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Removal of Cadmium from Water by Using Battery Industry Waste as Low-Cost Adsorbent

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Abstract: A cheaper adsorbent has been prepared utilizing battery industry waste and investigated for the removal of cadmium from aqueous solutions. Its adsorption on prepared adsorbent was studied as a function of contact time, concentration and temperature. The results have shown that prepared adsorbent adsorbs cadmium to a sufficient extent (32.8 mg g^{-1}). The adsorption has been found to be exothermic and data conform to Langmuir equation. The analysis of kinetic data indicates that adsorption is a first order process and pore diffusion controlled. As the prepared adsorbent shows satisfactory results in removing cadmium from water, therefore, it can be fruitfully used for the removal of metal ions from waste waters.

Key words: Waste management, battery industry waste, low-cost adsorbent, cadmium removal, water treatment, batch and kinetic studies

Introduction

The rapid industrialization and modern day domestic and agricultural activities have placed heavy demand for good quality water. Not only this, the water after use becomes highly polluted due to the addition of a number of inorganic and organic pollutants. As a result of development of better analytical systems and better health monitoring technologies, the acceptable minimum concentration of these pollutants is progressively decreasing. As such, stringent regulations have been introduced by most countries with respect to presence of these pollutants in water and which binds industries and other bodies to minimize the concentrations appreciably before the wastewater is discharged into natural bodies containing good quality water. In view of importance of pollution control, a number of technologies have been developed (Pontius, 1990). Some of them are coagulation, sedimentation, floatation, filtration, ion exchange, membrane process, adsorption, chemical precipitation and disinfection.

Among them, adsorption process is considered better as compared to other methods because of convenience, easy operation and simplicity of design. Further, this process can remove/minimize different type of pollutants and thus it has a wider applicability in pollution control (Faust and Aly, 1987). Activated carbon has been found to be a versatile adsorbent which can remove diverse type of pollutants such as metal ions, dyes, phenols and a number of other organic and inorganic compounds and bio-organisms. However, its use is sometimes restricted due to higher cost. Attempts have therefore, been made to utilize low cost natural materials or agricultural/industrial wastes as alternative adsorbents. The aim behind this is to minimize the cost of adsorbent so that the regeneration can be dispensed with. A wide variety of natural materials as well as agricultural and industrial wastes have been investigated for this purpose and excellent reviews have been published so far on the topic (Pollard *et al*., 1992; Babel and Kurniawan, 2003).

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Since last few decades, utilization of industrial wastes is of vital concern for researchers as these wastes cause major disposal problems. If the solid wastes could be used as low cost adsorbents, it will provide a two fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low cost adsorbent if developed can reduce the pollution of waste waters at a reasonably cost. Thus, a number of industrial wastes (Panday *et al*., 1985; Çengeloğlu *et al*., 2002; Calce *et al*., 2002; Yamada *et al*., 1986; Dimitrova, 1996; López *et al*., 1995; Jallan and Pandey, 1992) have been investigated with or without treatment as adsorbents for the removal of pollutants from waste waters. However, utility of battery industry waste has not been widely explored.

The aim of this study was to determine the efficiency of battery industry waste as low-cost adsorbent for the removal of Cd from aqueous solutions. Cadmium is selected for the present studies as it is highly toxic and has been implicated in some cases of poising through food. Minute quantities of Cd are suspected of being responsible for adverse affects in arteries of human kidneys. Cadmium also causes generalized cancers in laboratory animals and has been linked epidemiologically with certain human cancers. Cadmium concentration of 200 $\mu g\ L^{-1}$ is toxic to certain fish. Cadmium may enter in water as a result of industrial discharges or the deterioration of galvanized pipes.

Materials and Methods

Materials

Stock solution of Cd was prepared by dissolving the metal salt in doubled distilled water and was diluted further to obtain the lower concentration solutions. Battery industry waste was collected from M/S Prakash Metal Industries, Mohkampur, Phase I, Meerut.

Preparation of Battery Industry Waste as Adsorbent

The battery industry waste was first washed with double distilled water and dried at 200°C overnight. Then, it was treated with H_2O_2 to oxidize the adhering organic material. It was then washed with distilled water and heated at 200°C. The activation of this material was done at different temperatures in muffle furnace for 1 h in the presence of air. After activation, the ash content was removed by washing with distilled water and dried. Different mesh sizes were obtained after sieving and kept in desiccator for further use. It was found after preliminary adsorption studies that the activation at 450°C imparts maximum adsorption characteristics and, therefore, all investigations were carried out on the samples activated at this temperature only.

Apparatus

Atomic Absorption Spectrophotometer (AAS) from Hitachi model no. Z-7000 has been used to determine the concentration of cadmium in solutions.

Methods

Adsorption Studies

The adsorption of cadmium on battery industry waste was studied at room temperature by employing the batch method. A known volume (10 mL) of metal solutions of varying initial concentrations, taken in 50 mL stoppered glass tubes, was shaken with a fixed dose of adsorbent (0.01 g) for a specified period of contact time in a thermostated shaking assembly. After equilibrium, the concentration of the adsorbate in the residual solution was determined by AAS. The experiments were repeated a number of times and average values are reported. Standard deviations were found to be within±3.0%. The adsorption was studied as a function of contact time, concentration and temperature. Kinetic studies of adsorption were also carried out at two different concentrations of the adsorbates where the extent of adsorption was investigated as a function of time.

Results and Discussion

Effect of Contact Time and Concentration

In order to find equilibrium time for maximum uptake of cadmium on battery industry waste, the adsorption of Cd at fixed concentration was studied as a function of contact time and the results are shown in Fig. 1. It is clear from Fig. 1 that rate of uptake of Cd is rapid in the beginning and 50% adsorption is completed within 2 h. The Fig. 1 also indicates that the time required for equilibrium adsorption is 8 h. Thus for all equilibrium adsorption studies, the equilibration period was kept 10 h. The effect of concentration on equilibrium time was also investigated at different concentrations. It was found that time of equilibrium as well as time required to achieve a definite fraction of equilibrium adsorption is independent of initial concentration. These results indicate that the adsorption process is first order, which is confirmed by Lagergren's plots discussed later under dynamic modelling.

Adsorption Isotherms

In order to determine the efficacy of battery industry waste, the equilibrium adsorption studies were carried out and the adsorption isotherms are shown in Fig. 2. It is shown from Fig. 2, that the adsorption capacity of the adsorbent for Cd is 33 mg g^{-1}.

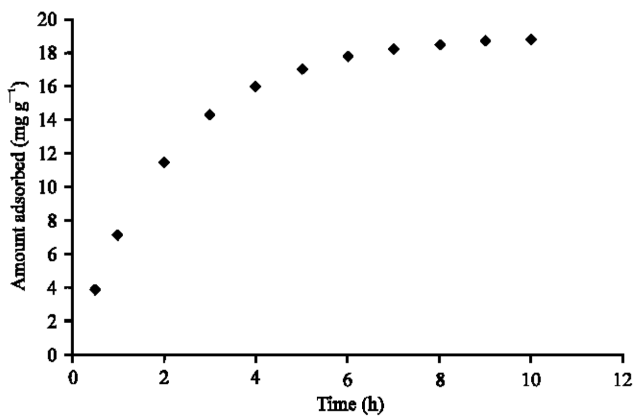

Fig. 1: Effect of contact time on uptake of cadmium on battery industry waste

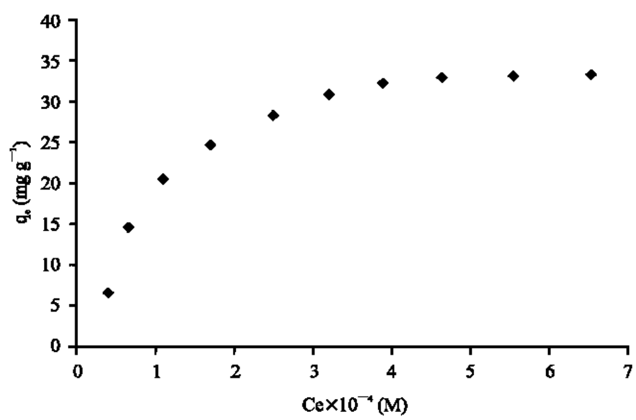

Fig. 2: Adsorption isotherm of cadmium on battery industry waste at 25°C

Effect of Temperature

To determine the effect of temperature on the adsorption of Cd, experiments were also conducted at 45°C. A comparison of adsorption isotherms at 25 and 45°C shows that adsorption decreases with increase in temperature indicating that the adsorption of Cd is exothermic. The adsorption data was further analyzed and found to conform best to following Langmuir equation

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m bC_e} \tag{1}$$

where 'q_e' is the amount adsorbed at equilibrium concentration C_e, q_m the Langmuir constant representing maximum monolayer capacity and 'b' the Langmuir constant related to energy of adsorption.

The free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated using following equations

$$-\Delta G^0 = R\,T\,\ln(b) \tag{2}$$

$$\ln(b_2 / b_1) = -\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{4}$$

for adsorption process in order to know the nature of adsorption and are summarized in Table 1.

Dynamic Modelling

Kinetics of sorption is one of the important characteristics in defining the efficiency of sorption. Various kinetic models have been proposed by various workers where the adsorption has been treated as first order (Panday *et al*., 1985; Haribabu *et al*., 1993) pseudo first order (Tutem *et al*., 1998; Ho and McKay, 1999) and pseudo second order process (Ho *et al*., 2001). Different systems conform to different models. The Lagergren's (1898) rate equation is the one most widely used (Panday *et al*., 1985; Haribabu *et al*., 1993) for the sorption of a solute from a liquid solution. Thus this first order equation

$$\log(q_e - q) = \log q_e - \frac{k_{ads}}{2.303} t \tag{5}$$

where q_e and q are amount of Cd adsorbed at equilibrium and at time t, in mg/g respectively and k_{ads} the first order rate constant, was applied to the present studies of Cd adsorption. As such, the values of log (q_e-q) were calculated from the kinetic data of Fig. 1 and plotted against time in Fig. 3. The plots are found to be linear indicating that Lagergren's equation is applicable to the Cd adsorption on battery industry waste and the adsorption is first order process.

The kinetic data were further used to learn about the slow step occurring in the present adsorption system. The applicability of following Bangham's equation (Aharoni and Ungarish, 1977).

Table 1: Thermodynamic parameters for adsorption of Cd on battery industry waste at different temperatures

Temperature (°C)	$-\Delta G^0$ (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	$-\Delta H^0$ (kJ mol^{-1})
25	19.1	91.8	6.8
45	21.4	92.2	

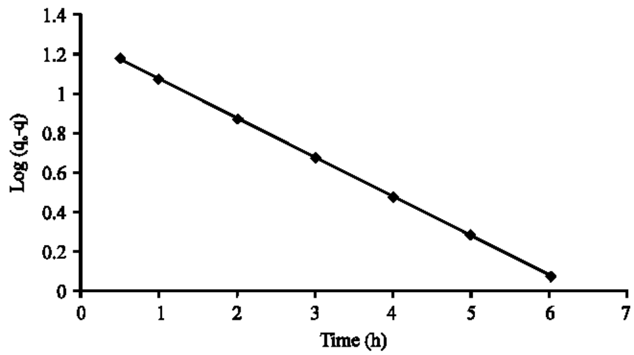

Fig. 3: Lagergren's plot for cadmium adsorption on battery industry waste

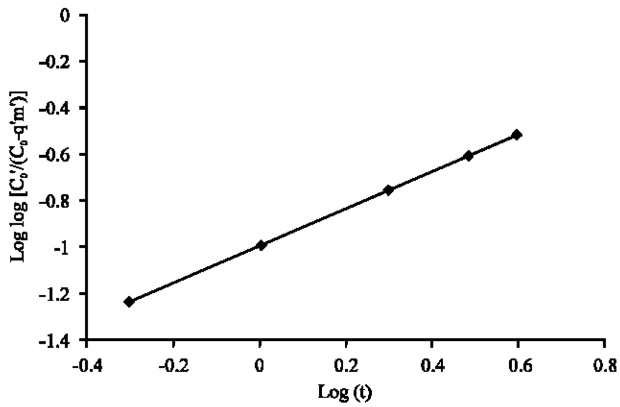

Fig. 4: Bangham's plot for cadmium adsorption on battery industry waste

$$\log\log\left(\frac{C_0'}{C_0' - q'm'}\right) = \log\left(\frac{k_0 m'}{2.303V}\right) + \alpha \log t \tag{6}$$

where C'_0 is initial concentration of the adsorbate in solution (mmol L^{-1}), V the volume the solution (mL), m' the weight of adsorbent used per liter of solution (g L^{-1}), q (mmol g^{-1}) the amount of adsorbate retained at time t and α (<1) and k_0 constants, to present adsorption studies was tested. As such, log log [C_0'/ (C_0'-q' m')] was plotted against log t, as shown in Fig. 4. The linearity of these plots confirms the applicability of Bangham's equation and indicates that the diffusion into pores of the adsorbent controls the adsorption process.

Conclusions

The present studies clearly reveal that battery industry waste can be fruitfully employed in treating industrial effluents containing toxic metal ions. The proposed technology (utilization of industrial wastes for effluent treatment) provides a double-fold aim of wastewater treatment and solid waste minimization.

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