

INVESTIGATIONS OF ADSORPTION BEHAVIOUR OF LEAD ON LOW COST ADSORBENT THROUGH EQUILIBRIUM AND KINETICS STUDIES

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ABSTRACT

Roasted china clay (RCC) was successfully employed to remove lead from aqueous solutions through batch process. The optimum contact time and pH for the maximum removal of lead (96.7 %) was 60 minutes and 4, respectively. The equilibrium data was analysed by the Langmuir and Freundlich isotherms. The value of correlation coefficient, $R^2 = 0.966$ for Langmuir isotherm indicates that adsorption of Pb(II) on RCC obey Langmuir isotherm more appropriately than Freundlich. The kinetic studies revealed that adsorption of lead by RCC followed both first and second order kinetics. These results suggested that RCC is a potential, cost free and environment friendly adsorbent which can be effectively used to remove heavy metals in aqueous system.

Keywords: *Adsorption, batch process, Freundlich, Langmuir, intra-particle diffusion, Pseudo-first order, Roasted china clay (RCC) and second order.*

I. INTRODUCTION

Heavy metals are non-biodegradable and tend to accumulate in human body causing various disorders [1]. Lead as a pollutant is a major concern as it has been used as one of the raw materials for battery manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing. It is highly toxic metal and as a result of related health concern as its presence in drinking water even at low concentration may cause disease such as anaemia, hepatitis and nephritic syndrome. According to the United States Environmental protection Agency (USEPA) the maximum permissible limits in wastewater and potable water are 0.1 mg/L and 0.015 mg/L respectively for lead (II) [2]. Therefore, it becomes necessary to remove these lead from wastewater by as appropriate treatment before releasing them into the environment [3].

Many conventional techniques have been used to reduce the concentration of heavy metals present in wastewater but adsorption was found to be superior both in terms of cost and efficiency of the process. In this context many researchers used number of clay based adsorbents to remove heavy metals from aqueous systems. Among them gyttja (which has multilayer coal deposits with clay and calcareous gyttja partings) [4], pottery glaze [5], natural kaolinite clay [6], natural bentonite [7] have recently been reported. In the present study potential of roasted china clay has been investigated to remove lead from aqueous solutions.

II. MATERIALS AND METHODS

2.1 Collection and preparation of adsorbent

Roasted china clay is obtained as waste when moulded ceramic articles broken down or get deshaped during heating in the furnace. These broken or deshaped articles were collected, grinded into fine particles and sieved through 300 μ mesh size and used as adsorbent for Pb(II) ions uptake from aqueous solution.

2.2 Batch studies

The adsorption of lead ions on to RCC was studied at room temperature by batch process by varying pH, contact time, adsorbent dose and adsorbate concentration. 0.5 gm RCC was taken in 100ml conical flask containing 50 ml of Pb(II) ions solution of concentration 50 mg/L at optimum pH. These solutions were shaken in a rotary shaker for prerequisite time interval to attain equilibrium. The effect of pH on the efficiency of adsorption of Pb(II) was verified by varying pH of adsorbate solution from 1 to 10 and initial concentration was varied from 10 to 200 mg/L to observed the effect of adsorbate concentration on lead ions uptake. 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. After that the mixture was filtered and final concentration of lead ions in the filtrate was analysed by AAS.

The removal percentage (R%) of Pb(II) ions and Adsorption capacity, q_e (mg/g) adsorbent were calculated for each run by the following expression-

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100$$

$$q_e = \frac{(C_i - C_e)}{m} \times V$$

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

III. RESULTS AND DISCUSSION

3.1 Batch studies

3.1.1 Effect of pH

The lead ions uptake is greatly affected by the pH of the solution. The amount of Pb(II) adsorbed at different pH values is shown in "Fig. 1". The amount of Pb(II) adsorbed on RCC was found to increase from 13.2 % to 97.6 % by increasing pH from 1 to 4 and then decrease slightly. At pH 1 there is competition between H^+ ions and Pb(II) ions for binding sites of adsorbent, therefore the adsorption of Pb(II) ions was least (13.2%). When the initial pH of the solution increases to 2 the adsorption percentage increases to 21.5%, possibly due to little less competition of Pb(II) ions and H^+ ions. However, when initial pH raised to 4 the adsorption of Pb(II) increased up to maximum of 96.7 % and will remain almost same when the initial pH adjusted to 6 as a result of maximum adsorption of Pb^{2+} ions along with H^+ ions. Further increase in pH of the solution to 8 and 10 results slightly decrease in the adsorption of Pb(II) ions to 95.1 and 94.1 %, respectively.

3.1.2 Effects of time

The adsorption of lead ions increases with contact time till the equilibrium is attained as shown in "Fig 2". In the beginning, adsorption of Pb(II) was found to be fast which may be due to the presence more number of active

sites on the adsorbent surface. But as the number of active sites becomes less available, the adsorption is likely to become slower and become almost constant and thus attained equilibrium within 60 minutes [8].

3.1.3 Effects of dose

The effect of dose of RCC on adsorption capacity and percentage adsorption of Pb(II) is shown in “Fig. 3”. Percent adsorption increased up to 99.6 % while adsorption capacity, q_e (mgg^{-1}) decreased from 10.9 mg/g to 2.49 mg/g when adsorbent dose increased from 0.1 to 1.0 g. The increase in adsorption percent might be due to the fact that on increasing the adsorption dose, number of sites available for adsorption also increased [9]. The decrease in adsorption capacity with an increasing adsorbent dose might be due to the fact that at lower adsorbent dose almost all the adsorption sites are saturated by the Pb(II) uptake but at higher adsorbent dose, the adsorption sites would be excessive for the adsorption reaction [10].

3.1.4 Effects of initial Pb(II) ion concentration

The Adsorption of Pb(II) is highly dependent on the initial concentration of metal ions. It was observed that removal efficiency of lead ions decreases from 100 % to 69.5 % while adsorption capacity q_e , increases from 1 mg/g to 13.9 mg/g with increase in initial concentration of lead ions from 10 mgL^{-1} to 200 mgL^{-1} as shown in “Fig. 4”. The decrease in removal efficiency may be due to the presence of limited number of active sites, which become saturated at a certain concentration [11]. The increase in adsorption capacity may be due to increased concentration gradient between the bulk solution and adsorbent surface which lower down the resistance to mass transfer of Pb(II) from aqueous to solid phase [12].

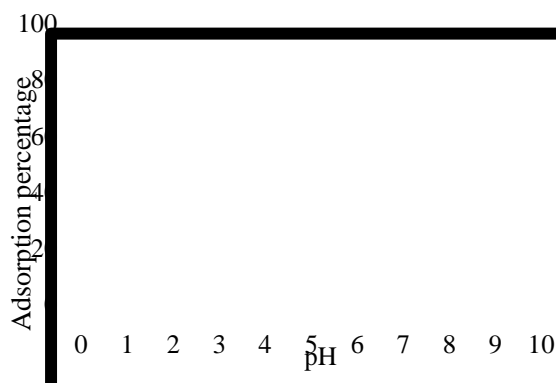


Fig. 1 Effect of pH on adsorption of Pb(II) on RCC

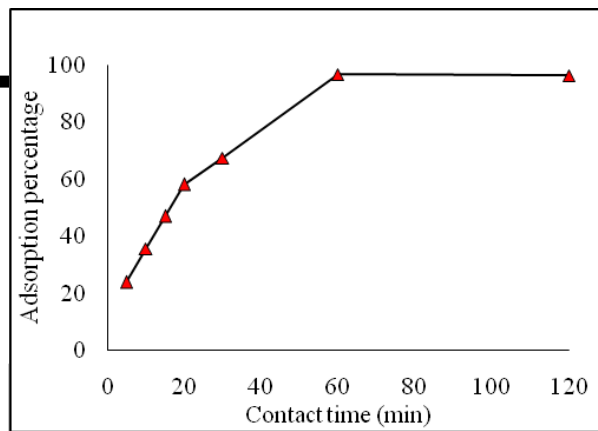


Fig. 2 Effect of contact time on adsorption of Pb(II)

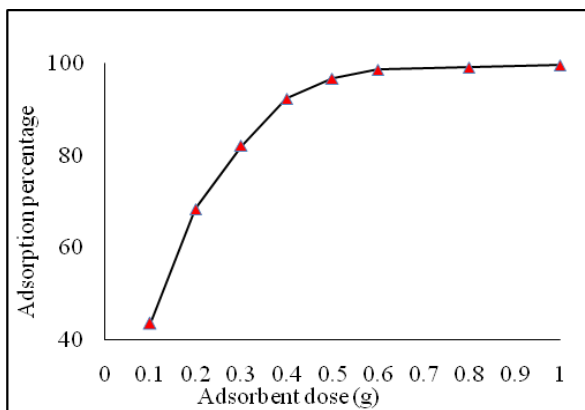


Fig. 3 Effect of dose on adsorption of Pb(II) on RCC

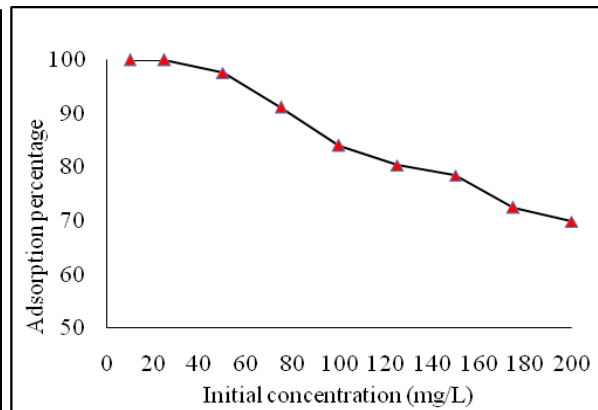


Fig.4 Effect of concentration on adsorption of Pb(II)

IV. ADSORPTION ISOTHERMS

Adsorption isotherms were studied to indicate how adsorbate molecules are partitioned between the adsorbent and liquid phase at equilibrium as a function of adsorbate concentration. The obtained data were analysed with the Langmuir and Freundlich isotherms.

According to Langmuir model the adsorption occurs on a homogeneous surface forming monolayer of adsorbate with constant heat of adsorption for all sites without interaction between adsorbed molecules. It can be represented by the equation:

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

where, C_e is the equilibrium concentration of adsorbate (mg/l), q_e is the adsorption capacity (mg/g), b and q_m are the Langmuir constants. The q_m is the amount of lead required to form monolayer (mg/g), and b is the constant related to energy of adsorption. The value of b and q_m can be calculated from the slope and intercept of the linear plot of C_e/q_e vs C_e as shown in “Fig. 5”.

The Freundlich equation has been used for the adsorption of lead on RCC is represented as-

$$\text{Log } q_e = \text{log } K_f + 1/n \text{ log } C_e$$

where, q_e is the amount of lead adsorbed, C_e is the equilibrium concentration of the lead ions in the solution (mg/L), and K_f and n are the constants for adsorption capacity and intensity of adsorption respectively. Plots of $\text{log } q_e$ vs. $\text{log } C_e$ has been shown in “Fig.6” and the values of K_f and n was calculated from slopes and intercepts of the plot.

The values of R^2 indicated that the adsorption of Pb(II) onto RCC was best fitted to Langmuir isotherm model with highest value of correlation coefficient $R^2=0.966$. The monolayer adsorption capacity (q_m) of Pb(II) ions on RCC is found to be 13.81 mg/g which is higher than number of clay based adsorbent reported. The Freundlich parameters, K_f , n and R^2 were calculated from slopes and intercepts of plot of $\text{log } C_e$ vs $\text{log } q_e$. The value of n indicated the degree of linearity between solution concentration and adsorption. If $n = 1$, then adsorption is linear, if $n < 1$, then adsorption is chemical process and if $n > 1$, then adsorption is a physical process. Since the value of n was found to be 2.88 ($n > 1$), this indicated that the lead ions on RCC are adsorbed by physical process. Thus, adsorption of Pb(II) ions occurs on heterogeneous surface of RCC through physical process by formation of monolayer followed by multilayer formation with uniform heat of adsorption [13, 14].

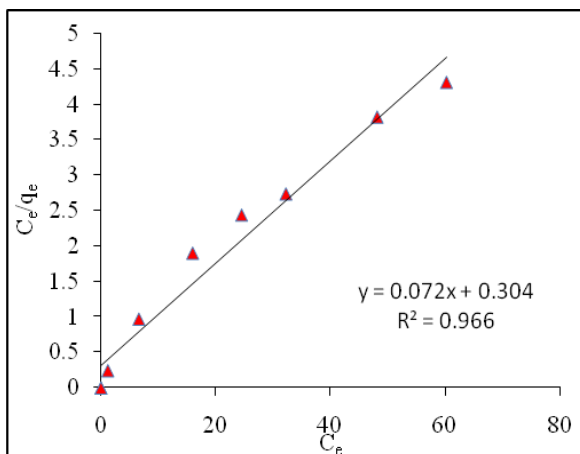


Fig. 5 Langmuir adsorption isotherm

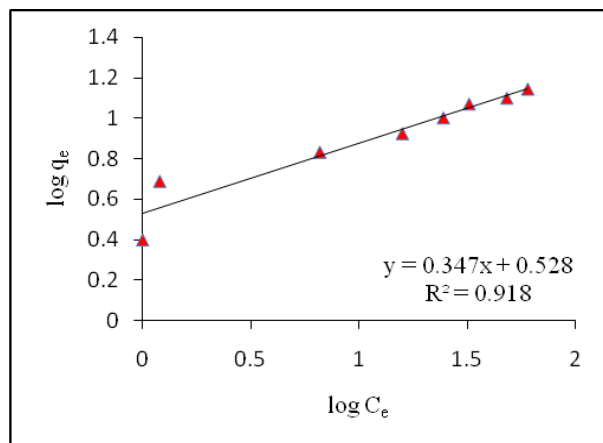


Fig. 6 Freundlich adsorption isotherm

V. ADSORPTION KINETIC STUDIES

In order to investigate the mechanism of adsorption of Pb(II) on RCC, the kinetic data was analysed using the Lagergren first order and pseudo second order.

The Lagergren first order rate equation is represented as :

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Or

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

where, q_e and q_t are the amounts of Pb(II) adsorbed (mg g^{-1}) at equilibrium and at time t , respectively. k_1 is the Lagergren rate constant (min^{-1}). Plots of $\ln (q_e - q_t)$ versus t has been shown in “Fig. 7” and values of q_e and k_1 have been calculated from the slope and intercept respectively.

The adsorption data have been applied to pseudo second-order kinetic model also. The equation is represented as:

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

where, K_2 (g/mg/min) is the rate constant of second order adsorption and can be obtained from plot of t/q_t against t which has been shown in “Fig. 8”

All kinetic data and comparative values of correlation coefficient for pseudo first order and pseudo second order kinetic models verifies that kinetic data is fitted for to both pseudo first and pseudo second order model as indicated by highest value of correlation coefficient, $R^2 = 0.997$ and $R^2 = 0.998$, respectively. The adsorption capacity, q_e (mg/g) is from first order kinetics is quite high indicated that RCC is a potential adsorbent for the removal of lead ions. Applicability of pseudo first and pseudo second order model implies that adsorption of Pb(II) on RCC involves the formation of one layer of molecules on the surface of adsorbent by physical adsorption and may be followed by additional layer of chemically adsorbed molecules [15].

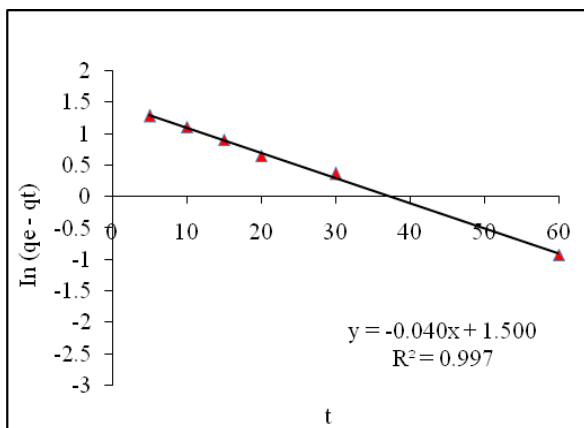


Fig. 7 Pseudo first order model

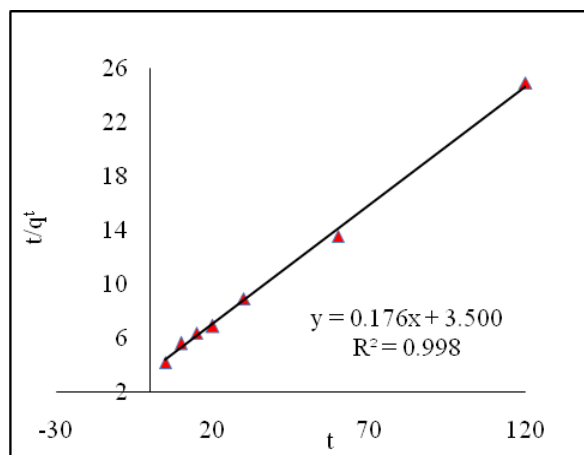


Fig. 8 Pseudo second order model

VI. CONCLUSION

The batch studies showed that RCC is a potential low cost and frequently available adsorbent can be used to remove Pb(II) ions from aqueous solution. Adsorption of lead on RCC is a fast process as equilibrium was established within 60 minutes. Adsorption of Pb(II) is a pH dependent and maximum amount of Pb(II) (96.7 %)

can be removed from aqueous solution at pH ranging 4-6 at concentration 50 mg/L. The experimental data is best fitted to Langmuir isotherm as indicated by the highest value of correlation coefficient ($R^2 = 0.966$). Kinetic data also suggest the applicability of both pseudo first and pseudo second order model as indicated by the values of correlation coefficients ($R^2 = 0.997$ and 0.998) which also confirms that adsorption of Pb(II) on RCC involve physical process followed by the chemisorption of adsorbate molecules. It may be concluded from the above results that RCC can be employed as potential adsorbent for the elimination of Pb(II) ions from aqueous solution since it is available free of cost in bulk.

VI. ACKNOWLEDGEMENT

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