Adsorption of Cd(II) and Pb(II) onto Clarified Sludge - Kinetics, Thermodynamics and Desorption and Application Study

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Abstract— *Clarified sludge is a major waste obtained from basic oxygen furnace during steel making process. In the present study clarified sludge has been characterized and used for the removal of Cd(II) and Pb(II) from aqueous solution. The effect of various physicochemical parameters such as pH, adsorbent dosage, adsorbate concentration, contact time and temperature on adsorption process was studied in batch experiments. Kinetics data for the adsorption of Cd(II) as well as Pb(II) were best described by pseudo-second order model. The effective diffusion co-efficient of for Cd(II) and Pb(II) adsorption were of the order of 10^{-11} m^2/s and 10^{-10} m^2/s respectively. The maximum uptake were 36.23 mg/g and 92.51 mg/g for adsorption of Cd(II) and Pb(II) respectively. The adsorption data for both the metal adsorption can be well described by Langmuir and Freundlich isotherm respectively. The result of the equilibrium studies showed that the solution pH was the key factor affecting the adsorption. The optimum pH for both the adsorption was 5. Mass transfer analysis was also carried out for the adsorption process. The values of mass transfer coefficients (β) obtained from the study indicate that the velocity of the adsorbate transport from bulk to the solid phase was quite fast. The thermodynamic studies indicated that the adsorption is spontaneous and exothermic for Cd(II) adsorption and endothermic for Pb(II) adsorption. The sorption energy calculated from Dubinin-Radushkevich isotherm model indicated that both the metal adsorption process were chemical in nature. Desorption studies were carried out using dilute mineral acids to elucidate the mechanism of adsorption. Application studies were carried out considering the economic viewpoint of wastewater treatment plant operations.*

Keywords— Clarified sludge, Adsorption, Pseudo second order, Freundlich adsorption isotherm, Mass transfer.

1. INTRODUCTION

Rapid industrialization has lead to increased disposal of heavy metals into the environment. Environmentalists are primarily concerned with the presence of heavy metals due to their toxicity and impact on human health and environment. The harmful effects of Cd(II) include acute and chronic metabolic disorders, such as itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy etc. [1-2]. Lead poisoning in human causes severe damage to kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead has been associated with sterility, abortion, stillbirths and neo-natal deaths etc. [3-4].

Cadmium is introduced into the water from smelting, metal plating, cadmium-nickel batteries, phosphate fertilizers, mining, pigments, pigments, stabilizers, alloy industries and sewage sludge. Where as Process industries, like battery manufacturing, printing and pigment, metal plating and finishing, ammunition, soldering material, ceramic and glass industries, iron and steel manufacturing units generate large quantities of lead.

Due to toxicity, the recommended maximum tolerance intake of Cd(II) by IS 10500 for discharge in inland surface water and public sewers are 2.0 and 1.0 mg/L respectively [5]. The permissible level of Pb(II) in water according to World Health Organization is 0.05 mg/L [6] and in wastewater as set by Environment Protection Agency [7] is 0.05 mg/L. Where as the tolerance limit of Pb(II) according to Bureau of Indian Standards (BIS) is 0.1 mg/L [8].

The safe and effective disposal of metal containing wastewater is a challenging objective for industries because cost-effective treatments alternatives are not readily available. Conventional technologies for the removal of heavy metal are chemical precipitation, ion exchange, electrochemical precipitation, solvent extraction, membrane separation, concentration, evaporation, reverse osmosis, emulsion per traction and adsorption. Among these technologies, adsorption is a cost-effective and user friendly technique which can be used only at the tertiary stage for the removal of heavy metal [9].

2. MATERIALS AND METHODS

The clarified sludge was collected from the sludge thickener of Basic Oxygen Furnace of Rourkela Steel Plant, Rourkela, Orissa, India. The sludge initially in the dust form in the basic oxygen furnace was arrested by hydro jetting followed by passing through venture scrubbers and then collected from clarifier after settling.

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Clarified sludge, after collection it was ground, homogenized and dried at 105 ± 5 ^{0}C for 3 hr and cooled to ambient temperature in a desiccators.

All the necessary chemicals used in the study were of analytical grade. Cadmium nitrate tetra hydrate [$Cd(NO_3)_2$, $4H_2O$] and Lead nitrate [$Pb(NO_3)_2$] were obtained from E. Merck Limited, Mumbai, India. Stock solution of the above heavy metals was made by dissolving exact amount of respective metal salt.

Different initial concentration of metal solutions was prepared by proper dilution from stock 1000-ppm metal standard. pH of the solution was monitored in a 5500 EUTECH pH Meter using FET solid electrode calibrated with standard buffer solutions. Necessary amount of clarified sludge was then added and contents in the flask were shaken for the desired contact time in an electrically thermo stated reciprocating shaker @ 120-130 strokes/min at 30^{0}C. The remaining metal concentration in the sample was analyzed using Atomic Absorption Spectrophotometer (VARIAN SPETRA AA 55, USA) as per procedure laid down in APHA, AWWA standard methods for examination of water and wastewater, 1998 edition [10].

3. RESULTS AND DISCUSSION

3.1 Effect of pH, contact time, adsorbent dosage

In order to evaluate the influence pH on the adsorption, the experiments were carried out at different initial pH values. The pH range was chosen as 2-7 in order to avoid metal hydroxides. The effect of pH on adsorption efficiencies are shown in Figure 1. The uptake of Cd(II) by clarified sludge increased as the pH increased. Although a maximum uptake was noted at a pH of 8, as the pH of the solution increased to >7, Cd(II) started to precipitate out from the solution. Therefore experiments were not conducted over pH 7. The increased capacity of adsorption at pH >7 may be a combination of both adsorption and precipitation on the surface of the adsorbent. It is considered that clarified sludge had a maximum adsorption capacity at a pH = 5, if the precipitated amount is not considered in the calculation. The pH range was chosen as 3-7 in order to avoid precipitate in the form of lead chloride and lead hydroxides, which has been estimated to occur at pH<2.0 for $PbCl_2$ and pH>6.5 for $Pb(OH)_2$. The effect of pH on adsorption efficiencies are shown in Figure 1. Removal of Pb(II) increases with increasing solution pH and a maximum value was reached at an equilibrium pH of around 5.

The metal ions in the aqueous solution may undergo solvation and hydrolysis. The process involved for metal adsorption is as follows [11],

$$M^{2+} + nH_2O = M\,(H_2O)_n^{2+} \qquad (1)$$

$$M(H_2O)_n^{\;2+} = [M(H_2O)_{n-1}(OH)]^+ + H^+ \qquad (2)$$

$$M^{\,2+} + nH_2O \overset{K_a}{=} [M(H_2O)_{n-1}(OH)]^+ + H^+ \qquad (3)$$

The pK_a value for Cd(II) and Pb(II) are 10.1 and 7.7 respectively. Perusal of the literature on metal speciation shows that the dominant species is $M(OH)_2$ at pH > 6.0 and M^{2+} and $M(OH)^+$ at pH < 6.0. Maximum removal of metal was observed at pH 5 for adsorption. On further increase of pH adsorption decreases probably due to the formation of hydroxide of cadmium and lead because of chemical precipitation. The optimum pH value for adsorption was found to be 5.

The effect of shaking time on the adsorption of Cd(II) and Pb(II) ion are shown in Figure 2. During the experiment contact time was varied from 0 to 5 h for adsorption of Cd(II) and 0 to 3 h for adsorption of Pb(II). The effect of contact time variation in the Figure 2 indicates that the adsorption processes reach the equilibrium after 2 h and 1 h respectively for adsorption of Cd(II) and Pb(II). The initial rapid adsorption gives away a very slow approach to equilibrium.

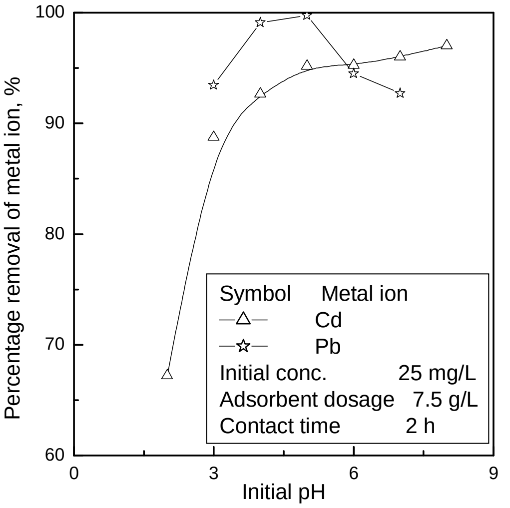

Fig. 1. Effect of pH on Cd(II) and Pb(II) removal.

Effect of adsorbent dosage on the removal of Cd(II) and Pb(II) was studied using Clarified sludge at concentration ranging from 1g/L to 30g/L. With an increase in adsorbent dosage, the metal ion removal increased to higher metal ion uptake by the increased amount of adsorbent. For higher adsorbent dosage, the incremental metal ion removal becomes very low as the surface metal ion concentration and the solution metal ion concentration comes to equilibrium with each other. The optimum adsorbent dosage on the Cd(II) and Pb(II) removal were found to be 7.5 g/L for both the cases.

3.2 Adsorption kinetics model

The study of adsorption kinetics describes the solute removal rate and evidently this rate controls the residence time of adsorbate removal at the solid - solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process. With the maximum shaking speed of 120 rpm, it was assumed to offer no mass transfer (both external and internal external) resistance to the overall adsorption process. Therefore kinetic can be studied through the residual metal ion concentration in the solution. The rate kinetics of metal ion adsorption on clarified sludge was analyzed using pseudo first-order

[12], pseudo-second order [13], and intraparticle diffusion models [14]. The conformity between experimental data and the model predicted values was expressed by correlation coefficients, r^2 and Chi-square test, χ^2.

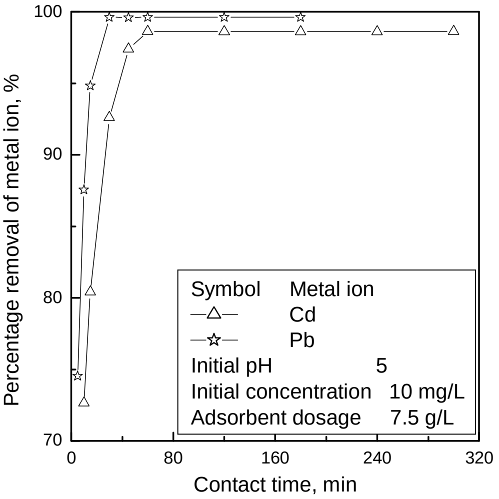

Fig. 2. Effect of contact time on Cd(II) and Pb(II) removal.

3.2.1 Pseudo first order model

The pseudo first order kinetic model was proposed by Lagergren [12]. The integral form of the model generally expressed as follows:

$$\log(q_e - q) = \log q_e - \frac{K_{ad} t}{2.303} \qquad (4)$$

3.2.2 Pseudo second order model

The kinetics of adsorption process may also be described pseudo second order rate equation [13]. The lineralized form of equation is expressed as

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (5)$$

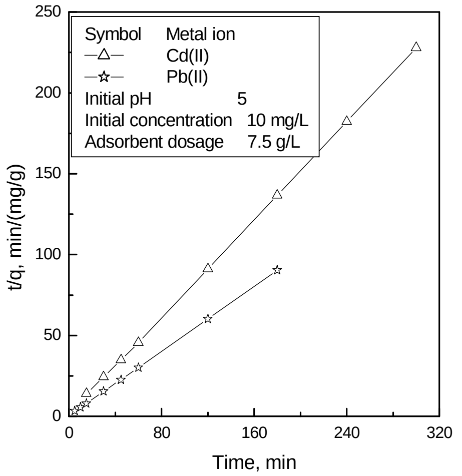

Fig. 3. Pseudo second order model for Cd(II) and Pb(II) removal.

3.2.3 Intraparticle diffusion model

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion and the adsorption on the pore surface, or a combination of more than one steps. Generally, a process is diffusion controlled if its rate dependent upon the rate at which components diffuse towards one another. The intraparticle diffusion model is based on the theory proposed by Weber and Moris [14]. According to this theory

$$q = K_{id} t^{0.5} \qquad (6)$$

The values of rate constants and correlation coefficients for each model are shown in Table 1. In addition, the Chi-square test was also done to support the best fit adsorption model. The equation for evaluating the best fit model is to be written as

$$\chi^2 = \sum \frac{(q_t - q_{tm})^2}{q_{tm}} \qquad (7)$$

It has been found that χ^2 values are much less in pseudo second order model (Figure 3) than that of pseudo first order and intraparticle diffusion model (Table1). Thus based on the high correlation coefficient and low χ_t^2 value, it can be said that adsorption of Cd(II) and Pb(II) onto clarified sludge follow pseudo second order model.

3.2.4 Mass transfer analysis

Mass transfer analysis for the removal of Cd(II) and Pb(II) from aqueous solutions by clarified sludge were carried out using the following equation as proposed by McKay et al.[15].

$$\ln\left(\frac{C_t}{C_o} - \frac{1}{1+MK_{bq}}\right) = \ln\left(\frac{MK_{bq}}{1+MK_{bq}}\right) - \left(\frac{1+MK_{bq}}{MK_{bq}}\right)\beta S_s t \qquad (8)$$

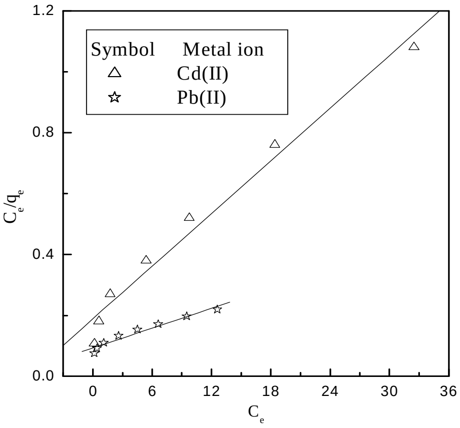

Fig. 4. Langumir plot for adsorption of Cd(II) and Pb(II) removal.

Table 1. Rate Kinetics for adsorption of Cd(II) and Pb(II) by clarified sludge

Metal	Lagergren 1st Order			Pseudo 2nd Order			Weber and Moris		
	$K_{ad}x10^{-2}$ min^{-1}	r^2	χ^2	K_2 $g.mg^{-1}.min^{-1}$	r^2	χ^2	K_{id} $x10^{-2}$ $mg.g^{-1}.min^{-1/2}$	r^2	χ^2
Cd(II)	7.37	0.998	2.045	1.606	0.999	0.026	6.40	0.931	1.179
Pb(II)	16.47	0.958	8.389	0.467	0.999	0.019	14.89	0.869	0.847

Table 2. Langmuir and Freundlich adsorption isotherm constants for Cd(II) and Pb(II) removal

Metal	Langmuir Constants				Freundlich Constants			
	q_{max} (mg g^{-1})	B (L mg^{-1})	r^2	χ^2	K_f	n	r^2	χ^2
Cd(II)	36.23	0.14	0.992	1.184	4.37	1.77	0.994	1.475
Pb(II)	92.51	0.115	0.953	0.676	8.872	1.304	0.998	0.539

Table 3. Thermodynamic parameters for the adsorption of Cd(II) and Pb(II) on clarified sludge

Metal	T (K)	$-\Delta G^0$ (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)	r^2
Cd(II)	303	10.621	-25.741	-0.050	0.928
	313	9.693			
	323	9.632			
Pb(II)	303	11.092	28.384	0.130	0.999
	313	12.369			
	323	13.698			

The values of mass transfer coefficients (β) were 2.514×10^{-5} cm s^{-1} and 4.873×10^{-5} cm s^{-1} with a high value of co-relation co-efficient for the removal of Cd(II) and Pb(II) respectively. Mass transfer coefficients (β) obtained from the study indicate that the velocity of the adsorbate transport from bulk to the solid phase was quite fast.

3.2.5 Determinatin of diffusivity

Kinetic data could be treated by the models given by Boyd et al.[16] which is valid for the experimental conditions used. Diffusion found to be rate controlling in the adsorption of Cd(II) and Pb(II) onto the particles of spherical shape. For the range $0 \le F(t) \le 1$ in the solution of divalent exchangeable ions, Boyd equation can be simplified as [17-19]

$$\ln\left[\frac{1}{1-F^2(t)}\right] = \frac{\pi^2}{R_a^2} D_e t \qquad (9)$$

The value of diffusion co-efficients as calculated from the equation (9) were found to be 2.3×10^{-11} and 1.7×10^{-10} m^2/s for the adsorption of Cd(II) and Pb(II) onto clarified sludge respectively. For the present system, the value of D_e, fall within the values reported in literature, especially for chemisorptions system (10^{-9} to 10^{-17} m^2/s) [20].

3.3 Adsorption isotherms model

The adsorption isotherm for the removal of metal ion was studied using initial concentration of between 10 and 300 mg/L at an adsorbent dosage level of 7.5 g/L for Cd(II) and Pb(II) at 30°C.

3.3.1 Langmuir isotherm model

The Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. The Langmuir adsorption isotherm [21] applied to equilibrium adsorption assuming mono-layer adsorption onto a surface with a finite number of identical sites and is represented as follows,

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \qquad (10)$$

Linear plots of C_e/q_e vs. C_e (Figure 4) were employed to determine the value of q_{max} (mg/g) and b (L/mg).

3.3.2 Freuindlich isotherm model

The Freundlich adsorption isotherm [22] is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor, n. The linear form of Freundlich adsorption isotherm takes the following form

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{11}$$

The Freundlich isotherm constants K_f and n were calculated from Equation (11) and Freundlich plots (Figure 5).

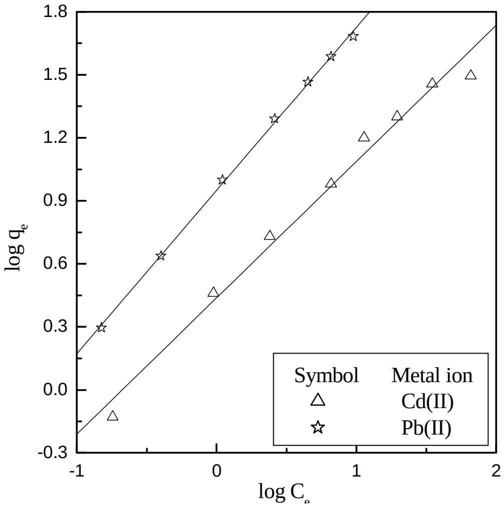

Fig. 5. Freundlich plot for Cd(II) and Pb(II) removal.

From the Table 2, it was seen that for Cd(II) adsorption, χ^2 value of Langmuir is lower than the Freundlich adsorption isotherm model. Therefore uptake of Cd(II) preferably follows the Langnuir adsorption model but it is reverse for the adsorption Pb(II) on clarified sludge.

3.3.3 Dubinin-Radushkevich (D-R) isotherm model

D-R isotherm relates the heterogeneity of energies close to the adsorbent surface. If a very small sub-region of the sorption surface is chosen and assumed to be approximately by the Langmuir isotherm, the quantity, $\sqrt{\lambda}$ can be related to the mean sorption energy, E, which is the free energy for the transfer of 1 mole of metal ions from the infinity to the surface of the adsorbent. The D-R isotherm [23] was employed in the following linear form:

$$\ln C_{abs} = \ln X_m - \lambda\varepsilon^2 \tag{12}$$

The Polanyi potential, ε, can be expressed as,

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \tag{13}$$

A plot of C_{abs} vs ε^2 is shown in Figure 6. Using the calculated value of λ, it is possible to evaluate the mean sorption energy, E, from

$$E = \frac{1}{\sqrt{-2\lambda}} \tag{14}$$

The estimated value of E were11.03 kJ/mol and 9.902 kJ/mol for Cd(II) and Pb(II) adsorption respectively which indicates the process are chemisorptions in nature.

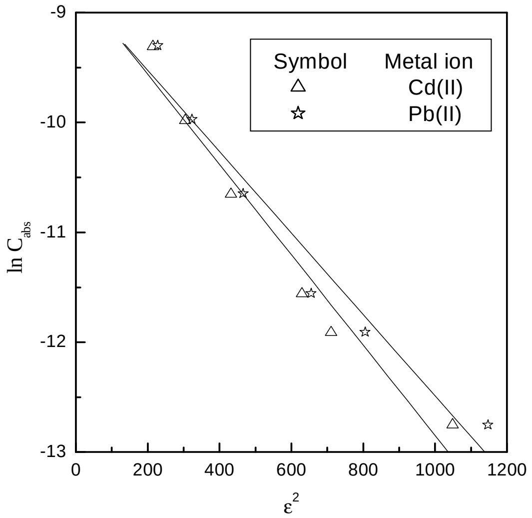

Fig. 6. D-R isotherm for Cd(II) and Pb(II) removal.

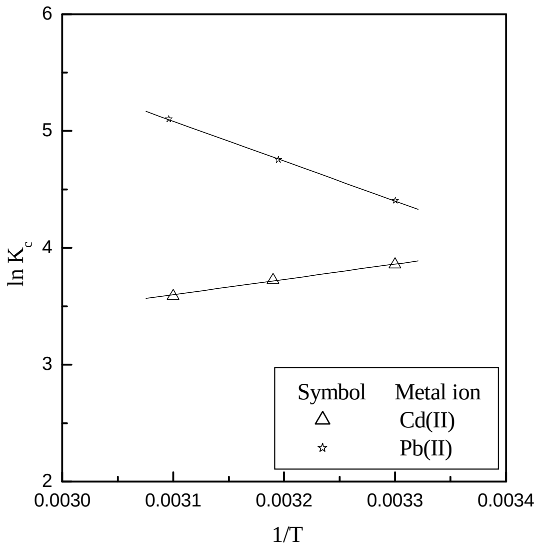

Fig. 7. Determination of thermodynamic parameter.

3.4 Thermodynamic study

The variation in the extent of adsorption with respect to temperature has been explained on the basis of thermodynamic parameters viz. changes in Gibbs free energy, enthalpy and entropy. The dependence on temperature of adsorption of Cd(II) and Pb(II) on the clarified sludge were evaluated using the following equations :

$$\ln K_C = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{15}$$

$$\Delta G^0 = -RT\ln K_C \tag{16}$$

From the slope and intercept of the plot (Figure7), the values of ΔH^0 and ΔS^0 had been computed, while ΔG^0 were calculated using equation (16). The values of these parameters thus calculated are recorded in Table 3.

Table 4. Desorption of Cd(II) and Pb(II) from loaded Clarified sludge

Strength of HCl (M)	% Desorption of Cd(II)	Strength of HNO_3 (M)	% Desorption of Pb(II)
0.01	22.45	0.1	68.90
0.025	26.7	0.25	87.8
0.05	79.82	0.5	98.42
0.075	93.75	0.75	98.43
0.1	98.21	1	98.42
0.125	98.30		
0.15	98.28		

Table 5. Application studies using clarified sludge

Test Parameter	Untreated effluent	Treated Effluent	Untreated effluent	Treated Effluent	Remarks
PH	4.7	5	PH	2.7	--
Conductivity (μmhos/cm)	2760	2735	Conductivity (μmhos/cm)	1737	--
Cd(II) (mg/L)	3.8	0.076	Pb(II) (mg/L)	2.84	Successfully meet the IS 10500 1992 [6] norms of Cd(II) and Pb(II)
Fe (mg/L)	1.06	0.78	Fe (mg/L)	1.2	--
Ca (mg/L)	180	154	Ca (mg/L)	214	--
Mg (mg/L)	48	34	Mg (mg/L)	64	--
Chloride (mg/L)	28	24	Chloride (mg/L)	18	--
TSS (mg/L)	32	27	TSS (mg/L)	26	--

3.5 Desorption studies for Cd(II) and Pb(II) –clarified sludge system

Batch desorption experiments were carried out to further elucidate the mechanism of adsorption. Attempts were made to desorb Cd(II) and Pb(II) from clarified sludge using different concentration of HCl or HNO_3 solution having good potential to dissolve metal ions under study by batch desorption technique maintaining the same conditions similar to batch adsorption studies. The experiments conducted for 2 h and 1 h for Cd(II) and Pb(II) desorption respectively. The results of desorption experiments with various concentrations of HCl or HNO_3 are shown in Table 4.

3.6 Application studies using industrial effluents

Industrial effluent containing Cd(II) and Pb(II) were collected from electroplating unit and battery manufacturing unit located near Kolkata, India. The characteristics of effluent samples were shown in Table 5. Batch adsorption studies were carried out with the collected industrial effluent samples using clarified sludge as metal adsorbent at under under optimum condition as obtained from batch adsorption studies. The final concentration of Cd(II) and Pb(II) fall within the limit of the IS 10500 1992 norms.

4. CONCLUSIONS

In this study, batch adsorption experiments for the removal of Cd(II) and Pb(II) from aqueous solutions have been carried out using clarified sludge

(1) Maximum adsorption of Cd(II) and Pb(II) occurred at pH 5

(2) The experimental data were better described by pseudo 2nd order model as evident from correlation co-efficient (r^2) and χ^2 values for both the metal ions.

(3) The effective diffusion co-efficient of Cd(II) and Pb(II) adsoption process were 2.3×10^{-11} m^2/s and 4.873×10^{-10} m^2/s respectively.

(4) Langmuir adsorption isotherm model was better fitted than Freundlich adsorption isotherm model for Cd(II) but it was reverse for Pb(II) adsorption. The monolayer adsorption capacity were obtained 36.23 mg/g and 92.51 mg/g for Cd(II) and Pb(II) adsorption respectively. (5) Sorption energy for the Cd(II) and Pb(II) were 11.03 kJ/mol and 9.902 kJ/mol respectively which indicated that adsorption process were chemical adsorption in nature.

(6) Thermodynamic parameters studies showed that both Cd(II) and Pb(II) adsorption were spontaneous in

nature. The enthalpy change of the adsorption indicated that process were exothermic for Cd(II) and endothermic for Pb(II) removal.

NOMENCLATURE

B = Langmuir constant ($\mathrm{Lmg^{-1}}$)
C_{abs} = Conc. of metal ion on adsorbent at equilibrium, ($\mathrm{mgL^{-1}}$)
C_e = Conc. of metal ion in solution at equilibrium, ($\mathrm{mgL^{-1}}$)
C_0 = Initial conc. of metal ion in solution, ($\mathrm{mgL^{-1}}$)
C_t = Conc. of metal ion in solution at time t, ($\mathrm{mgL^{-1}}$)
K_2 = Pseudo-second-order rate constant of adsorption [(mg/g) min]
K_{ad} = Lagergren rate constant, ($\mathrm{min^{-1}}$)
K_c = Thermodynamic equilibrium constant
K_f = Measure of adsorption capacity, (mg/g)
K_{id} = Intra-particle rate constant, [(mg/g) $\mathrm{min^{1/2}}$]
K_{bq} = Constant obtained by multiplying q_{max} and b
M = Metal ion in Equation (9)
n = Freundlich constants, intensity of adsorption
q = Amount adsorbed per gm of the adsorbent, (mg/g)
q_e = Amount adsorbed per g of adsorbent at equilibrium, (mg/g)
q_{max} = Maximum adsorption capacity, (mg/g)
q_t = Amount adsorbed per g of adsorbent at time t
r^2 = Correlation coefficient
S_s = External surface area of adsorbent per unit volume, ($\mathrm{m^{-1}}$)
D_e = Diffusion coefficient ($\mathrm{m^2/s}$)
t = Time, (min.)
F(t) = Amount adsorbed per g of adsorbent at time/amount adsorbed per g of adsorbent at equilibrium
X_m = Maximum adsorption capacity, (mmol/g)
E = Mean sorption energy, (kJ /mol)
ΔG^0 = Gibbs free energy, ($\mathrm{kJmol^{-1}}$)
ΔH^0 = Heat of adsorption, ($\mathrm{kJmol^{-1}}$)
ΔS^0 = Entropy of adsorption, ($\mathrm{kJK^{-1}mol^{-1}}$)

Greek letter

β = mass transfer coefficient, (m/s)
λ = constant related to energy ($\mathrm{mol^2/kJ^2}$)
ε = Polanyi potential ($\mathrm{kJ^2/mol^2}$)

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