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An evaluation of cadmium sorption potential of waste aluminium dross

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ABSTRACT

The removal of Cd(II) from aqueous solution onto aluminium dross surface was investigated. The influence of pH, contact time, initial metal ion concentration and temperature on the effectiveness of the removal process was studied. The variation of adsorption efficiency with pH indicates that the aluminium dross has residual negative charge on the surface. At low pH, H^+ ion gets adsorbed preferentially than Cd(II) ion but at higher pH, Cd(II) ion gets adsorbed in larger numbers. It has been further observed that the adsorption efficiency increases with temperature indicating an increase in kinetic energy of the solute ions or decrease in boundary layer resistance to mass transfer. Kinetic study indicated that in the present work the adsorption process follows mainly pseudo-first-order rate model. The low activation energy ($18.3\,\text{kJ mol}^{-1}$) reveals that the process is spontaneous and physical in nature. The value of ΔG° is negative which further decreases with temperature indicating spontaneity of the adsorption process. The positive value of ΔH° indicates that the process is endothermic. The present study revealed that waste aluminium dross can be a potential sorption material for cadmium in an aqueous system under conditions of pH (4–9), temperature of about 42℃ and reaction time of 2 h.

Keywords: Cadmium; Sorption; Aluminium dross; Kinetics; Thermodynamics

1. Introduction

Due to rapid industrial development, there are increased level of metal concentration in the waste water posing a serious problem to the biosphere. Metal industries, refining, mine drainage, dye and leather industries, domestic effluents, laboratory effluents, land fill leachate and agricultural run off generate waste water that contain heavy metal ions [1]. According to World Health Organization, the metals of concern are cadmium, chromium, zinc, copper, lead, mercury, etc. [2]. Most of the metal ions are non-degradable and therefore pose threats to public health if the problem of their removal is not addressed properly. There are several methods for the treatment of metal effluents such as precipitation, ion exchange, membrane processes and adsorption. Adsorption is often chosen for the abatement of such problems particularly when the adsorbent selected is a low cost or a waste material.

Cadmium is one of the main heavy metals, which is highly toxic to humans, plants and animals. It enters the food chain and forms strong complexes with bio molecules [3]. The major sources of cadmium

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Table 1
Chemical composition of washed aluminium dross

Compound/element	Al_2O_3	SiO_2	MgO	Fe_2O_3	CaO	C
Percentage (%)	68.1	4.2	3.35	1.57	1.0	1.75

into the waste streams are electroplating, use of phosphatic fertilizers, smelting, alloy manufacturing, pigments, plastics, battery and mining [4–6]. Cadmium is one of the most mobile pollutants, because it is most weakly bound to the soil constituent [7]. In the present study cadmium has been chosen as the contaminant in aqueous medium.

Waste secondary aluminium dross generated during remelting of primary dross with salts, such as KCl, NaCl, etc., is considered as a pollutant when it is kept stockpiled for a longer period. It leaches out several pollutants like Na, K, etc. and emits harmful gases like NH_3, SO_2, CH_4, etc. to the water stream and atmosphere, respectively. Several processes [8,9] were developed to treat such material, but majority of the dross are still used as land fill material. Utilization of this material as adsorbent has been carried out in the present study after thorough washing. The alumina present in the dross may be responsible for its adsorptive capacity. In recent years, adsorption techniques have been investigated for the removal of cadmium from waste water streams [3,7,10–15]. In majority of the cases activated carbon obtained from various sources [11,12,15–19] are utilized. Activated alumina was also used as adsorbent for cadmium [10,20]. Various clays, natural zeolite, olive stones, cellulosic materials, nut and wall nut shells, waste tea [6,21–24], etc. were also tried.

Aluminium dross being a waste material is available almost freely and apart from that one has to spend money for its stock piling. Therefore, its use as an adsorbent can be an alternative option. Hence, in the present work, aluminium dross was used to evaluate its effectiveness for the adsorption of cadmium. Due to seasonal variation of temperature in tropical countries, studies on the temperature dependence of adsorption have been carried out. Variation of pH, Cd(II) concentration along with kinetics and thermodynamic studies were also taken up.

2. Materials and methods

2.1. Adsorbent: aluminium dross

The aluminium dross obtained from a domestic supplier containing 65% Al_2O_3, 4% SiO_2 and oxides of Mg, Ca and Fe along with some salts, such as NaCl and KCl, was ground in a ball mill and then passed through a screen to obtain a product of 100 mesh (Tyler). This powdered mass was then washed in a beaker at 80°C with stirring for 4 h to leach out all soluble impurities such as KCl, NaCl, etc. The slurry was then filtered and the residue was washed several times to ensure there are no more soluble impurities in it. The residue was then dried in an oven at 110°C for 24 h. This dried mass was used as adsorbent for further studies. The chemical composition of this aluminium dross is given in Table 1. Fig. 1 shows the X-ray diffraction (XRD) pattern of washed aluminium dross. The major phases observed are α-alumina, Mg-aluminate, quartz and graphite. Scanning electron micrograph (SEM) of aluminium dross is also shown in Fig. 2, which indicates that particles are highly porous.

2.2. Adsorbate

A stock solution of $CdSO_4$ ($10\,g\,L^{-1}$) was prepared by taking analytical grade reagent (Merck, India). Solutions with required cadmium concentration were prepared by diluting the stock solution with distilled water. A 100 mL of solution was used in every experiment.

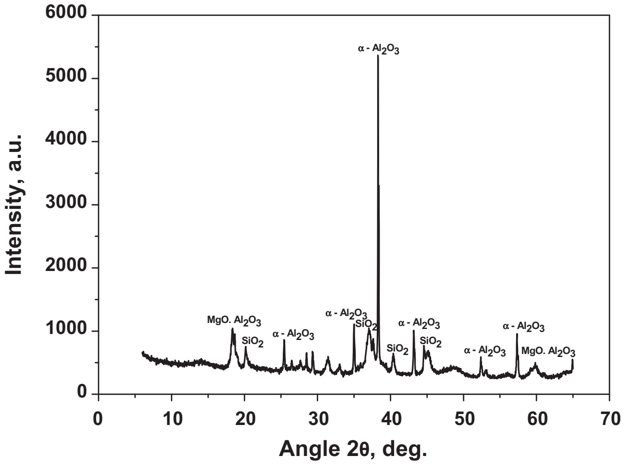

Fig. 1. XRD pattern of aluminium dross showing different phases.

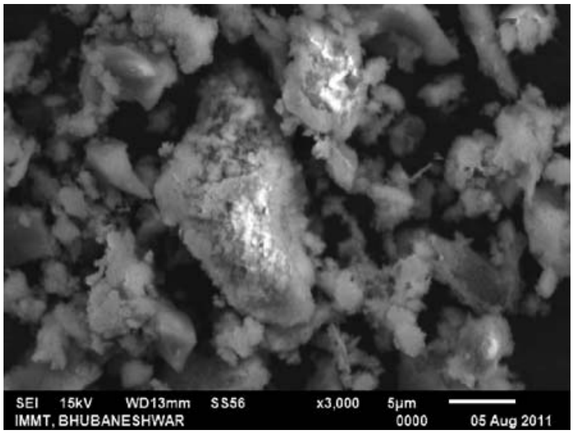

Fig. 2. SEM of washed aluminium dross.

2.3. *Adsorption procedure*

Adsorption tests were conducted in a 250 mL glass beaker with 100 mL of cadmium solution as adsorbate and 0.5 g of dross as adsorbent. The solution was stirred at RPM of 100 ± 5 using a mechanical stirrer having a variable speed regulator. Samples were withdrawn at various time intervals and analysed for Cd concentration by AAS (Perkin Elmer). Each experiment was continued for 3 h. The tests at higher temperatures were carried out in a constant temperature bath (Julabo, Germany).

3. Results and discussion

3.1. *Effect of adsorbate concentration*

The percent adsorptions at different initial cadmium concentrations are shown in Fig. 3. In these experiments, amount of adsorbent was kept constant and cadmium concentration was varied to know the equilibrium concentration at each initial cadmium concentration. It was observed that with increase in initial cadmium concentration of adsorbate, the percentage adsorption has declined but the equilibrium reached at around 120 min in all the cases. The effective adsorbate concentration was found to be about 10–15 ppm Cd(II) in the presence of 0.5 g of adsorbent, where nearly 100% adsorption efficiency was achieved at 25˚C.

3.2. *Effect of pH*

Since cadmium adsorption is very much pH dependent, effect of initial pH of the solution on the adsorption characteristics was studied keeping the cadmium concentration constant. In this case, adsorbent quantity used was 0.5 g. The temperature of the study was 25˚C. According to Namasivayam and Ranganathan [14], precipitation of cadmium starts at pH 8.2. But as the solute concentration is very low, cadmium precipitation is unlikely at slightly higher pH than 8.2. Therefore, in this study, the effect of pH was studied in the range of 2–9. Fig. 4 shows the effect of pH variations on the adsorption efficiencies. It is clear that at higher pH (4–9) the adsorption efficiency is more than 90%. However, at lower pH of 2 or 3 the adsorption efficiency is low and remains below 50%. In highly acidic medium (pH 2), due to the presence of higher concentration of protons (H^+), the adsorption of Cd(II) is diminished as a result of simultaneous adsorption of protons onto the adsorbent surface. It is evident from the fact that pH of the solution increased from 2 to 4.05 at the end of the study due to H^+ ions depletion in the solution. At higher pH, adsorption efficiency increased due to depletion of H^+ ions or presence of OH^- ions which

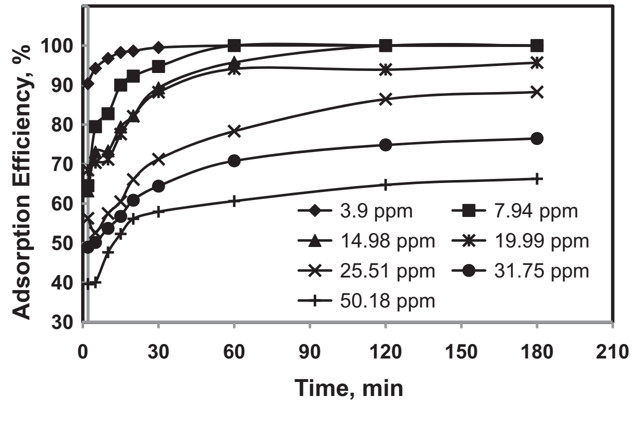

Fig. 3. Variation of adsorption efficiency with time at different initial concentrations of adsorbate. pH—6, adsorbent—0.5 g and temperature—25˚C.

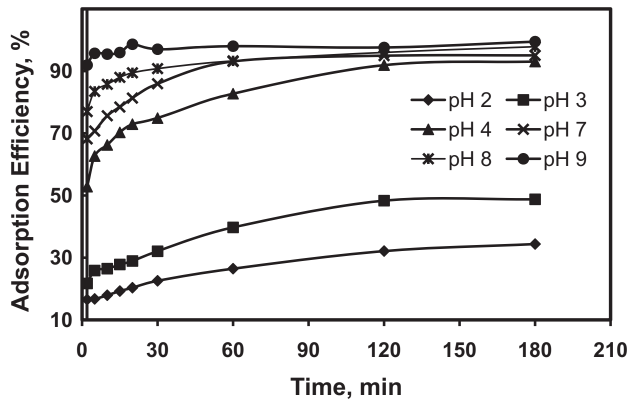

Fig. 4. Variation of adsorption efficiency with time at different pHs. Adsorbent—0.5 g, adsorbate—21.86 ppm and temperature—25˚C.

did not get attached to the adsorbent surface. Therefore, there are more vacant sites for cadmium to be adsorbed. This indicates that the aluminium dross is having residual negative charge on the surface. Similar results of increased adsorption due to increase in pH were noticed by other authors [7,15].

3.3. *Effect of temperature*

Fig. 5 shows the effect of temperature on Cd(II) adsorption varied with time. Adsorption efficiency of the aluminium dross was found to be increased with temperature. It can be noted that at a particular time of 120 min, Cd(II) adsorption efficiencies were found to be 76, 88, 94 and 95% at 25, 35, 42 and 50˚C, respectively. The increase in adsorption efficiency with temperature may be due to decrease in boundary layer resistance to mass transfer and increase in kinetic energy of Cd(II) ions. The increase in adsorption with temperature confirms the endothermic nature of the adsorption process. The optimum temperature for an efficient adsorption was found to be about 42˚C.

3.4. *Adsorption kinetics of cadmium*

Kinetics of metal ion adsorption determines the rate, which simultaneously calculates the residence time in batch/continuous mode operations and efficiency of an adsorbent [17]. This also provides information on the minimum time required for considerable adsorption to take place and the possible diffusion control mechanism between the metal ions as it moves from the bulk solution towards the adsorbent surface. In this study, kinetic analyses were made on the basis of effect of temperature on cadmium adsorption for which a fixed concentration of solute was taken and temperature was varied. The data obtained in this study were fitted into two types of kinetic models, such as (i) pseudo-first-order rate equation [25] and (ii) pseudo-second-order rate equation [26].

3.4.1. *Pseudo-first-order rate equation*

The first-order rate equation is generally expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

where q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively, and expressed in mg g^{-1}. k_1 (L min^{-1}) is the first-order rate constant for adsorption. When the values of $\ln(q_e - q_t)$ are plotted as a function of time (t), a linear relationship is obtained, from which k_1 can be found out.

3.4.2. *Pseudo-second-order rate equation*

The second-order rate equation is generally expressed as:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{2}$$

where q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively, and expressed in mg g^{-1}. k_2 ($\text{g mg}^{-1}\,\text{min}^{-1}$) is the second-order rate constant and can be obtained from the slope of the linear Eq. (2).

In all the adsorption processes it has been noticed that adsorption is rapid during the initial stages and then it slows down before attaining an ultimate

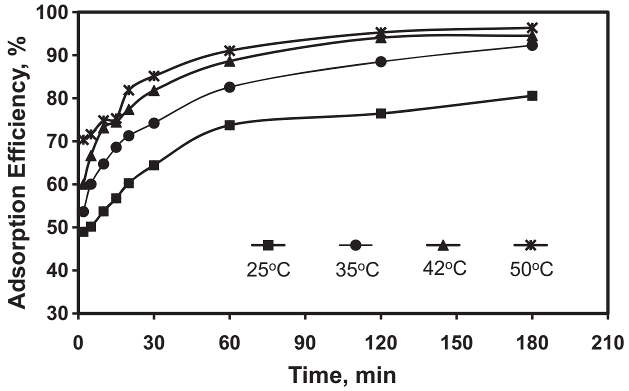

Fig. 5. Variation of adsorption efficiency with time at different temperatures. Adsorbent—0.5 g, adsorbate—31.75 ppm and pH—6.

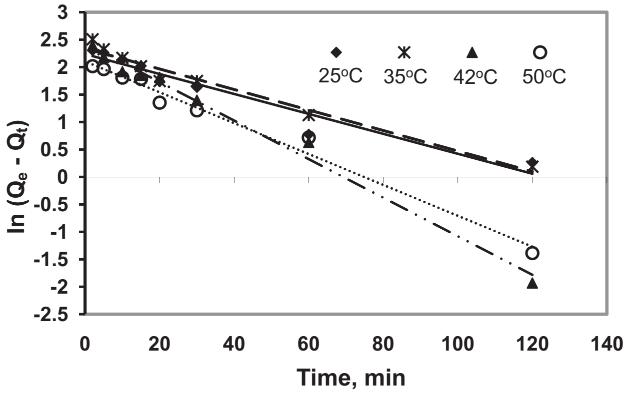

Fig. 6. The pseudo-first-order rate plot at four different temperatures.

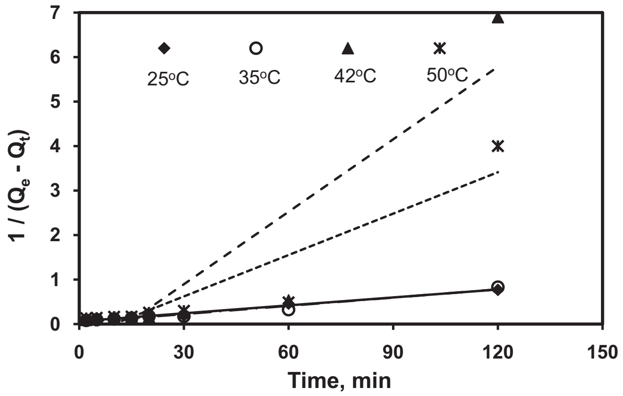

Fig. 7. The pseudo-second-order rate plot at four different temperatures.

equilibrium. Initially, adsorption occurs instantaneously due to vacant sites and then slowly it decreases due to covering of vacant sites.

Figs. 6 and 7 show the pseudo-first-order and pseudo-second-order rate plots, respectively, measured at four different temperatures. The correlation coefficients (R^2) and rate constants were calculated and given in Table 2. The correlation coefficients for all temperatures were quite high (>0.93) for pseudo-first-order reaction, whereas for pseudo-second-order reaction the correlation coefficients for 25 and 35°C are quite high (>0.96), but for 42 and 50°C they are low (<0.86). From the above, it is clear that as the correlation coefficient of pseudo-first-order equation is greater than 0.93 for all temperatures experimented, Cd(II) ion adsorption process onto aluminium dross is mainly following pseudo-first-order equation.

The activation energy for Cd(II) adsorption onto aluminium dross is calculated by using the Arrhenius equation as shown below:

$$k = A\mathrm{e}^{-E/RT} \tag{3}$$

$$\text{or } \ln k = \ln A - \frac{E}{RT} \tag{4}$$

where k is the rate constant at temperature T (K), A is the frequency factor, R is the universal gas constant ($8.314\,\mathrm{J\,mol^{-1}\,k^{-1}}$) and E ($\mathrm{J\,mol^{-1}}$) is the activation energy for the process. When ln$k$ values are plotted against $1/T$, activation energy value can be calculated from the slope of the straight line.

The effect of temperature on the rate constants of Cd(II) adsorption onto aluminium dross was investigated by determining the activation energy. The pseudo-first-order rate constants were utilized for determination of activation energy. The resultant

Table 2
Kinetic constants and calculated correlation coefficients for rate equations

Temperature (K)	Pseudo-first-order equation		Pseudo-second-order equation		Equilibrium constant
	K_1	R^2	K_2	R^2	K_C
298	0.0182	0.9387	0.006	0.9873	4.1375
308	0.0187	0.9709	0.0062	0.9672	11.9592
315	0.0351	0.9884	0.0543	0.8312	17.2997
323	0.0281	0.9828	0.0311	0.8526	21.2028

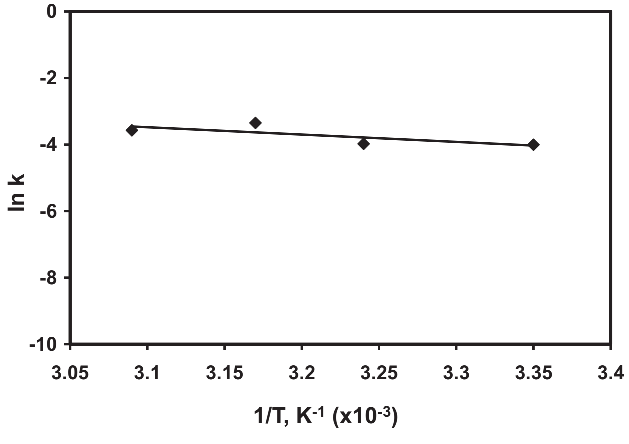

Fig. 8. The resultant Arrhenius plot for pseudo-first-order rate reaction.

Arrhenius plot is shown in Fig. 8. The calculated activation energy value for the adsorption process is 18,319 J mol^{-1}. The low value of activation energy indicates the spontaneous nature of the adsorption and the process is governed by physical forces.

3.5. Thermodynamic parameters

Some thermodynamic evaluations were made from the results obtained from the pseudo-first-order rate study. The values for standard Gibbs free energy change (ΔG°), standard entropy change (ΔS°) and standard enthalpy change (ΔH°) were calculated for the adsorption of Cd(II) onto aluminium dross and reported in Table 3.

The standard free energy change (ΔG°) was calculated according to the following equation:

$$\Delta G^\circ = -RT \ln k_C \tag{5}$$

where k_C is the characteristic equilibrium constant [27] and it can be evaluated as:

$$K_C = C_A/C_E \tag{6}$$

Table 3
Thermodynamic parameters for adsorption of Cd(II) onto aluminium dross

Temperature (K)	ΔG° (J mol^{-1})	ΔH° (J mol^{-1})	ΔS° (J mol^{-1} K^{-1})
298	−3,518.38	52,024	187.8
308	−6,354.41		
315	−7,465.69		
323	−8,201.64		

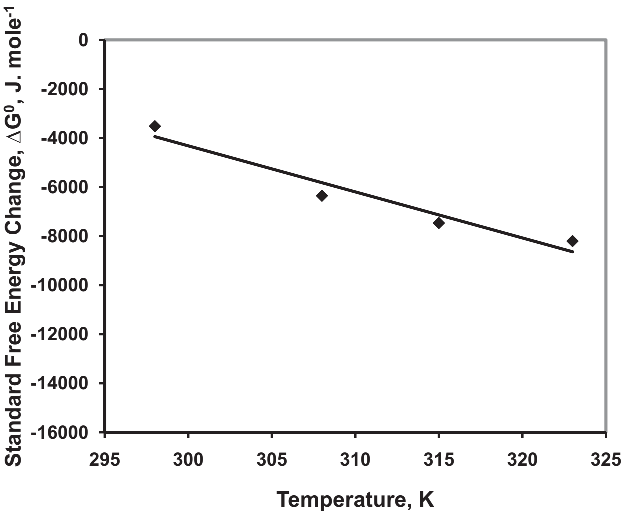

Fig. 9. Variation of standard free energy change (ΔG°) with temperature.

where C_A (mg L^{-1}) is the amount of cadmium adsorbed at equilibrium and C_E (mg L^{-1}) is the amount of cadmium remaining in adsorbate solution at equilibrium. R is the universal gas constant (J mol^{-1} k^{-1}) and T is the absolute temperature in Kelvin (K).

ΔH° and ΔS° are calculated from the intercept and slope of the linear equation as shown below:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{7}$$

Fig. 9 shows the plot of ΔG° against T. The positive value of ΔH° (52,024 J mol^{-1}) confirms the endothermic nature of the adsorption process. The negative value of ΔG° indicates the spontaneity of the adsorption process. The positive value of ΔS° (187.8 J mol^{-1} K^{-1}) shows the increased randomness at the interface (solid–liquid) during adsorption process.

4. Conclusions

Aluminium dross being a waste product seems to be a good option as adsorbent for cadmium removal in aqueous system. The use of waste secondary aluminium dross as metal ion sorption material has not been reported in the literature earlier. The residual surface charge of aluminium dross particles was found to be negative in aqueous solution. At low pH, the adsorption efficiency was low as compared to that of at higher pH (4–9) because at low pH, H$^+$ ion gets adsorbed preferentially than Cd(II) ion due to smaller ionic radius, but at higher pH the solution will have less protons and therefore Cd(II) ion gets adsorbed in larger numbers. The process of cadmium adsorption by aluminium dross can be efficiently carried out in 2 h of reaction time. It has been further observed that the adsorption efficiency increases with temperature indicating an increase in kinetic energy of the solute ions or decrease in boundary layer resistance to mass transfer. Kinetic study indicated that in the present work the adsorption process follows mainly the pseudo-first-order rate model. The low activation energy reveals that the process is spontaneous and physical in nature. The value of ΔG° is negative which further decreases with temperature indicating spontaneity of the adsorption process. The positive value of ΔH° indicates that the process is endothermic.

The adsorbed cadmium from the surface of aluminium dross can be recovered by desorption followed by precipitation as its compounds and cadmium free aluminium dross which is non-hazardous can be reutilized. As aluminium dross was found to be an effective adsorbent for cadmium, similar studies can be explored for other heavy metal ions.

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