

RICE STRAW FOR HEAVY METALS REMOVAL FROM EFFLUENTS

Abdel – Rahman, M.E.

Department of Soil Chemistry and Physics, Desert Research Center, El-Matareya, Cairo, Egypt.

Rice plant produces large quantities of rice straw which has been used in agriculture, construction, metal recovery and water pollution control. The removal of cadmium and copper by rice straw was investigated. Data obtained reveal that rice straw is an effective metal absorbent for these two metals. The adsorption capacity of this material increases as the initial metal concentration decreases. Adsorption equilibria were established rapidly at the early stage of reaction and decreased markedly after 1 hr.

The removal phenomenon appears to be that the rice straw neutralizes the metal solution due to its alkaline nature. The presence of high ionic strength does not have any significant effect on the adsorption of these metals by rice straw. The effect of solution pH on adsorption was also studied.

Keywords: rice straw, cadmium, copper, adsorption.

Effluents from metal industries increase the levels of toxic heavy metals in water and soil. Awareness of the hazards of heavy metals covers a wide spectrum of metals as Pb, Cd, Cr, Cu and Zn (Dean *et al.*, 1972). Among these, Cd poisoning in humans is the most serious as it causes severe dysfunction of the kidneys, reproductive system, liver, brain and central nervous system (Manahan, 1994).

Methods used to remove heavy metals from wastewater include ultra filtration, precipitation, electrolytic processes, reverse osmosis, ion exchange, activated carbon, solvent extraction and biological systems (Panday *et al.*, 1984; Evan, 1985; Elliot *et al.*, 1986; Narayan and Bandyripadhyay, 1992 and Vega Farfan *et al.*, 1996). Most of these methods are expensive, involving both elaborate and costly equipment or high operation costs and energy requirements. The ultimate disposal of the contaminants may also be a problem in these techniques (Lin and Huang, 1994). Recently, the recovery and recycling of organic residues (agricultural, urban industry, etc.) became a major area of investigation in developed countries. Agricultural wastes such as tree bark, peanut skin and hull and

growing plants (tobacco and tomato root tissue) have been used to remove heavy metals from water (Randall and Hantala, 1975; Scott, 1992 and Lujan *et al.*, 1994).

Rice straw, for many years, has been considered a waste material, the quantities of which continued to increase (2.5 million ton/year), hence the motivation to look for possible industrial and environmental application is of interest. One of these is the potential use in soil pollution control.

In this study, an investigation of the treatment of metal effluents (Cd and Cu) using rice straw is conducted.

MATERIALS AND METHODS

Rice straw used in this study was obtained from mature rice plants in two fractions (0.5-1.0 mm and < 0.5 mm). Both fractions were analyzed for their chemical composition (Table1) where the rice straw fractions were melted with a mixture of 1:1 w/w boric acid and lithium carbonate at 950°C. Then, the fused mixture was treated with deionized water and concentrated nitric acid to obtain the sample solution (Julia *et al.*, 1998). The surface area was measured by the BET nitrogen desorption method.

X-ray diffractogram for the fine fraction (<0.5 mm) showed that the major components of rice straw are aluminum silicates, iron oxychloride and silicon phosphide (Fig.1). Cadmium and Cu solutions were prepared from analytical reagent grade CdSO₄ and CuSO₄, respectively. Sulfuric acid and NaOH were used to prepare the different metal solutions.

TABLE (1). Chemical composition of rice straw.

Component	<0.5 mm	1.0-0.5 mm
Al ₂ O ₃	32.40	33.1
SiO ₂	49.00	48.7
Fe ₂ O ₃	6.90	6.60
CaO	4.81	5.10
MgO	1.70	1.20
Na ₂ O	0.64	0.61
K ₂ O	4.00	3.70
Cd	0.014	0.020
Cu	0.267	0.357
S.A.cm ² /g*	12200	9830

* = Surface area

The adsorption experiments were carried out in polyethylene bottles by mixing fly ash with Cd and Cu metallic solutions, shaken at room temperature and then allowed to separate by gravity. The supernatant liquid was analyzed for pH, cadmium and copper.

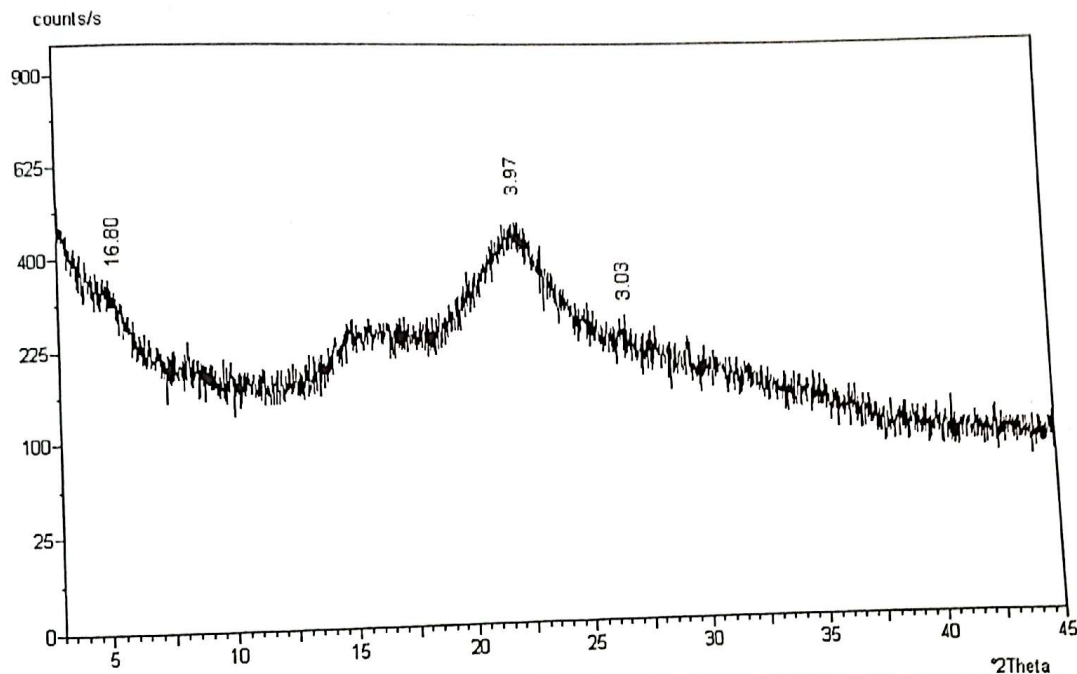


Fig. (1). X- ray diffractogram of rice straw (fine fraction).

Different parameters were then studied: initial metallic concentration, pH, contact time, adsorbent concentration, grain size and ionic strength.

The adsorption was studied with different initial metallic concentrations: 0.25, 0.50, 1.00, 1.50 and 2.00 mg/l Cd and 2.00, 3.00, 5.00, 10.00 and 20.00 mg/l Cu, all of them adjusted at pH 5.0. The adsorption kinetics were studied at pH 5.0 using 2.00 mg/l Cd and 20.00 mg/l Cu, the samples were shaken for 5, 15, 30 and 60 minutes.

The effect of pH of the initial solutions on the adsorption process was studied using solutions having pH range between 1 and 5 adjusted with H_2SO_4 acid and NaOH.

The effect of ionic strength was studied using Na_2SO_4 and potassium sulphate in the range of 10^{-1} to 10^{-4} M.

RESULTS AND DISCUSSION

Effect of Initial Concentration

For the different initial Cd concentrations, adsorption equilibrium was rapidly achieved. The results indicate that the adsorption capacity increases

as the initial Cd concentration decreases for both fractions of rice straw, but the adsorption capacity of the finest fraction is distinctly better than that of the coarser one. It is also found (Fig. 2) that the lower initial concentration of the metal (0.25 and 0.50 mg/l), the greater percent of the metal removal when compared to the higher initial metal concentrations (1.5 and 2.0 mg/l).

Additionally, the results further show that the ultimate removal of Cd with the initial Cd concentration of 0.25 – 0.50 mg/l ranged from 60 to 88 % and from 40 to 67 % for both straw fractions (<0.5 mm and 0.5- 1.0 mm, respectively), while that of Cu seems to be in a little bit lower range (32 – 66 % and 33 – 50 %) with the initial concentration of 2.0 – 3.0 mg/l for the same fractions (Table 2). Figure (3) shows an example of this comparison, indicating that Cd has more affinity for adsorption on rice straw than Cu.

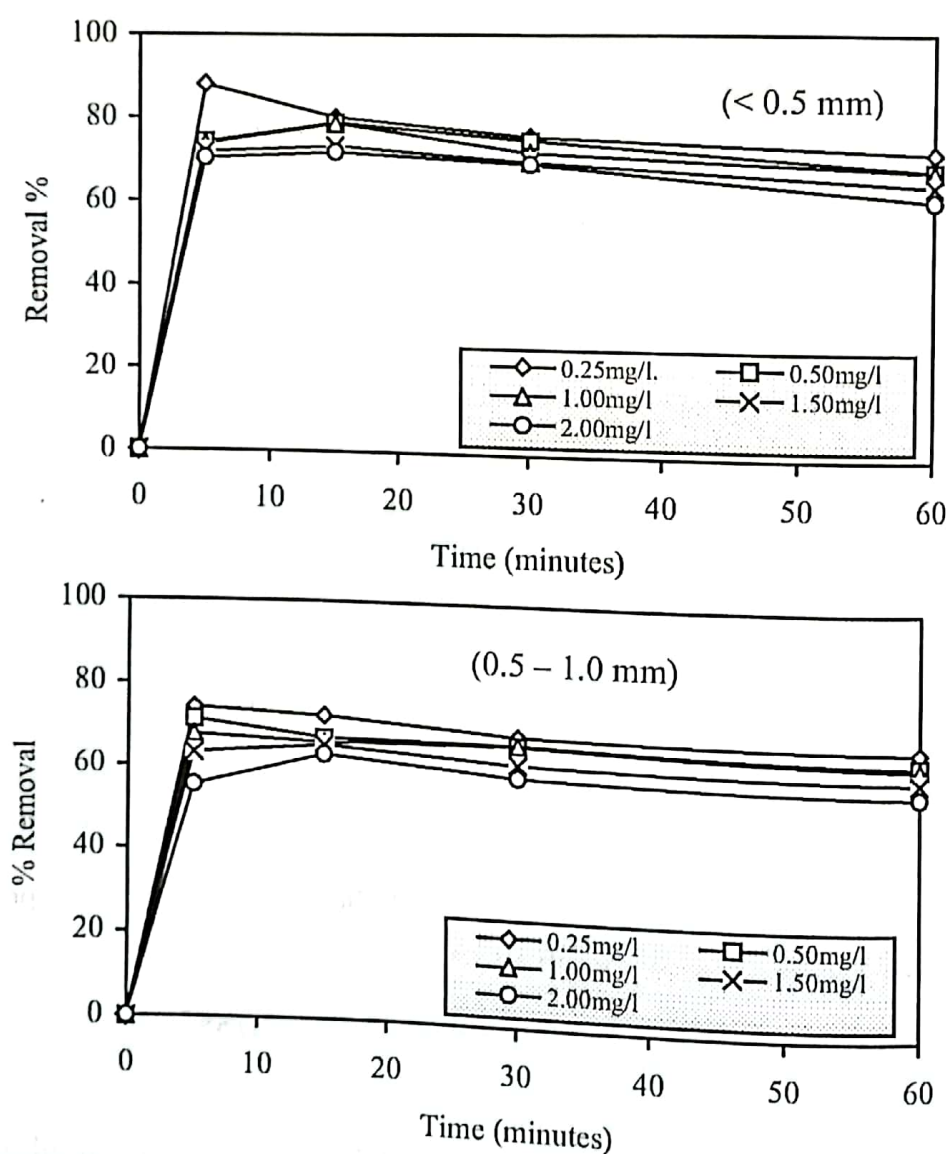


Fig.(2). Effect of initial concentration on Cd removal (Rice straw: 40g/l).

Values of metal uptake can be reported in metal sorbed/g. Data in table (3) show that the higher values (0.123 and 1.313 mg/g) for Cd and Cu, respectively were observed with the adsorbent amount of 10 g/l only. The maximum Cd and Cu adsorption capacity of rice straw can be attributed to the interaction of metal with surface silica sites as well as only a small contribution from alumina sites.

TABLE (2). Changes in suspension pH values and percent removal of Cu by rice straw as affected by adsorbent amount.

Adsorbent amount g/l		initial Cu concentration, mg/l									
fine fraction	coarse fraction	2.0		3.0		5.0		10.0		20.0	
		pH	% removal	pH	% removal	pH	% removal	pH	% removal	pH	% removal
10		8.05	32.79	8.07	37.01	7.98	52.69	7.80	52.18	7.48	50.95
20		8.12	40.37	8.10	48.36	8.11	53.03	8.09	56.47	7.81	54.95
40		8.31	66.20	8.27	55.17	8.13	55.41	8.11	57.01	7.89	58.85
	10	7.72	33.90	7.75	34.70	7.55	30.95	7.43	29.13	7.15	21.83
	20	7.75	36.65	7.75	37.19	7.64	35.52	7.48	35.69	7.29	26.25
	40	7.82	50.42	7.61	42.59	7.64	45.99	7.56	41.21	7.42	32.24

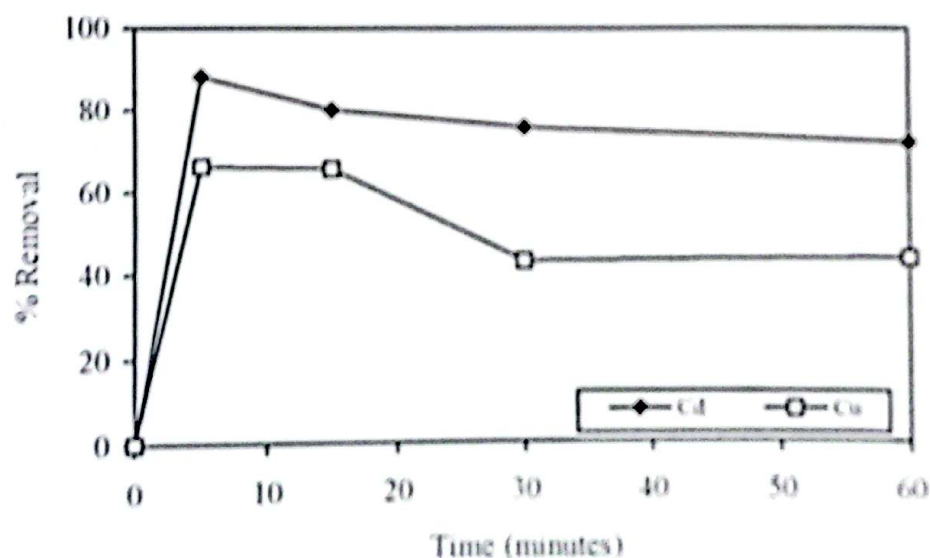
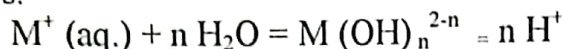


Fig. (3). Adsorption of Cd and Cu on rice straw. Adsorbent concentration: 40 g/l; fraction (<0.5 mm); Cd, initial concentration: 0.25 mg/l; Cu, initial concentration: 2.0 mg/l.

Effect of pH

The pH in solution has been identified as the most important variable governing metal adsorption on biosorbents. As the pH increase, aqueous cations hydrolyse according to the generalized expression for divalent metals.



This hydrolysis may be accompanied by precipitation of metal hydroxide (Panday *et al.*, 1984 and Elliot *et al.*, 1986). The effect of pH on sorption of cadmium and copper on rice straw was studied at room temperature by varying the pH of metal – rice straw suspension from 1 to 5.

Figure (4) shows that Cd retention capacity by rice straw depends on the pH of the initial metal solution, where retention decreases with decreasing pH. The same behaviour was observed with Cu solutions (Table 4). Rice straw can neutralize initial solutions having pH = 3 when adsorbent amount reaches 10 g/l. When the metal solution has a pH value less than 3, it is necessary to use more amount of rice straw to neutralize the solutions.

TABLE (3). Cadmium and Cu removal reported in mg metal sorbed /g.^a

initial concentration mg/l		adsorbent amount, mg/l		
Cd	Cu	10.0	20.0	40.0
0.25		0.016	0.009	0.005
0.50		0.027	0.017	0.009
1.00		0.057	0.033	0.020
1.50		0.089	0.052	0.030
2.00		0.123	0.073	0.037
	2.00	0.105	0.061	0.046
	3.00	0.175	0.092	0.049
	5.00	0.298	0.164	0.088
	10.00	0.633	0.321	0.161
	20.00	1.313	0.748	0.492

a = Temperature: 25°C, pH :5.0, contact time :15 min and fraction (< 0.5mm).

TABLE (4). Effect of initial pH on Cu adsorption and pH of the final solution.

adsorbent amount g/l	initial pH									
	1		2		3		4		5	
	Final pH	% removal	Final pH	% removal	Final pH	% removal	Final pH	% removal	Final pH	% removal
10	4.34	10.98	7.10	53.12	7.68	60.14	7.25	38.56	7.79	59.86
20	5.99	43.30	7.62	54.02	7.96	59.88	7.66	51.54	7.94	69.82
40	6.96	47.58	7.86	66.52	8.13	61.74	8.01	55.54	8.03	75.75

Effect of Contact Time

The adsorption equilibrium is rapidly achieved and only 5 mins. contacting time is enough to achieve equilibrium conditions (Fig. 5). For 2.0

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mg/l Cd at pH 5, with a low amount of adsorbent (10g/l), the removal after 5 mins was 65 % and 45 % for both fractions (< 0.5 mm and 0.5 – 1.0 mm, respectively). The same percentages were obtained after 24 hrs. contacting time. Similar behaviour was observed with copper solution (20.0 mg/l), under the same conditions (Table 5).

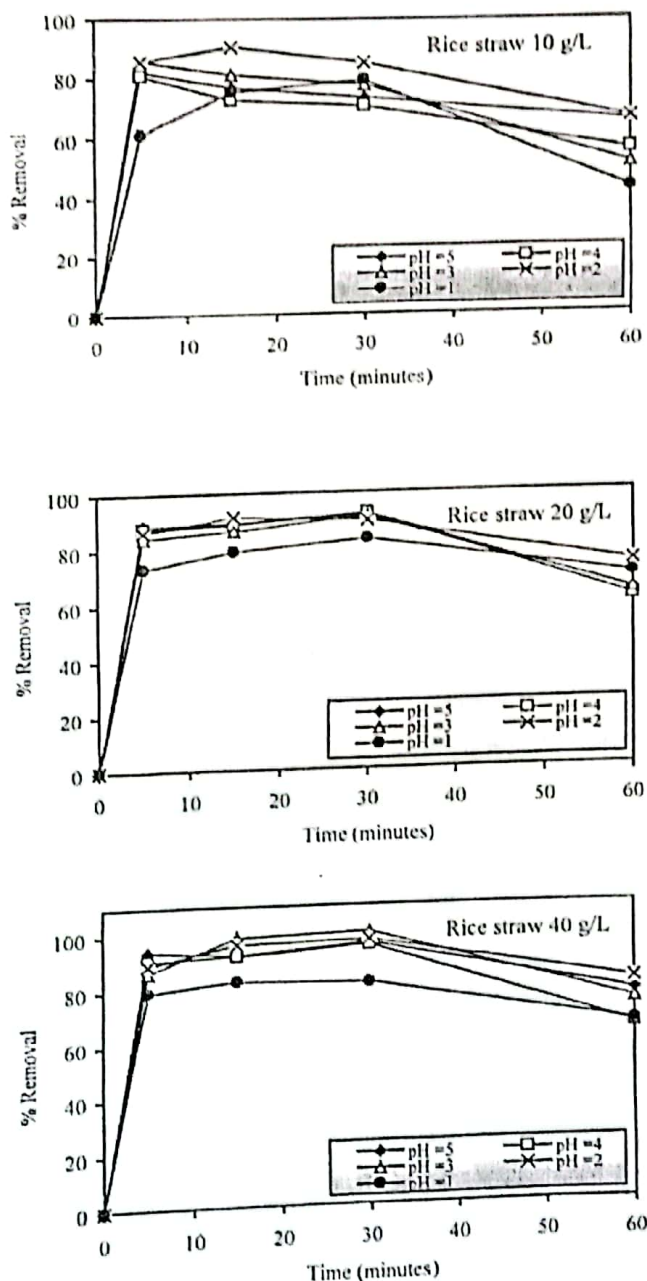


Fig.(4). The effect of pH on Cd removal through rice straw adsorption. Temperature 25C, equilibrium time 1 h and initial concentration: 2.0 mg/L.

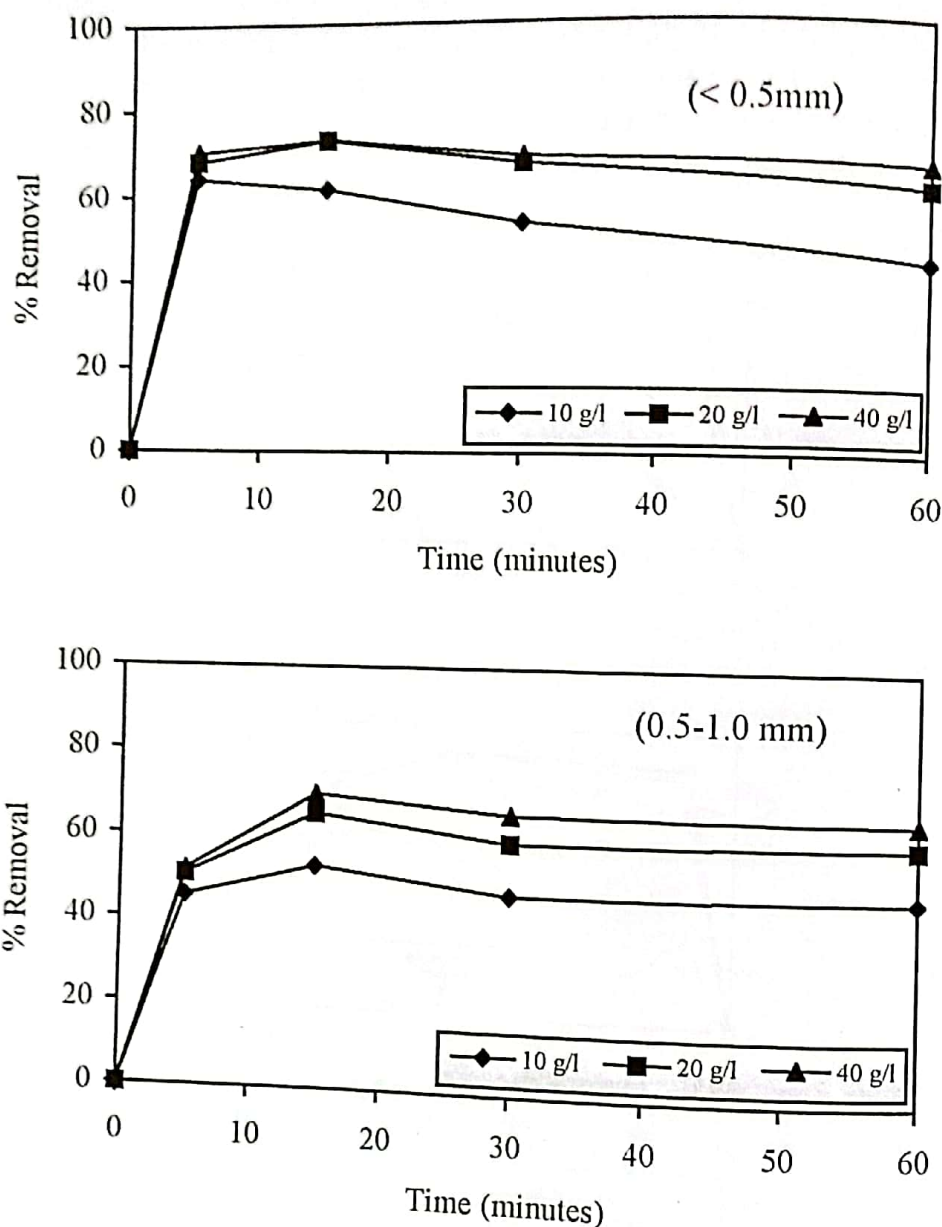


Fig. (5). Sorption kinetic of Cd (II) with different contacting time.

Effect of Adsorbent Amount

The dependence of Cd and Cu sorption on rice straw amount was studied at room temperature by varying the sorbent amount from 10 to 40 g/l, while keeping the other parameters such as pH and solution volume (50 ml) constant.

From this experiment, it is clear that for Cu and Cd adsorption to rice straw was quite similar regardless of magnitude. Firstly, the rate of metal removal is higher at the beginning in all cases, such as rice straw amounts of 40, 20, and 10 g/l, respectively. This is clearly due to the affinity of the rice

straw surface area. Secondly, in a certain time, the percent metal removal reached maximum, it is about 1 hr for both Cd and Cu. Fig. (6) demonstrates this effect and presents a comparison of the two metals, Cd and Cu.

TABLE (5). Adsorption kinetics of Cu and pH of the final solution with different contacting time.

contacting time (mins)	< 0.5 mm						1.0 – 0.5 mm					
	10 g/l		20 g/l		40 g/l		10 g/l		20 g/l		40 g/l	
	pH	% *	pH	% *	pH	% *	pH	% *	pH	% *	pH	% *
5	7.48	50.95	7.81	54.95	7.89	58.85	7.15	21.83	7.29	26.25	7.42	32.24
15	7.47	65.67	7.79	74.83	7.92	98.35	7.04	25.66	7.24	29.70	7.37	43.29
30	7.38	57.88	7.75	63.08	7.86	63.44	7.02	28.41	7.25	39.05	7.36	45.65
60	7.37	63.03	7.67	63.68	7.84	65.44	6.91	30.83	7.12	37.71	7.29	47.39

* = % removal

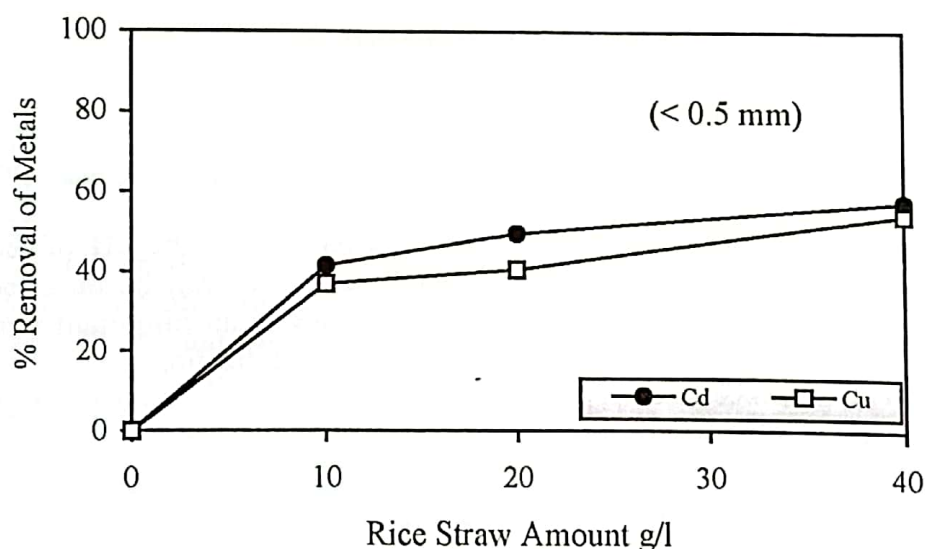


Fig (6). Effect of rice straw amount on the removal of Cd (II) and Cu (II). Initial concentration of Cd and Cu: 2.0 mg/l, contact time: 1 hr.

Effect of Ionic Strength

Ionic strength is one of the most important factors, which has an effect on the aqueous phase equilibrium. Wastewater has many other compounds that can influence metal retention. Data tabulated in table (6) show the effect of ionic strength on metal adsorption. This study was obtained with 2.0 mg/l for Cd and 20.0 mg/l for Cu at 60 mins of contacting

time. Data show no influence on the removal of metal as a result of the presence of these electrolyte concentrations.

TABLE (6). Effect of some substances on Cd and Cu removal and the pH of final solution.

Electrolyte concentration, M		Cd		Cu	
Na ₂ SO ₄	K ₂ SO ₄	pH	%	pH	%
10 ⁻¹ M		7.11	60.22	7.48	65.41
10 ⁻² M		7.24	59.95	7.37	64.88
10 ⁻³ M		7.31	59.74	7.52	63.55
10 ⁻⁴ M		7.28	58.86	7.74	63.21
	10 ⁻¹ M	7.26	61.45	7.68	65.11
	10 ⁻² M	7.32	61.02	7.62	64.85
	10 ⁻³ M	7.20	60.75	7.96	64.02
	10 ⁻⁴ M	7.22	60.25	7.86	63.58

CONCLUSION

Significant data were obtained through this study for the removal of Cd and Cu by rice straw adsorption. Rice straw appears to be a promising adsorbent for the removal of Cd and Cu.

Metal retention using rice straw decreases when the pH of the initial solution decreases. The metal removal mechanism can be described as a neutralizing process. The amount of rice straw is an important parameter. Very acid solutions need more rice straw for neutralization.

The presence of high ion strength does not have a significant effect on the removal of Cd and Cu.

At these adsorption levels, a process using rice straw for the removal of heavy metals is shown to be potentially more economical than current process technology.

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قش الأرز لإزالة العناصر الثقيلة من المحاليل

محمد عيسى عبد الرحمن

قسم كيمياء وطبيعة الأراضى - مركز بحوث الصحراء - المطرية - القاهرة - مصر .

تم دراسة إمكانية إزالة كلا من الكاديوم والنحاس من المحاليل بواسطة قش الأرز، حيث أظهرت النتائج أن قش الأرز يعتبر مادة جيدة لأدمصاص كلا العنصرين وأن السعة الأدمصاصية تزداد بنقص التركيز الابتدائي للعنصر المدمص، كما أن عملية الأدمصاص تصل إلى مرحلة الاتزان بعد دقائق قليلة من بداية التفاعل وتتناقص بدرجة ملحوظة بعد ساعة واحدة. وتوضح ظاهرة إزالة العناصر أن قش الأرز يعمل على معادلة المحاليل نظرا لطبيعته القلوية، كما أوضحت النتائج أن وجود الأيون المصاحب لم يؤثر على عملية الأدمصاص لكلا العنصرين بواسطة قش الأرز في حين أن تأثير رقم الحموضة كان واضحا.