at room temperature using four different initial lead concentrations at pH 5.0 and five different initial copper concentrations at pH 7.0. The amount of sawdust was 40 g/l and the contact time was 1 h. The loaded sawdust was filtered and re-suspended in redistilled water of the same volume with a pH adjusted to 2.0 using HNO_3. The metal ions in both the sorption and loading status were determined using the usual method.

Data tabulated in tables (3 and 4) show that the loading of ions on sawdust increases with increasing metal concentration. Data also show that the percent recovery of copper is higher than that of lead which confirms the assumption that lead has more affinity for adsorption on sawdust compared to copper. Also, it can suggest that there are two major types of sorption mechanisms, the ion exchange and the mono ion-layer physical adsorption.

Ion exchange may be the important mechanism for the removal of heavy metals such as Pb (II) and Cu (II). The major components in sawdust are lignin, tannins or other phenolic compounds. These types of materials increase the capability of capturing heavy metals. It can be said that lignin; tannins or other phenolic groups are the active ion exchange compounds.

Based on the structure of these phenolic compounds, a possible mechanism of ion exchange could be considered as a divalent ion (M^{2+}) attaches itself to two adjacent hydroxyl groups and two oxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution (Ajmal *et al.*, 1998).

TABLE (3). Desorption of Pb (II) from sawdust (SD). [a]

Initial concentration	ECS [b]	Loading of Pb (II) mg/g (SD).	Recovery from SD (%)
10.0 mg/l	0.332	0.2417	86.1
25.0 mg/l	1.112	0.5972	87.5
50.0 mg/l	2.848	1.1788	88.2
100.0 mg/l	8.352	2.2912	89.7

a = Sawdust concentration: 40 g/l; Temperature: 25°C; pH: 5.0 for adsorption and 2.0 for desorption; contact time: 1 h.
b = Equilibrium concentration of sorption.

TABLE (4). Desorption of Cu (II) from sawdust (SD). [a]

Initial concentration	ECS [b]	Loading of Cu (II) mg/g (SD)	Recovery from SD (%)
2.0 mg/l	0.296	0.0426	97.6
3 .0 mg/l	0.460	0.0635	95.1
5 .0 mg/l	0.748	0.1063	96.9
10 .0 mg/l	1512	0.2122	94.6
20 .0 mg/l	3.432	0.4142	95.8

a = Sawdust concentration: 40 g/l; Temperature: 25°C; pH: 7.0 for adsorption and 2.0 for desorption; contact time: 1 h.
b = Equilibrium concentration of sorption.

Effect of Anions

Data in table (5) show that sawdust adsorbed Pb (II) and Cu (II) ions much more efficiently from acetate solution than from sulfate, chloride and nitrate. In all the cases, the metal sorption was affected by the activity of hydrogen ions. The hydrogen ions in solution of strong acids like HCl, HNO_3 and H_2SO_4 are almost completely dissociated, while it is partially dissociated in acetic acid.

TABLE (5). Effect of anions on the adsorption of metal ions on sawdust [a]

Compound	Initial cation concentration (mg/l)	Equilibrium cation concentration (mg/l)	Adsorption %
$Pb(NO_3)_2$	20.00	8.38	58.1
$PbCl_2$	20.00	6.7	66.5
$PbSO_4$	20.00	4.72	76.4
Pb (Ac)$_2$	20.00	2.04	89.8
$Cu(NO_3)_2$	20.00	9.44	52.8
$CuCl_2$	20.00	8.92	55.4
$CuSO_4$	20.00	7.54	62.3
Cu (Ac)$_2$	20.00	5.28	73.6

[a] = Sawdust concentration: 40 g/l; temperature: 25°C; pH: 5.0 (Pb), 7.0 (Cu); contact time: 15min.

It is well known that heavy metals exit in acidic solution as cations. At lower pH, the existing of relatively large quantities of hydrogen ions may change the direction of reversible ion exchange equilibrium back to start materials. At higher pH, the metal ions will be associated with OH^- and become neutral at a certain pH range. A neutral compound possesses hydrophobicity makes the metal precipitated or lipophilicity, which makes the metal easily, adsorbed by sawdust (Ya *et al.*, 2001).

In a higher pH range, existing of counter ions might result in lower efficiency of adsorption and ion exchange. This trend is clearly shown in Fig. (5).

CONCLUSION

Data obtained from this study reveal that sawdust appear to be a good material for the removal of lead and copper from aqueous solution and may also be suitable for other heavy metals. At these adsorption levels, using sawdust for the removal of heavy metals is potentially more economical than the classical methods. The removal of Pb and Cu was heavily dependent on pH, amount of sawdust, contact time as well as the initial metal concentration.

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إزالة بعض العناصر الثقيلة من المحاليل المائية باستخدام نشارة الخشب

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تم دراسة إدمصاص كل من الرصاص والنحاس علي نشارة الخشب ، وقد أثبتت النتائج أن عملية الأدمصاص تتأثر كثيرا برقم حموضة المحلول و زمن التفاعل وكذلك تركيز العنصر المد مص ، بالإضافة إلى النسبة بين المحلول ونشارة الخشب.

كما بينت النتائج أن أعلي إدمصاص لكل من الرصاص والنحاس كان عند رقم حموضة ٥ ، ٧ علي التوالي. كذلك أوضحت الدراسة أن نشارة الخشب تعتبر من المواد الفعالة في إزالة العناصر الثقيلة ، كما أنه يمكن تجديدها باستخدام محلول حامضي ، حيث أوضحت النتائج أن النشارة المجددة يمكنها إدمصاص كميات أكبر من العناصر الثقيلة بالمقارنة بالنشارة الغير معاملة بالمحلول الحامضي.