Kinetics Study of Lead ion Adsorption on Active Carbon

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The kinetics of the adsorption of lead ions on active carbon from aqueous solutions was studied at room temperature at different lead ion concentrations (i.e. 0.1-0.5 g/L). The kinetics of the lead ion adsorption on active carbon is explained through mass transfer adsorption phenomena and the rate determining step was found to be film diffusion.

Introduction

The presence of heavy metal ions in the environment has been a matter of major concern due to their toxicity to human life. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions will not degrade into harmless end-products[1]. The treatment of aqueous wastes containing soluble heavy metal ions requires the concentration of metal ions followed by recovery for secure disposal. Many techniques such as chemical precipitation, ion exchange, reverse osmosis, solvent extraction and adsorption are used for wastewater treatment (removal of metal ions). The adsorption technique, both bio and chemical adsorption, has a definite edge over the other techniques[2]. The adsorbent used is material containing organic carbon such as activated carbon, charcoal, lignite, wood bark and many inorganic chemicals and clay. The adsorptive properties of the active carbon for the removal of the pollutants are well documented[3]. Lead is a metal ion toxic to the human biosystem, and is among the common global pollutants arising from increasing industrialization. The assimilation of relatively small amounts of lead over a long period of time in the human body can lead to the malfunctioning of the organs and chronic toxicity. The toxic effects of lead ions on humans, when present above the threshold level in the hydrosphere, are well documented[4]. Previously, various researchers have studied the adsorption of lead on oxide of silicon, manganese, aluminum[5−6], bentonite[7], hydrated titanium dioxide[8], modified silica gel [9−10], polycarbonate filters [11], dithizone-anchored poly (EDGMA-HEMA) microbeads[12], resin[13], anionic microgel[14], bacterially oxidized manganese[15], ZnS surface[16], magnetite[17], pedogenic oxides, ferrihydrite and leaf compost[18], sawdust[19], Brazilian oxisols[20], limestone and dolomite[21] and lateritic minerals[22]. Few reports are available in the literature on carbon and carbon- related compounds[23−25]. All these studies were

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carried out from different points of view. The present communication describes the kinetic study of lead ions adsorption on active carbon from aqueous solutions.

Experimental

A commercial active carbon (Riedel de Haen; item no. 18001) was used in this study. The B.E.T. surface area, determined by nitrogen adsorption using the Quantasorb Sorption System (Quantachrom Corporation, N.Y., USA), was found to be 950 m^2/g. The pore volume and porosity were determined by mercury intrusion to be 1.53 cm^3/g and 60.26%, respectively. A carbon analyzer (model CS-244 by M/S LECO) determined the carbon content to be 87.28%. The active carbon was dried at 100 ^oC before use. Lead nitrate supplied by Riedel de Haen (product code: 11520) was used to prepare solutions of lead ions in deionized water. The adsorption of lead ions onto active carbon was carried out using a batch technique at room temperature (23 $\pm$ 1 ^oC). Details of the adsorption procedure employed were similar to those described elsewhere[26]. The concentration of lead ions in solution was measured using an atomic absorption spectrometer (M/S Hitachi, Japan, model no. 180-80). The percentage of adsorption of lead ions was computed in the usual way.

Results and Discussion

Figure 1 represents the variation in lead ion adsorption on active carbon with shaking time at different lead ion solution concentrations (0.1 to 0.5 g/L). This figure indicates that while the adsorption of lead ions is quite rapid initially, the rate of adsorption becomes slower with the passage of time and reaches a constant value in ca. 60 min (equilibrium time). The initial faster rate may be due to the availability of the uncovered surface area of the adsorbents, since the adsorption kinetics depend on the surface area of the adsorbent[27]. It is quite evident from this figure that the percentage adsorption at equilibrium, as well as prior to equilibrium, decreases with an increase in lead ion concentration.
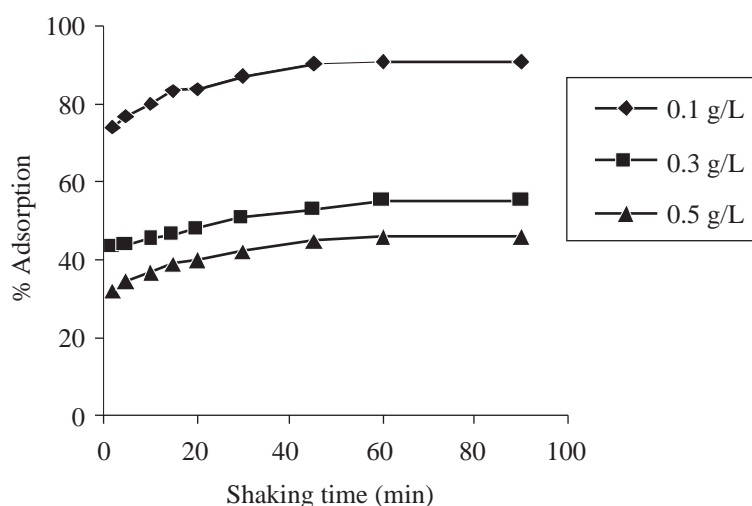

Figure 1. Variation of % adsorption with shaking time for the adsorption of lead ions on active carbon from aqueous solutions.

The equation developed by Lo and co-workers[28-29] was employed to study the kinetics of lead ions adsorption on active carbon:

$$C - C_e = D \exp(K_o t) \tag{1}$$

where C is the lead ion solution concentration (g/L) and C_e is the lead ion concentration at equilibrium (g/L); t is shaking time (min); D is a fitting parameter and K_o is a constant $= k_o M$; M is the mass of active carbon and k_o is the mass transfer adsorption coefficient. To apply Equation 1 to the experimental data in Figure 1, the equation 1 is rearranged as follows:

$$ln(C - C_e) = lnD + K_o t \tag{2}$$

Straight lines were obtained by plotting $ln(C-C_e)$ against t, as shown in Figure 2, indicating that the system acts in accordance with the equation developed by Lo and co-workers. Values of K_o and ln D, evaluated from the slopes and intercepts of the plots shown in Figure 2, are given in Table 1 along with the values of the correlation coefficient.
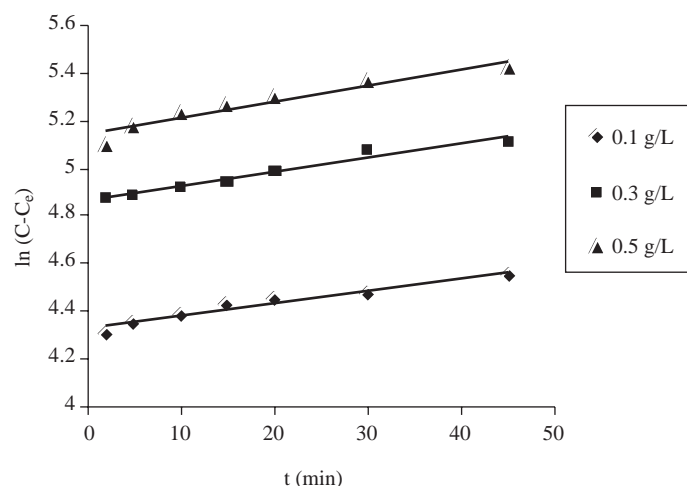

Figure 2. Plot of ln $(C-C_e)$ with t (min) for the adsorption of lead ions on active carbon from aqueous solutions.

Table 1. Calculated values of parameters for lead ions adsorption on active carbon.

Lead ion conc. (g/L)	K_o (min^{-1})	ln D	R^2, correlation coefficient
0.1	0.0051	4.3209	0.9782
0.3	0.0060	4.8557	0.9866
0.5	0.0068	5.1373	0.9582

Using the values of K_o and equilibrium concentration, C_e (g/L), determined from Figure 1 (given in Table 2), one can predict the rate determining step for the adsorption of lead ions on active carbon. In the adsorption process, the metal ions from the bulk solution should travel to the thin liquid film surrounding the adsorbent. There are 2 possibilities: either the thin liquid film may produce a diffusion barrier for the metal ions to penetrate or the diffusion barrier may be negligible. The former process is known as film diffusion controlled and the latter is known as adsorption controlled. If film diffusion is the rate determining step, then the bulk concentration will be greater than the interfacial concentration. Therefore the net rate of

adsorption will approach zero. Under these circumstances, Lo and co-workers found a correlation, as shown below:

$$k_o = K_m S C_o M / (C_o - C_e) \qquad (3)$$

where S is the specific surface area of the active carbon, C_o is the initial concentration of lead ions and K_m is the mass transfer coefficient between the bulk and carbon particle. The K_m value was reported [30-31] to depend on the particle size of the adsorbate and the rate of energy dissipation per unit mass of fluid. Therefore, for the same agitation rate, the K_m value will be constant. The specific surface area of the charcoal, S, is presumed to be constant. If film diffusion is the rate determining step, then $K_m S$ should be constant. Table 2 shows that the magnitude of the quantity $K_m S$ at constant temperature for different concentrations of lead ion solutions is more or less the same; therefore, it can be concluded that film diffusion is the rate determining step for the adsorption of lead ions on active charcoal. The desorption rate constant, k_d, can be calculated from the following relation[27,32].

$$K_o = k_d C_o / C_e \qquad (4)$$

K_o in Equation 4 is independent of the lead ion concentration. k_d values can be calculated from Equation 4 and are also given in Table 2. This table shows that the calculated values of k_d increase with the increase in lead ion concentration.

Table 2. Calculated kinetics parameters for lead ions adsorption on active carbon.

Lead ion conc. (g/L)	k_o (min^{-1}.g^{-1})	K_m S (dm^3./g.min)	C_e (g/L)	C_e/C_o	$k_d \times 10^3$ (min^{-1})
0.1	0.051	0.500	0.0033	0.033	0.168
0.3	0.060	0.330	0.1350	0.450	2.700
0.5	0.068	0.314	0.2700	0.540	3.670

Conclusion

Active carbon is a good adsorbent for lead ions, and the kinetics of the adsorption were rapid in the initial stage followed by a slow rate. The kinetic of lead ion adsorption on active carbon was explained through mass transfer adsorption phenomena and the rate determining step was found to be film diffusion.

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