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THE REMOVAL OF HEAVY METALS BY USING AGRICULTURAL WASTES

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ABSTRACT

The removal of heavy metals from wastewater using adsorbants such as waste tea, Turkish coffee, exhausted coffee, nut and walnut shells has investigated. 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) metalions. 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. These results were compared with those obtained using activated carbon as adsorbent. The batch adsorption kinetics and adsorption equilibria were examined and described by a first order reversible reaction and Freundlich isotherm, respectively. The first order rate and isotherm constants have been calculated.

KEYWORDS

Adsorption, agricultural wastes, metal ions, equilibrium isotherms.

INTRODUCTION

The presence of heavy metals in the environment can be detrimental to a variety of living species. The most important feature that distinguishes heavy metals from other toxic pollutants is their nonbiodegradability and that even have a tendency to accumulate in living material. Therefore, the elimination of heavy metals from wastewater is an important subject for public health. According to some surveys from the Public Health Services of different countries, significant numbers of people have been exposed to the hazards of excess metals in different ways (WHO, 1971). Many methods have been proposed for the removal of heavy metals. Chemical precipitation, membrane filtration, ion exchange, alum coagulation, iron coagulation and adsorption are some of the most commonly used processes; each has its merits and limitations in applications (Patterson, 1975). Activated carbon adsorption appears to be a particularly competitive and effective process for the removal of heavy metals at trace quantities (Huang and Blankenship, 1984). However, the use of activated carbon is not suitable for developing countries because of its high cost (Panday *et al*, 1985). For that reason, the use of low cost materials as possible media for metal removal from wastewater have been highlighted recently. These materials range from industrial products such as waste rubber tyres (Knocke and Hemphill, 1981), to agricultural products such as wool, rice straw, coconut husks and peat moss (Macchi *et al.*, 1986). New research shows the effective adsorption of heavy metals from wastewater using the agricultural products and by-products; walnut expeller meal, peanut skins, wool, rice straw, plumpit shells, peanut hults, sugar cane bagasse (Ferro-Garcia *et al., 1988*). Recently, the use of waste tea leaves and coffee powder for heavy metals removal of Hg (II) has been reported (Macchi *et al.*, 1986).

The aim of the present work is to study the influence of the agricultural material, namely waste tea, Turkish and exhausted coffee, nut and walnut shells, on the removal of heavy metals from wastewater.

EXPERIMENTAL

Five adsorbents such as waste tea, Turkish and exhausted coffee, nut and walnut shells were used in this study. Adsorbents were washed in distilled water constantly all day. The suspension was then left to settle to allow the supernatant to be poured off; this was repeated three times. Finally, the washed adsorbents were dried in an oven at 105°C until constant weight, cooled and kept in dessicators for subsequent use. The containers used were bottles of 150 ml capacity. Each container was filled with synthetic wastewater containing 5 mg/L of Cd (II), Cr (VI) and Al (III). Batch adsorption experiments were carried out by shaking 0.3 g of adsorbent with 100 ml synthetic wastewater at constant speed at room temperature. At the end of a preselected reaction time, approximately 2 hours, the adsorbents were separated by either centrifugation or filtration. The remaining concentration of heavy metals in each sample after adsorption at various time intervals was determined spectrophotometrically. The amount of total heavy metals removed is taken as the concentration difference between originally added and that finally remaining. Using activated carbon in the same adsorption process, the results were compared with their capacities to remove metal ions.

RESULTS

The aim of batch experiments is to study the influence of some adsorbents used in the adsorption process of metal ions. Waste tea, Turkish and exhausted coffee, nut and walnut shells have been used as adsorbent s to remove Cr (VI), Cd (II) and Al (III) from wastewater. Figures 1–5 show the adsorption of heavy metals by adsorbents as a function of time. The curves showed strong adsorption During the 60 minutes; equilibrium is established in approximately 120 minutes. From these figures, a pattern is recognized: adsorption increases with time to reach a peak value and then remains at this level. A waiting time of 120 minutes has been assumed to be suitable for batch experiments. The capacity values reported in Table 1 were calculated from batch experiments data.

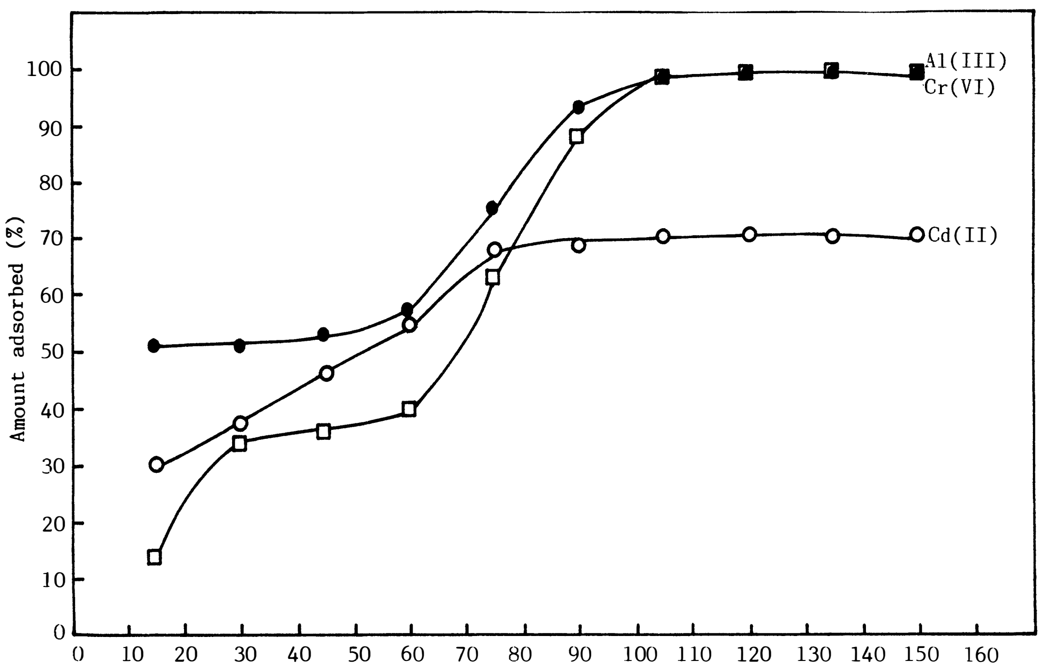

Figure 1. Adsorption of heavy metals on Turkish coffee.

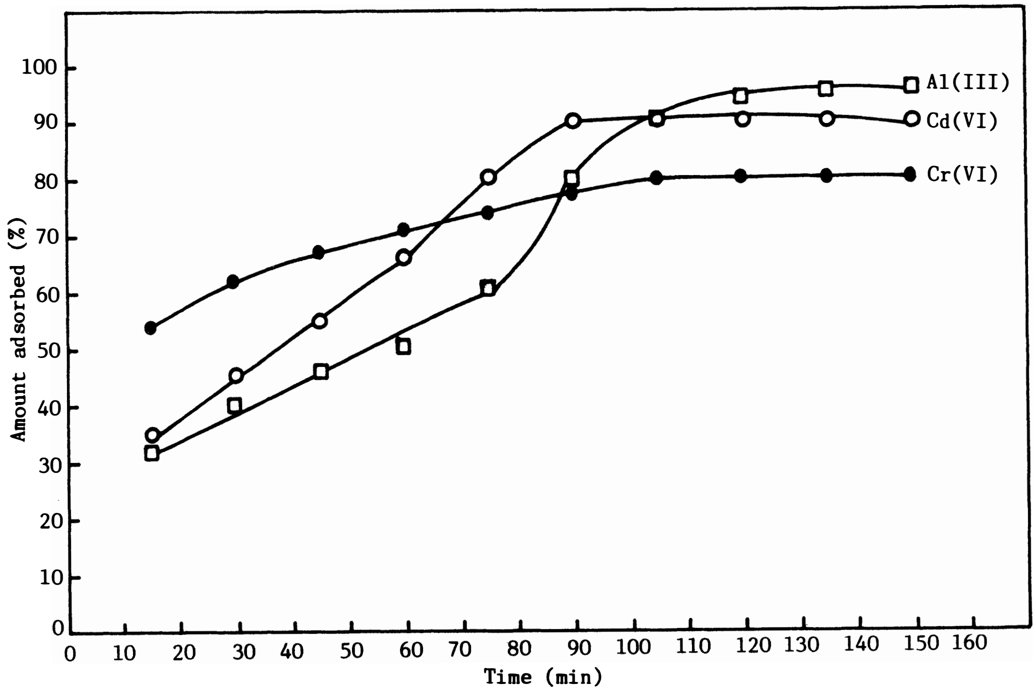

Figure 2. Adsorption of heavy metals on exhausted coffee.

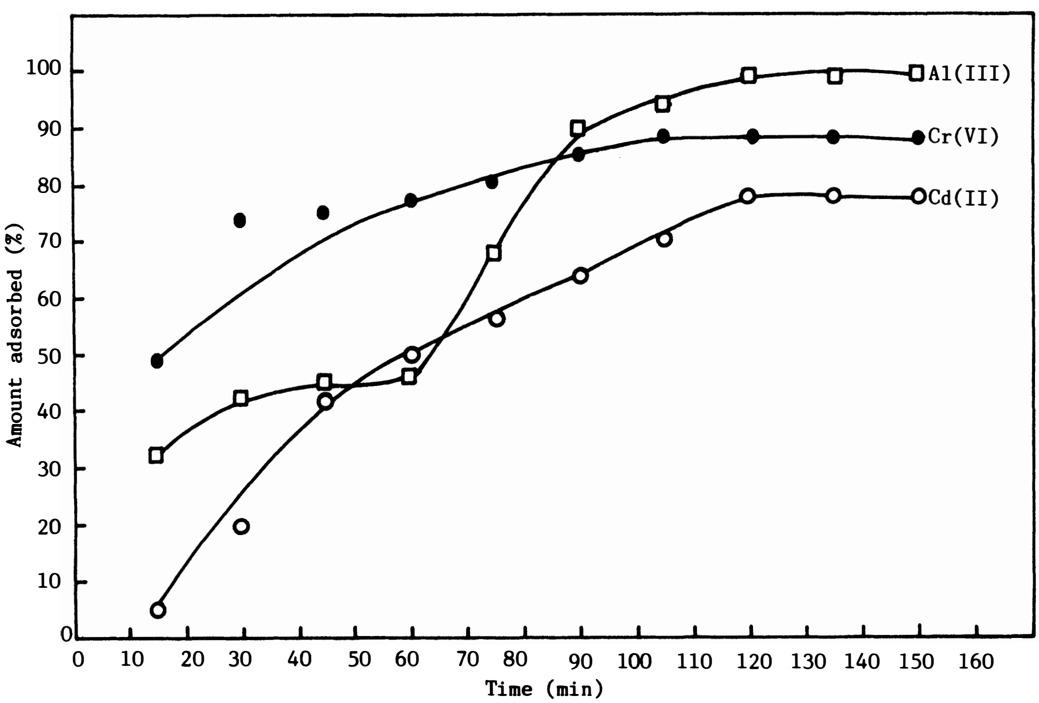

Figure 3. Adsorption of heavy metals on nut shell.

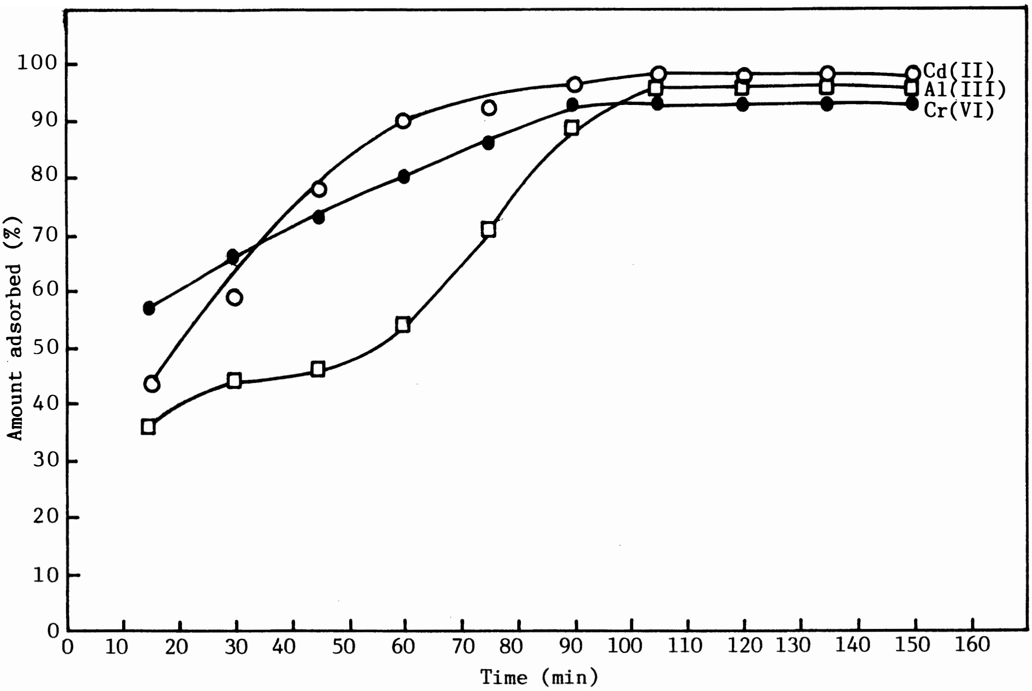

Figure 4 Adsorption of heavy metals on waste tea.

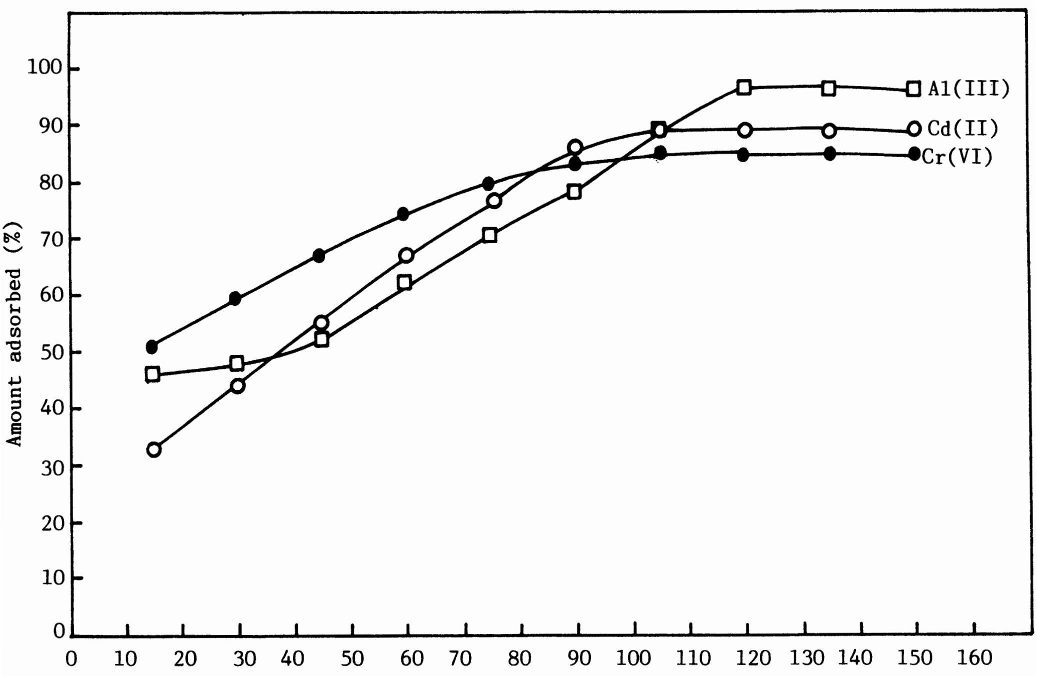

Figure 5. Adsorption of heavy metals on nut shell.

Table 1. Batch Capacities of Heavy Metals by Various Adsorbents.

Metals	Amount Absorbed (%)				
	Waste Tea	Turkish Coffee	Exhausted Coffee	Nut Shell	Walnut Shell
Cr (VI)	93.0	98.0	85.0	88.0	80.0
Cd (II)	98.0	70.0	89.0	78.0	90.0
Al (III)	98.0	99.0	96.0	99.5	96.0

According to the experimental results, all adsorbents seem to have the highest adsorption capacity for all of the heavy metals studied. The activated carbon was used in the sample adsorption process to compare the performance of agricultural wastes and adsorption ratios of Cr (VI), Cd (II) and Al (III) were 98.5, 99.0 and 99.8% of that by activated carbon. These values are similar to those found for the heavy metal adsorption by agricultural wastes and these adsorbents seem to be suitable for the removal of heavy metals from wastewater. Batch experiments results showed the possible use of agricultural wastes for heavy metal removal and the adsorbents have good potential as metal scavengers from wastewaters.

The two important aspects for parameter evaluation of the adsorption study are the kinetic and the equilibria of adsorption. The adsorption of heavy metals from liquid phase to solid phase can be considered as a reversible reaction with an equilibrium being established between two phases (Bhattacharya and Venkobachar,C. 1984). A simple first order reaction kinetic model was used to establish the rates of reaction which can be expressed as

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \tag{1}$$

If the first order reversible kinetic model holds true, the rate equation for the reaction is expressed as

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} = C_{Ao}\frac{dX_A}{dt} = k_1 C_A - k_2 C$$

$$= k_1 (C_{Ao} - C_{Ao} X_A) - k_2 (C_{Bo} + C_{Ao} X_A) \tag{2}$$

in which C_B is the concentration of heavy metal on the adsorbent and C_A is the concentration of heavy metal in solution at any time. C_{BO} and C_{AO} are the initial concentration of heavy metals on adsorbent and solution, respectively. X_A is the fractional conversion of heavy metal, and k_1 and k_2 are the first order rate constants. At equilibrium conditions

$$\frac{dC_B}{dt} = \frac{dC_A}{dt} = 0 \tag{3}$$

$$\text{and} \quad X_{Ae} = \frac{K_c - \dfrac{C_{Bo}}{C_{Ao}}}{K_c + 1} \tag{4}$$

in which X_{AE} is the fractional conversion of heavy metal at equilibrium, and K_C is the equilibrium constant defined as

$$K_C = \frac{C_{Be}}{C_{Ae}} = \frac{C_{Bo} - C_{Ao} X_{Ae}}{C_{Ao} - C_{Ao} X_{Ae}} = \frac{k_1}{k_2} \tag{5}$$

in which C_{BE} and C_{AE} are the equilibrium concentration for heavy metals on the adsorbent and solution, respectively. The rate equation in terms of equilibrium conversion can be obtained from Eqs. 2,4 and 5

$$\frac{dX_A}{dt} = (k_1 + k_2) (X_{Ae} - X_A) \tag{6}$$

Integration of Eq. 6 and substituting for k_2 from Eq. 5 gives

$$-\ln \left(1 - \frac{X_A}{X_{Ae}} \right) = k_1 \left(1 + \frac{1}{K_C} \right) t \tag{7}$$

Eq. 7 can be rewritten in a different from as

$$\ln (1 - U(t)) = -k' t \tag{8}$$

in which k' is the overall rate constant. Further

$$k' = k_1 \left(1 + \frac{1}{K_C} \right) = k_1 + k_2 \tag{9}$$

$$\text{and} \quad U(t) = \frac{C_{Ao} - C_A}{C_{Ao} - C_{Ae}} = \frac{X_A}{X_{Ae}} \tag{10}$$

U(t) is called the fractional attainment of equilibrium (7). Plots as per Eq. 8 were made for all adsorbents and the result for Al (III) by nut shells is shown in Fig 6. A near straight line fit was generally observed for all metals and indicated that the adsorption reaction can be approximated to first order reversible kinetics. Constants k_1, k_2 and K_C were calculated using Eqs.5 and 9 and presented in Tables 2–4.

Table 2 The Values of First Order Reaction Rate Constants (k', k_1, k_2) for Cr (VI) Metal Ion

Adsorbent	k'	k_1	k_2
Waste Tea	0.1516	0.0772	0.0742
Turkish Coffee	0.1738	0.0969	0.0769
Exhausted Coffee	0.1585	0.0829	0.0756
Nut Shell	0.1549	0.0822	0.0727
Walnut Shell	0.1349	0.0718	0.0631

Table 3 The Values of First Order Reaction Rate Constants (k', k_1, k_2) for Cd (II) Metal Ion

Adsorbent	k'	k_1	k_2
Waste Tea	0.1516	0.0772	0.0742
Turkish Coffee	0.1738	0.0969	0.0769
Exhausted Coffee	0.1585	0.0829	0.0756
Nut Shell	0.1549	0.0822	0.0727
Walnut Shell	0.1349	0.0718	0.0631

Table 4 The Values of First Order Reaction Rate Constants (k', k_1, k_2) for Al (III) Metal Ion

Adsorbent	k'	k_1	k_2
Waste Tea	0.1045	0.0553	0.0492
Turkish Coffee	0.1949	0.1191	0.0758
Exhausted Coffee	0.1315	0.0739	0.0576
Nut Shell	0.1698	0.0949	0.0748
Walnut Shell	0.1738	0.1000	0.0738

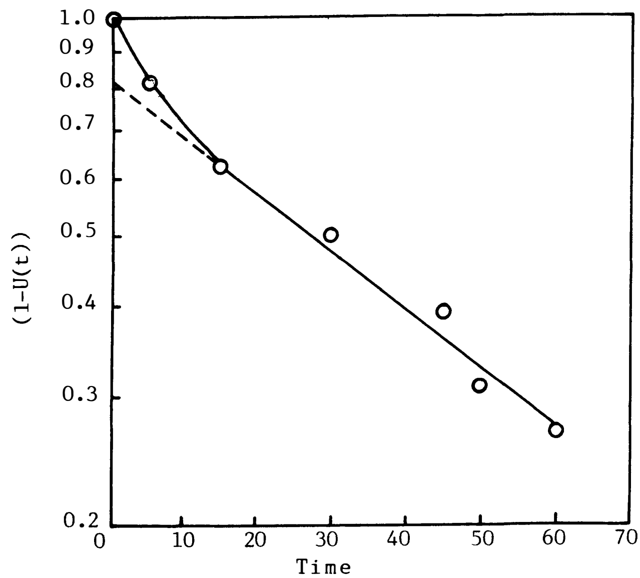

Figure 6. First order reversible kinetic fit of Cd(II) adsorption data on nut shell.

k_1, k_2 represent sorption of solute from solution on to the adsorbent to solution, respectively. It can be observed that k_1 is generally higher for Turkish coffee than other adsorbents. The reverse reaction rate constant k_2 is also faster for Turkish and exhausted coffee. In the case of these adsorbents, as the ratio of adsorbents to adsorbates decreases, k_1 also decreases. Thus, the adsorption reaction can be described by the simple first order reversible reaction. The equilibria data were correlated both by Langmuir and Freundlich equations giving better correlation for Freundlich equation,

$$\log Q_E = \log k + n \log C_{Ae} \qquad (11)$$

in which Q_E is the amount of heavy metal adsorbed per unit weight of adsorbent (mg/g), k is a measure of adsorption capacity and 1/n of adsorption intensity. The validity of fitting the data to the Freundlich isotherm is tested by determining the standard error of estimate of regression line. The Freundlich isotherm line of regression constants, correlation coefficients and standard error of estimate have been calculated and presented in Tables 5 and 6. The data fitted to the Freundlich isotherm for Al (III) by nut shell are shown in Fig. 7. The isotherm data can also be used to calculate the ultimate sorption capacity of the adsorbent by substituting the initial concentration for equilibrium concentration in Freundlich isotherm equations. The following equations are obtained for Cr (VI), Cd (II) and Al (III) using nut shell, respectively.

$$\frac{X}{M} = 1.9\ C_{Ae}\ 0.0230 \quad (12)$$

$$\frac{X}{M} = 1.6\ C_{Ae}\ 0.9230 \quad (13)$$

$$\frac{X}{M} = 2.4\ C_{Ae}\ 0.0700 \quad (14)$$

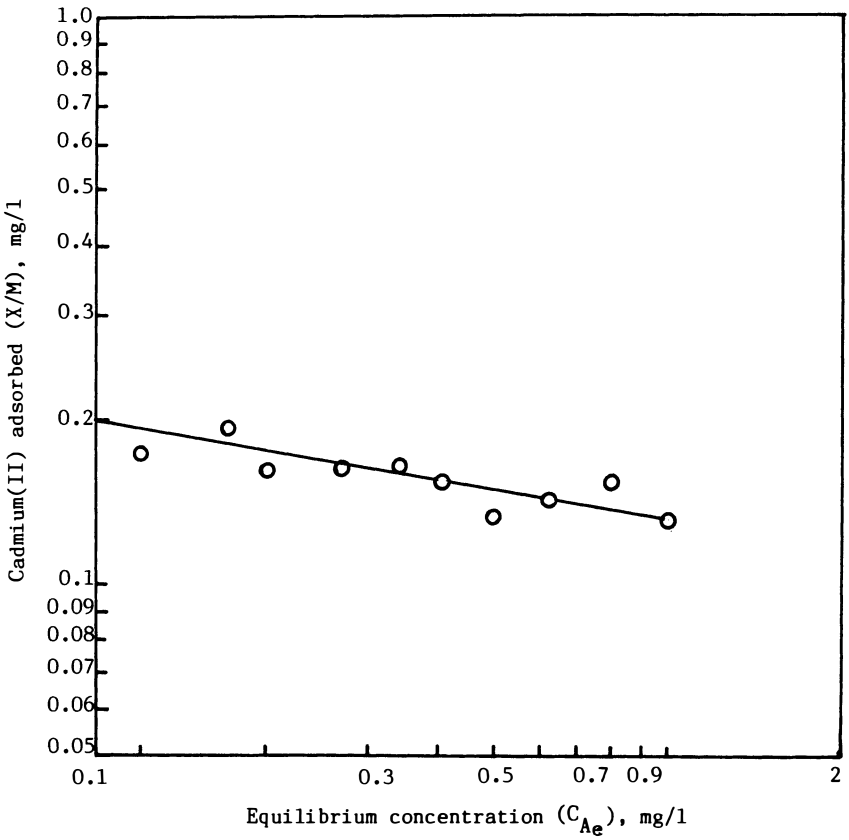

Figure 7. Linearized adsorption data for Cd(II) adsorption on nut shell.

Table 5 Freundlich Isotherm Constants

Metal	Waste Tea		Turkish Coffee		Exhausted Coffee		Nut Shell		Walnut Shell	
	k	n	k	n	k	n	k	n	k	n
Cr (VI)	1.4	0.3379	0.8	0.8414	2.3	0.1627	1.9	0.0230	2.7	0.0590
Cd (II)	1.6	0.7590	1.5	0.8040	1.5	0.9020	1.6	0.9230	3.5	0.5120
Al (III)	2.7	0.2710	2.7	0.1040	2.8	0.7460	3.4	0.0700	1.7	0.9820

Table 6 Correlation Coefficients (R) and Standard Error of Estimation of Regression Line (SE)

Metal	Waste Tea		Turkish Coffee		Exhausted Coffee		Nut Shell		Walnut Shell	
	R	SE	R	SE	R	SE	R	SE	R	SE
Cr (VI)	0.89	0.028	0.86	0.052	0.95	0.021	0.98	0.052	0.90	0.028
Cd (II)	0.79	0.066	0.90	0.007	0.72	0.013	3.93	0.006	0.73	0.226
Al (III)	0.80	0.081	0.60	0.184	0.88	0.051	0.81	0.083	0.71	0.110

CONCLUSIONS

From these results, agricultural wastes appear to be suitable for the removal of Cr (VI), Cd (II) and Al (III) from wastewater. Batch studies shown that the adsorption reaction can be described by the first order reversible reaction and the sorption equilibria data can be approximated to Freundlich isotherm.

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