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SIMULTANEOUS REMOVAL OF LEAD AND CADMIUM IONS FROM AQUEOUS SOLUTIONS USING CERAMIC INDUCTRY WASTE AS AN ADSORBENT

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ABSTRACT

In the present research work, a comparative potentiality ofceramic industry wastefor the removal of Pb(II) and Cd(II) has been investigated. Batch method had been employed to studied the effects of various adsorption controlling parameters such as contact time (5 - 120 min.), pH (1 - 10) of solution, metal ions concentration (10 - 200 mgL^{-1}) and adsorbent dose (0.1 - 1.0 g) on adsorption of Pb(II) and Cd(II) ions from aqueous solutions. The optimum set of conditions for maximum adsorption of Pb(II) ions (96.32%) were found to be initial concentration 50 mgL^{-1}, dosage 0.5 g and pH 4 and while at the same concentration and dosage the maximum removal of Cd(II) ions was found to be 52.3 % at pH 6. Ceramic industry waste showed better adsorption capacity for lead (11.9 mg/g) than cadmium (2.34 mg/g). The experimental data was agreed with almost all isotherm models applied but best fitted to Langmuir models as indicated by high values of correlation coefficient for lead (R^2 = 0.9917) and cadmium (R^2= 0.971). The Langmuir monolayer adsorption capacity for Pb(II) and Cd(II) was found to be 12.210 mg/g and 5.476 mg/g, respectively. Kinetic data of both Pb(II) and Cd(II) were best fitted to Pseudo- second order model. Thus ceramic industry waste have greater adsorption capacity for Pb(II) than Cd(II) and can be employed as efficient adsorbent for treatment of lead and cadmium contaminated wastewaters.

Key words: Adsorption, batch process, ceramic industry waste, Freundlich, Langmuir, monolayer and kinetics

I. INTRODUCTION

Water contaminated with metallic effluent can cause several health problems. The release of these heavy metals poses a significant threat to the environment and public health because of their toxicity and bioaccumulation in the food chain and persistent in nature [1]. The heavy metals such as cadmium, chromium, lead and copper are the most common pollutants found in industrial effluents [2, 3] which are extremely toxic in relatively low dosages. Lead for instance, can interfere with enzymes activities and formation of RBCs. It is extremely toxic to the nervous system, kidney and reproductive system. Higher doses may damage the foetus [4, 5]. Cadmium

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being one of the most toxic elements, even at low concentration in the food chain has been found to cause itai-itai disease killing scores of population in Japan. Its exposure causes renal dysfunction, bone degeneration, liver and blood damage. It has been reported that there is sufficient evidence for the carcinogenicity of cadmium [6]. In order to improve the quality of treated effluent before it is released in to the environment, a number of physicochemical methods have been used such as reduction and precipitation [7], coagulation, flotation [8], adsorption on activated carbon [9, 10], ion exchange, reverse osmosis and electro-dialysis [11]. Many of them are restricted due to their disadvantage and economic constraints like generation of the sludge in the precipitation method poses challenges in handling, treating and land-filling of the solid sludge [12]. Therefore, there is a need for the development of a low cost process to remove heavy metals economically.Adsorption has been developed as an effective and economic method to treat wastewater containing low concentrations of metal pollutants. Compared with conventional treatment methods, adsorption has advantages such as high efficiency and selectivity for absorbing heavy metals, energy-saving, easy reclamation of heavy metal, and easy recycling of the sorbent [13]. This study is designed to examine comparative potentiality of roasted china clay for the removal of cadmium and lead from aqueous solution. Attempts has been made to investigate the comparative effect of pH, metal ion concentration, sorbent dose and contact time of roasted china clay on the removal of Pb(II) and Cd(II) from aqueous solutions. The pseudo first-order and pseudo second-order were studied to analyze the kinetic data. The experimental data was also compared with Langmuir, Freundlich and Temkin isotherms.

II. MATERIALS AND METHODS

2.1 Preparation of adsorbent

Khurja, U.P, India, a town famous for its glazed ceramic industries. The ceramic powder is converted into a semi-solid paste called ceramic slurry which is in turn moulded into various shapes to manufacture different articles. The ceramic slurry exhibits excellent binding property after heating. The moulded articles are dried and heated in a roasting furnace to provide rigidity, this process is called Firing. But during the process of Firing, some of the articles breaks or gets deshaped which are thrown away as waste. This thrown away waste known as roasted china clay (RCC) were collected and brought to the laboratory. RCC was washed, dried and grinded to fine particles to be used as adsorbent to remove metal ions from synthetic waste water.

2.2 BATCH ADSORPTION STUDIES

Adsorption studies were carried out by batch process at room temperature. An accurately weighed 0.5 gm of adsorbent was placed in 100 ml stoppered conical flask containing known volume (50 ml) of metal ions solution of known concentration (50 mg/L). This solution was shaken in a rotary shaker for predetermined time interval to attain equilibrium with intermittent manual shaking. All the operations were conducted with 50 ml solutions of 50 mg/L metal ion concentration except during the study of effect of concentration in which 10 to 200 mg/L metal ion concentration solutions were used. The solutions were filtered to separate the adsorbent from supernatant liquid. The residual concentration of metal ions was determined by Atomic Absorption Spectrophotometer model GBC 902 using air Acetylene flame. The effect of pH on the efficiency of adsorption

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of Pb(II) and Cd(II) was verified by varying pH of adsorbate solution from 1 to 10. The contact time was varied between 5 to 120 minutes to study the effect of time on adsorption and adsorbent dosage was taken from 0.1 g to 1 g to get ratio of adsorbate to adsorbent.

The adsorption percentage (R%) of metal ions and adsorption capacity or amount of metal ions adsorbed per unit mass of adsorbent (q_e) were calculated for each run by the following expressions:

$$R\% = \frac{(Ci - Ce)}{Ci} X\ 100$$

$$q_e = \frac{(Ci - Ce)}{m} X\ V$$

where C_i is the initial metal ions concentration, C_e is the final metal ions concentration (in mg/L), V is the volume of the solution (in liter) and m is mass of the adsorbent (in g).

2.3 Adsorption isotherm models

Adsorption isotherm indicates how the adsorbed molecules distribute between the liquid and solid phase when adsorption reaches an equilibrium state [14, 15]. The adsorption capacity of RCC for Cd(II) and Pb(II) was investigated using Langmuir and Freundlich adsorption isotherms.

Langmuir isotherm assumes that the uptake of metal ions occurs on the homogeneous surface of the adsorbent by monolayer adsorption without any interaction between adsorbed metal ions [16]. The linearized form of Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = 1/q_m \times 1/b + C_e/q_m$$

Where, q_e is the amount of metal ions adsorbed per unit mass of the adsorbent (mg/g) at equilibrium, C_e is the concentration of metal ions solution (mg/L) at equilibrium, q_m is the quantity of metal ions required for a single monolayer on the unit mass of adsorbent (mg/g), b is a Langmuir constant related to the bonding energy of adsorption and monolayer adsorption capacity of adsorbent (mg/g), respectively.

A further analysis of Langmuir equation can be made on the basis of a dimensionless equilibrium parameter R_L which can be expressed by the equation given below:

$$R_L = 1/ (1 + b \times C_i)$$

where, b is the Langmuir constant, C_i is the initial metal ion concentration (mg/L), R_L is the dimensionless equilibrium parameter. The value of R_L provides important information about the nature of adsorption. It indicated the shape of Langmuir isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L > 1$), linear ($R_L = 1$) or unfavourable ($R_L < 1$).

The Freundlich isotherm equation is an empirical equation which is one among the most widely used equation to describe the adsorption which takes place on a heterogeneous surface through a multilayer mechanism [17]. The linear form of the Freundlich adsorption isotherm equation is expressed as:

$$\log q_e = \log K_f + 1/n \log C_e$$

where, C_e is the equilibrium concentration of metal ions (mg/L), q_e is the amount of metal ions adsorbed per unit weight of the adsorbent (mg/g), K_f is a Freundlich constant which indicates the relative adsorption capacity of the adsorbent related to bonding energy and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient.

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2.4 Adsorption kinetic models

The evaluation of kinetic models is an important aspect for designing and optimization of water and wastewater treatment process. The kinetic data was analysed by using the pseudo first-order kinetic model express by Lagergren [18]; [19] and pseudo second order kinetic model [20].

The pseudo first-order kinetic equation given by Lagergren was widely used for the adsorption of liquid/solid system on the basis of solid capacity is represented as:

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303$$

where k_1 is the Lagergren rate constant for adsorption (min^{-1}), q_e is the amount of metal adsorbed at equilibrium (mg/g), q_t is the amount of metal adsorbed (mg/g) at any time t.

Pseudo second order kinetic model suggests during adsorption metal ions react chemically with the specific binding sites on the surface of adsorbent.The equation of pseudo second order model is expressed as:

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t$$

where k_2 is the equilibrium rate constant of second order model (g mg^{-1} min^{-1}), q_e is the amount of metal adsorbed at equilibrium (mg/g), q_t is the amount of metal adsorbed (mg/g) at any time t.

III. RESULTS AND DISCUSSION

3.1 Batch Studies

3.1.1 Effect of metal ion concentration

The effect of initial metal ion concentration ranging from 10 to 200 mg/L on the adsorption of Cd(II) and Pb(II) on 0.5 g adsorbent is shown in Fig. 1. It was observed that the amount of metal adsorbed per gram of adsorbent increased while adsorption percentage decreased with the increase of initial metal ion concentration. The Fig. 1 reveals that adsorption efficiency (%) decreased from 98.36 – 26.45% and 100 – 59.2% while adsorption capacity (mg/g) was found to increase from 0.984 – 5.29, and 1 – 11.84 mg/g for the removal of Cd(II) and Pb(II), respectively.

3.1.2 Effect of pH

Solution pH has been identified as the most important factor governing metal adsorption. The pH can of solution influence the surface charge of the adsorbent, the degree of ionization and the species of adsorbate ions. Effect of pH on adsorption of Cd(II) and Pb(II) is shown in Fig. 2. The adsorption of Pb(II) ions was increased to maximum of 96.32% at pH 4 and remain almost constant upto pH 8. But further rise in pH results in decrease of adsorption efficiency of adsorbentdrastically. In case Cd(II) ions results was consistent as increase in pH results in increase of Cd(II) ions uptake slowly and reaches maximum of 52.3% at pH 6 and then no appreciable change was observed in adsorption of cadmium ions. At lower pH, adsorption efficiency was found to be very low which might be due to the competition of protons for active adsorption sites on adsorbent while at higher pH decrease in adsorption capacity of adsorbentmight be due to the precipitation of metal ions in the solutions.

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3.1.3 Effect of contact time

Adsorption of metal ions depends on the interaction of functional groups between the solutions and surface of adsorbent. The effect of contact time on adsorption of Cd(II) and Pb(II) by adsorbent is shown in Fig. 3. The metal uptake was rapid for all metal ions in first 30 minutes, accounting 49.7% and 67.5% of adsorption for Cd(II) and Pb(II), respectively and no appreciable changes in terms of metal ions removal was observed after 120 minutes. The maximum adsorption efficiency and equilibrium contact time was found to be 52.3% and 96.32% and 120 min, respectively for Cd(II) and Pb(II).

3.1.4 Effect of dose

The effect of dose of adsorbenton adsorption efficiency of Cd(II) and Pb(II) is shown in Fig. 4. It was observed that adsorption percent of all metal ions increased rapidly with an increase in the amount of adsorbent dose due to the availability of greater surface area on increasing concentration of adsorbent. Adsorption percentage was found to increase from 9.36 to 66.37 % and 47.64 to 99.45 % for Cd(II) and Pb(II), respectively. The metal ion removal capacity of adsorbent decreased from 2.34 to 1.65 mg/g for Cd(II) and 11.91 to 2.49 mg/g for Pb(II) on increasing the adsorbent dose from 2 mg/ml to 20 mg/ml. This might be due to the fact that at lower adsorbent dose almost all the adsorption sites are saturated by the metal ions but at higher adsorbent dose, the adsorption sites would be excessive for the adsorption since the concentration metal ions as well as the volume of the solution are constant. Thus, amount of Cd(II) and Pb(II) ions adsorbed per unit mass of adsorbent was decreased [21].

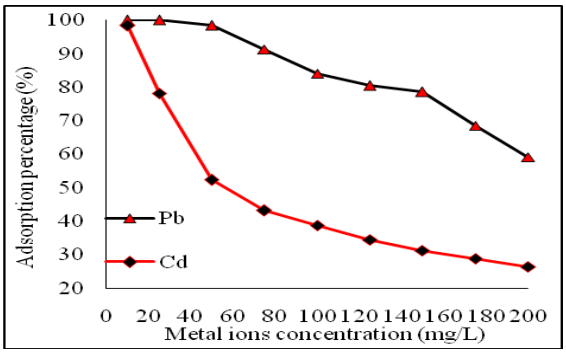

Fig. 1 Effect of metal ion concentration

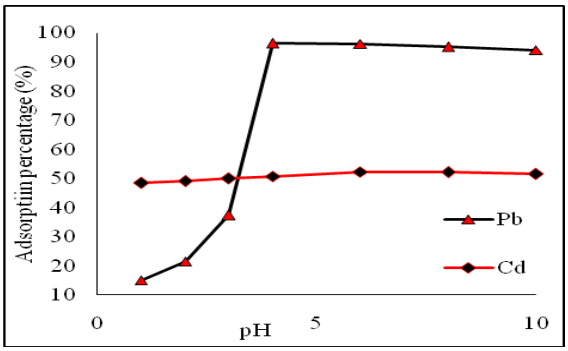

Fig. 2 Effect of solution pH

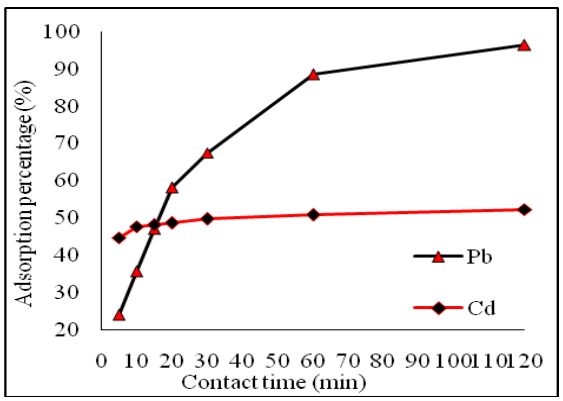

Fig. 3 Effect of contact time

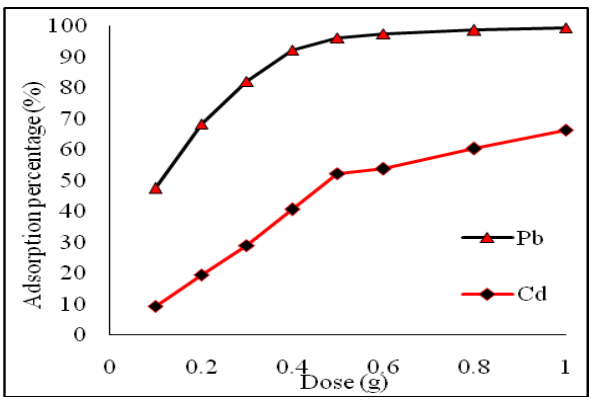

Fig. 4 Effect of adsorbent dose

3.2 Adsorption Isotherm Studies

The values of constants and regression coefficients (R^2) for Langmuir and Freundlich isotherms were calculated from slopes and intercepts of their linear plots shown in Fig. 5 and 6 are listed in table 1. The Langmuir plot of C_e/q_e vs $C_e$for Cd(II) and Pb(II) shown in Fig. 5 reveals that obtained experimental data of Pb(II) and Cd(II) were show better applicability as indicated by high values of correlation coefficient (R^2 = 0.9917). The monolayer adsorption capacity (q_m) of adsorbent for lead and cadmium was found to be 12.210 mg/g and 5.476 mg/g ions. Moreover the value of R_L was found to be 0.233 and 0.075 for Cd(II) and Pb(II), respectively indicated that the adsorption is favourable. The values of n, K_F and R^2 for Freundlich isotherm were calculated from the plot of log q_e vs log C_e shown in Fig. 6 and mentioned in table 1. The value of n for both Pb(II) and Cd(II) is greater than 1, this indicated that adsorption of Pb(II) and Cd(II) on adsorbent is the physical process. The value of K_F for Pb(II) and Cd(II) was found to be 1.6233 mg/g and 1.4210 mg/g, respectively. The value of 1/n for both metal ions lies between 0 and 1 indicated favourable adsorption.

Table: 1 Langmuir and Fruendlich constants for adsorption of Cd(II) and Pb(II)

Metal	Langmuir isotherm				Freundlich Isotherm			
	q_m(mg/g)	b (L/mg)	R_L	R^2	1/n	n	K_F(mg/g)	R^2
Pb^{+2}	12.210	0.338	0.075	0.991	0.537	1.86	1.623	0.826
Cd^{+2}	5.476	0.074	0.233	0.971	0.257	3.88	1.42	0.969

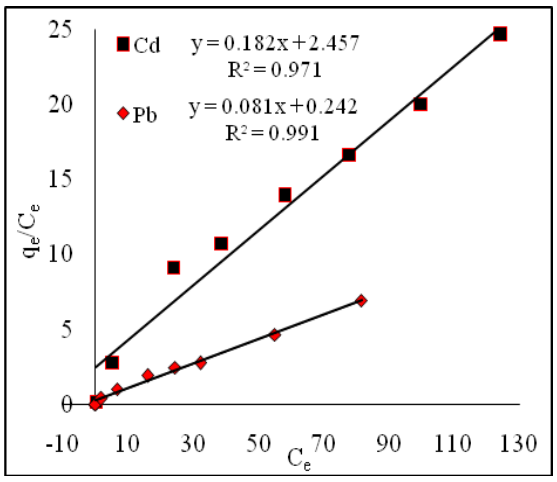

Fig. 5 Langmuir isotherm model

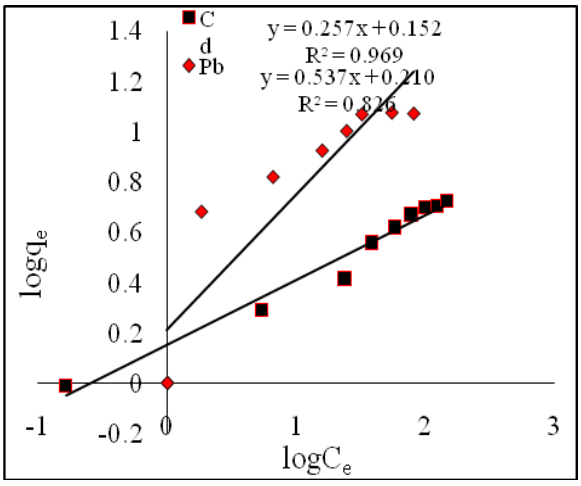

Fig. 6Freundlich isotherm model

3.3 Adsorption Kinetics Studies

The values of correlation coefficients and other kinetic parameters for pseudo first order and pseudo second order models were calculated from slopes and intercepts of their plots of log (q_e - q_t) vs t and t/q_t vs t shown in Fig. 7 and 8, respectively and listed in table 2. The high values of R^2 for pseudo second order comparing to other kinetic models for both Cd(II) and Pb(II) ions indicate the better applicability of this model. The values of R^2 for pseudo first order ($R^2 \approx 0.997$) and second order ($R^2 \approx 0.998$) was found to be quite high for experimental data obtained for Pb(II) than Cd(II), suggested that adsorption of Pb(II) ions on adsorbent fitted to both kinetic models more closely than Cd(II). This indicated the better applicability of adsorbent for the removal of Pb(II)

ions over other metal ions from wastewater. The value of adsorption capacity, q_e of adsorbent for Pb(II) and Cd(II) ions was found to be 5.659 mg/g and 3.425 mg/g, respectively. Thus ceramic industry waste has good adsorption capacity for Pb(II) than Cd(II).

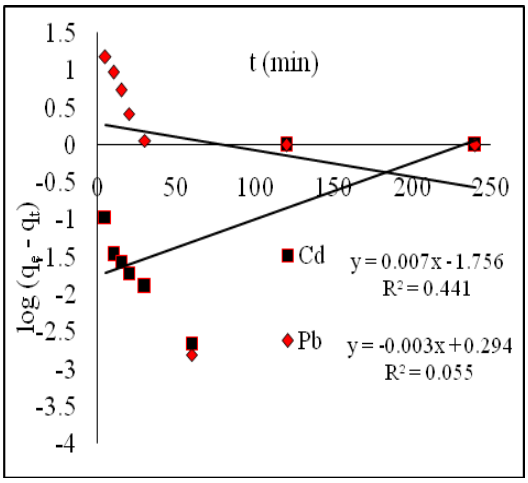

Fig. 7 Pseudo first order model

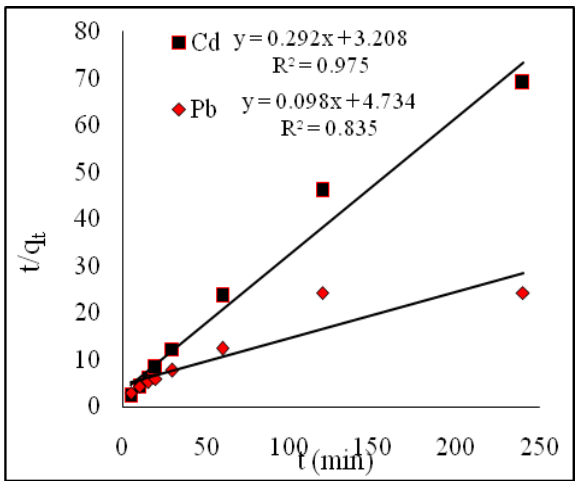

Fig. 8 Pseudo second order model

Table: 2 Pseudo first and second order constants for adsorption of Pb(II) and Cd(II)

Metal Ions	Pseudo first order			Pseudo second order		
	q_e	K_1	R^2	q_e	K_2	R^2
Pb^{+2}	31.681	0.0926	0.997	5.659	0.0089	0.998
Cd^{+2}	0.0175	-0.0175	0.4417	3.425	0.0266	0.9754

IV. CONCLUSION

Comparative study of adsorption capacity of an adsorbent for the removal of different heavy metals is always helpful in designing an economic and efficient wastewater treatment system. Comparative metal ions removal capacities of ceramic industry waste for Cd(II) and Pb(II) were studied found in order of Pb(II) >Cd(II). Investigations also found that adsorption of both metals ions used were quite fast and reaches to their maximum in a very short period of time. The maximum removal was found to be 96.32% in 2 hours and 52.3% in 2 hours for Pb(II) and Cd(II), respectively. Both Langmuir and Freundlich isotherm model were found fit very well for data of both metal ions. The monolayer adsorption capacity for Pb(II) and Cd(II) was observed, 12.210 mg/g and 5.476 mg/g, respectively. Furthermore, value of R_L for adsorption of both metal ions on adsorbent lies between 0 and 1 indicated that adsorption is favourable. Kinetics of adsorption was described by pseudo second order model more successfully than pseudo first order. Thus, investigations reveals that ceramic industry waste is a potential and economically feasible adsorbent and can remove Pb(II) and Cd(II) from their aqueous solutions. Desorption of metal ions and recovery of adsorbent was not conducted as adsorbent is available free of cost in bulk and can be disposed easily after use without causing any harm to the natural environment.

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