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Chemically modified low cost treatment for heavy metal effluent management

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Abstract *The removal efficiency of lead [Pb(II)], zinc [Zn(II)], nickel [Ni(II)] and chromium [Cr(VI)] from aqueous solutions by adsorption on non-conventional materials (rice husk and sawdust) in its natural form and on their chemically modified form is presented. It is found that adsorption potential varies as a function of contact time, concentration, particle size, pH and flow rate. Of all the low cost adsorbents used in this study, sawdust is found to possess greater adsorption efficiency for all metals than rice husk under identical experimental conditions. Chemically activated sawdust could remove 95 percent of Pb(II), 93 percent of Zn(II), 80 percent of Ni(II) and 75 percent of Cr(VI) from the metal bearing industrial effluents.*

Introduction

Heavy metal bearing wastes are considered to be hazardous to both human life and the environment due to their acute toxicity and non-biodegradability, even at tract concentrations. Most of the physio-chemical processes, which are in practice, are found to be non-effective and economically not feasible to achieve the required stringent disposal standards in surface water bodies. Hence in recent years attention has been focussed on the use of low cost adsorbents and their chemical modification to achieve technically feasible and cost-effective adsorption process.

Fly ash has been used for the removal of heavy metals, namely chromium (Viraraghavan and Rao Ganesh, 1991) and zinc (Alaerts *et al.*, 1989; Gaikwad and Bhadwaj, 1995). Adsorption of lead and chromium on activated slag has been investigated (Srivastava *et al.*, 1997). Blast furnace flue dust has been shown to remove hexavalent chromium from aqueous solutions (Patnaik and Das, 1995). Agricultural wastes such as sawdust (Gupta *et al.*, 1987); rice husk (Srinivasan *et al.*, 1988); tea leaves (Singh and Lal, 1992) and coconut fibre pith

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(Manju and Anirudhan, 1997) have been used for the removal of lead and chromium from aqueous solutions.

Recent investigations on the chemical modification of low cost adsorbents, such as chemically treated tea leaves (Singh *et al.*, 1993); polyacrylamide grafted sawdust (Raji and Anirudhan, 1997) polyacrylamide grafted tin (IV) oxide gel (Subha, 1996; Mckay and Porter, 1997; Ouki and Neufeld, 1997) and chemically modified sawdust (Muthukumaran *et al.*, 1995) revealed the possibility of maximizing the adsorption potential of non-conventional materials for the removal of heavy metals.

Hence the present paper aims at evaluating and maximizing the adsorption efficiency of commonly occurring heavy metals in industries using non-conventional materials as adsorbents, either in their natural form or in their chemically modified form.

Materials and methods

Rice husk and sawdust were used as adsorbents in the present study. The characteristics of the above adsorbents after their chemical activation are presented in Table I. The experimental parameters considered in this study are given in Table II.

Chemical activation

Rice husk or sawdust is activated by treating three parts of it (by weight) with one to two parts of chemicals (EDTA or activated carbon) and keeping it in an oven maintained at a temperature of 140-160°C for a period of 24 hours. The carbonized material was washed well with water to remove free acid and then dried at 105-110°C for one hour. The dried material was subjected to thermal activation in an atmosphere of carbon dioxide at 800-850°C for a period of 30 minutes. The material was then ground to produce particles of average diameter 170μm and 1300μm for sawdust and rice husk respectively.

Batch and continuous flow studies

Glass columns of 3cm diameter and heights 16cm (referred to hereafter as Adsorption Column-I i.e. ACI) and 47.5cm (referred to hereafter as Adsorption

Table I.
Characteristics of adsorbents after chemical activation

Characteristics	Rice husk	Sawdust
Apparent density (g/cc)	0.34	1.2
Mean particle size (mm)	1.30	0.17
Surface area (m^2/g)	370.00	130.00
Moisture content (%)	13.68	2.3
Porosity (m/g)	0.14	0.48
Ash content (%)	31.26	0.09
pH zpc	6.10	5.82

Table II. Experimental parameters

Description of parameter	Value
Height of adsorption bed (long column)	16cm
Height of adsorption bed (long column)	47.5cm
Volume of short adsorption column	60ml
Volume of long adsorption column	185ml
Volume of feed bottle	200ml
Inlet head	40ml
Flow rate	15ml/min

Column-II i.e. ACII) were used as adsorption columns. The weighed quantity of rice husk and sawdust before and after activation were filled into ACI and ACII. The quantity of materials required for ACI and ACII were estimated at 30gm and 93gm respectively. Synthetic samples were prepared for a wide range of concentrations from 10 to 100mg/l. For each trial, adsorption column was loaded with samples in batch mode and then continued for continuous flow experiments. Batch studies were performed by shaking 0.1gm of chemically activated rice husk or sawdust with 50ml aqueous solution of heavy metal of the desired concentration in different stoppered glass bottles. Initial pH was maintained with 0.05 M HNO_3 and NaOH.

In order to minimize variations in activity coefficients, a constant ionic media of 0.01M $NaNO_3$ was used. The contents were continuously agitated in a temperature controlled flask shaker. At the end of the predetermined time interval, the adsorbent was centrifuged and the supernatant was analysed for metal concentration using automatic absorption spectrophotometer (GBC 908 model). The quantity of metal ions adsorbed on the chemically activated rice husk/sawdust was calculated based on the initial and final concentrations of the solution. After batch mode, the synthetic sample fed into the adsorption column, percolates downwards under gravity, at a flow rate of 15ml/min, with a constant inlet head of 40cm.

It was observed that for each experiment, equilibrium is reached within 60 to 180 minutes. The operation of adsorption column is stopped after equilibrium in batch mode.

Results and discussion

Effect of contact time and initial concentration on adsorption

Removal of Pb(II), Ni(II), and Cr(VI) were found to increase from 22mg/g (95 percent) to 35mg/g (75 percent), when the metal concentration increases from 30 to 100mg/L, over a pH range of 2 to 9. It was observed that equilibrium was attained within 150 minutes and it was independent of the initial concentration. Removal curves for each of the above heavy metals were single, smooth and continuous indicating the possibility of a monolayer coverage of metal ion at the outer interface of adsorbents. At lower concentrations, the ratio of initial number of moles of metal ion to the available adsorption site was low and subsequently the fractional adsorption becomes independent of the initial concentration. Comparative results of the metal ions for various concentrations are summarized in Table III and in Figures 1 and 2.

Effect of pH

The adsorption efficiency of various heavy metals was studied at pH values ranging from 2 to 9. It was observed that the efficiency of removal of each metal at the effective pH of adsorption was found to be greater when chemically activated non-conventional adsorbents were used than when they were used in their natural form. Higher removal efficiencies were observed for activated carbon than for EDTA. The chemically activated sawdust yielded better efficiency than activated rice husk. The effective pH of adsorption of different metals was studied with respect to the dosage of adsorbent and the efficiency of removal. It was clear from Figures 3 and 4 that lead and zinc adsorptions are effective at pH 6 and 4-5.5 respectively. Effective pH values of adsorption for chromium and nickel were found at 2-3 and 3.5-4 respectively.

Adsorption isotherm

Experimental results of metal adsorption were analyzed for their fitness into Langmuir model of adsorption. The rearranged equation for Langmuir model can be expressed as shown in the following equation:

Table III. Comparison of experimental results – adsorption efficiency

		Non-conventional adsorbent				Chemically activated adsorbent			
Metal	Effective pH	Material	AC	DT (mts)	η (%)	Material	AC	DT (mts)	η (%)
Lead [Pb(II)]	5.5-6	SD	ACII	13.62	70.47	SD+AC	ACII	14.52	95.00
		RH	ACII	12.52	67.17	RH+AC	ACII	14.07	93.25
						SD+EDTA	ACII	13.68	89.68
Zinc [Zn(II)]	4-5.5					SD+AC	ACII	15.52	93.00
		SD	ACII	16.02	72.42	RH+AC	ACII	14.75	90.07
		RH	ACII	14.98	68.19	SD+EDTA	ACII	16.02	89.42
Nickel [Ni(II)]	3.5-4					SD+EDTA	ACII	15.64	80.00
		SD	ACII	14.28	60.08	SD+AC	ACII	13.72	78.46
		RH	ACII	13.52	58.62	RH+AC	ACII	13.95	75.69
Chromium [Cr(VI)]	2-3	SD	ACII	15.68	45.68	SD+AC	ACII	16.85	75.00
		RH	ACII	14.07	42.72	RH+AC	ACII	14.68	73.32
						RH+AC	ACII	15.54	72.65

Notes: ACII = Long adsorption column (47.5cm); DT = Detention time; mts = minutes; η = Efficiency of adsorption; SD = Sawdust; AC = Activated carbon; RH = Rice husk; EDTS = Ethylene diamine tetra acetic acid

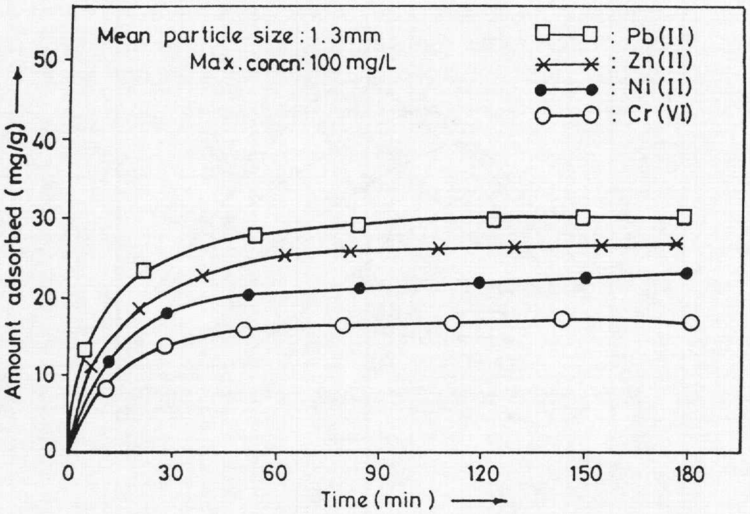

Figure 1. Effect of contact time and concentration on the adsorption of chemically activated rice husk

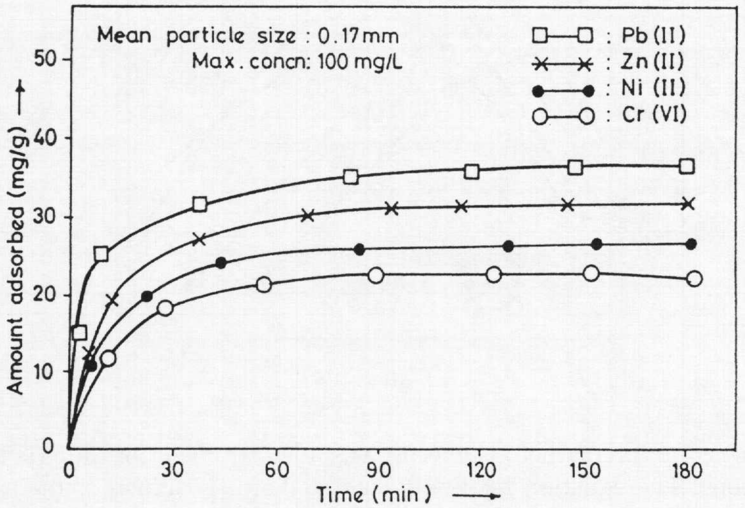

Figure 2. Effect on contact time and concentration on the adsorption of chemically activated sawdust

$$C_e/q_e = 1/Qb + C_e/Q$$

where, C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g) and Q and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The equation for rice husk and sawdust activated with EDTA and activated carbon is presented in Table IV. The plot of (C_e/q_e) and C_e for rice husk and sawdust (Figures 5 and 6) gives a straight line relationship indicating the applicability of Langmuir isotherm.

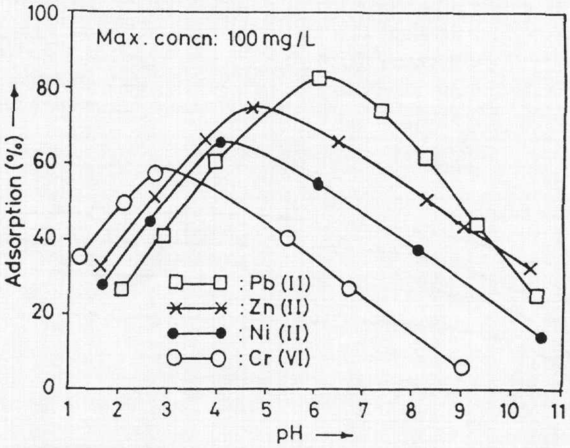

Figure 3.
Effect of pH on the adsorption of chemically activated rice husk

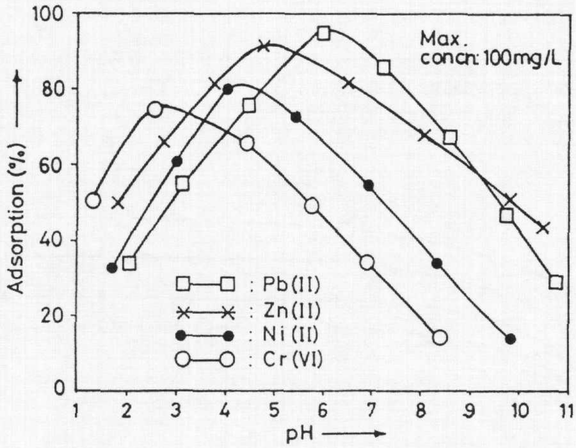

Figure 4.
Effect of pH on the adsorption of chemically activated sawdust

The fitness of Freundlich isotherm was also studied for different metal adsorptions. The equation for Freundlich isotherm is shown in the equation below:

$$\text{Log } q_e = \log k_f + (1/n) \log C_e$$

where C_e is the equilibrium concentration (mg/l) and q_e is the amount adsorbed (mg/g).

The equation for rice husk and sawdust activated with EDTA and activated carbon is presented in Table V. The values of k_f and n are determined from q_e and C_e and a linear plot is obtained for different metal adsorptions. The above plots for rice husk and sawdust are shown in Figures 7 and 8 respectively.

Metal	Adsorbent	Metal concentration (mg/l)	pH	Q (mg g^{-1})	b (1mg^{-1})
Lead [Pb(II)]	Sawdust	60	5.5-6	3.2756	0.0143
		100		3.2517	0.0135
	Rice husk	60		2.9572	0.0135
		100		2.8274	0.0139
Zinc [Zn(II)]	Sawdust	60	4-5.5	3.0125	0.0133
		100		3.0111	0.0125
	Rice husk	60		3.0012	0.0124
		100		3.0005	0.0123
Nickel [Ni(II)]	Sawdust	60	3.4-4	2.9217	0.0122
		100		2.9314	0.0119
	Rice husk	60		2.8522	0.0117
		100		2.7252	0.0116
Chromium [Cr(VI)]	Sawdust	60	2-3	2.8244	0.0102
		100		2.8112	0.0101
	Rice husk	60		2.8012	0.0101
		100		2.7562	0.0902

Table IV. Langmuir isotherm for chemically activated adsorbents

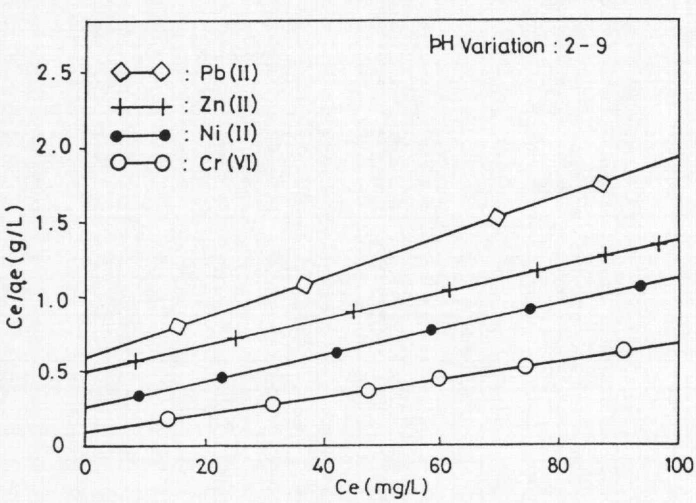

Figure 5. Langmuir isotherm for the adsorption on chemically activated rice husk

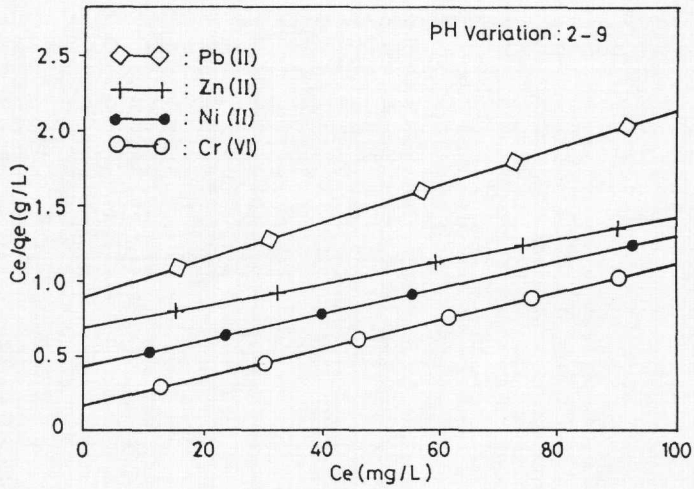

Figure 6.
Langmuir isotherm for the adsorption on chemically activated sawdust

Table V.
Freundlich isotherm for chemically activated adsorbents

Metal	Adsorbent	Metal concentration (mg/l)	pH	Adsorption capacity $k_f \times 10^5$	Adsorption intensity (1/n)
Lead [Pb(II)]	Sawdust	60	5.5-6	12.61	2.08
		100		11.85	2.05
	Rice husk	60		12.05	2.03
		100		11.65	2.01
Zinc [Zn(II)]	Sawdust	60	4-5.5	11.52	2.02
		100		11.45	1.98
	Rice husk	60		11.25	1.95
		100		11.05	1.91
Nickel [Ni(II)]	Sawdust	60	3.5-4	11.24	1.89
		100		11.01	1.84
	Rice husk	60		10.95	1.81
		100		10.82	1.72
Chromium [Cr(VI)]	Sawdust	60	2-3	10.75	1.74
		100		10.45	1.69
	Rice husk	60		10.21	1.68
		100		10.07	1.64

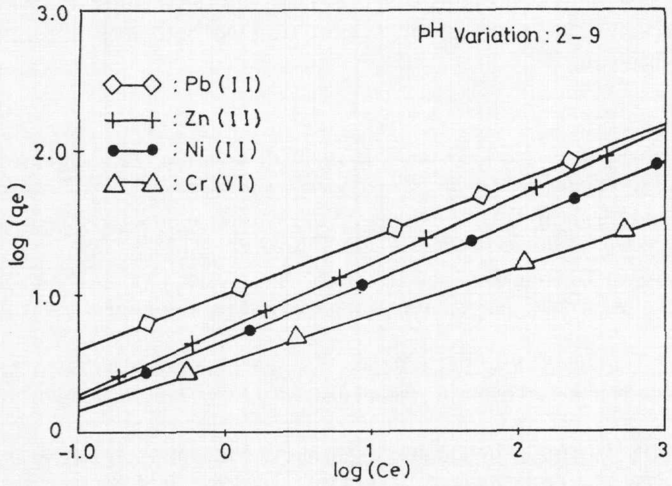

Figure 7. Freundlich isotherm for chemically activated rice husk

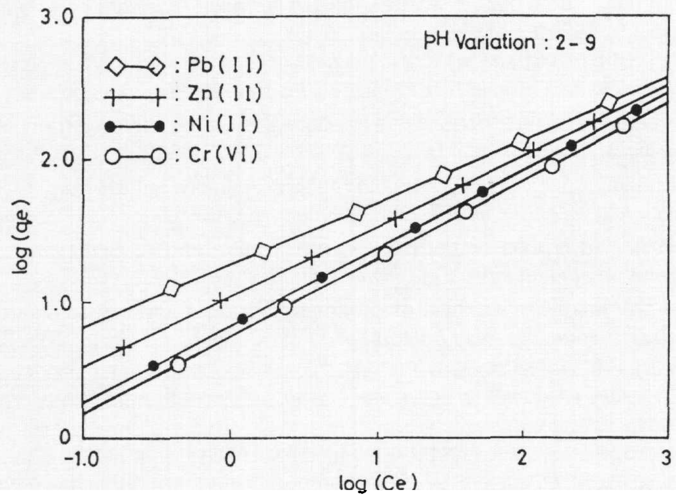

Figure 8. Freundlich isotherm for chemically activated sawdust

Conclusions

The following conclusions would be drawn from the detailed experimental investigations carried out using rice husk and sawdust as non-conventional adsorbents:

The ability of chemically activated rice husk and sawdust for the removal of Pb(II), Zn(II), Ni(II) and Cr(VI) has been very clearly established. The extent of removal depends on the metal concentration and pH.

The efficiency of sawdust as an adsorbent in its natural form is superior to that of rice husk. Activated carbon as an activator is found to be superior to that of EDTA, for sawdust and rice husk.

Maximum removal of all metals is observed for saw dust activated with activated carbon. The process of uptake obeys both the Langmuir and Freundlich isotherms.

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