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P Venugopalan
Sree Neelakanta Government Sanskrit College Pattambi, Palakkad, Kerala State, India 679306

N U Aswathy Unnikrishnan
Sree Neelakanta Government Sanskrit College Pattambi, Palakkad, Kerala State, India 679306

Correspondence
P Venugopalan
Sree Neelakanta Government Sanskrit College Pattambi, Palakkad, Kerala State, India 679306

Curcuminoids– a potent sorbent for the removal of lead (II) ions from aqueous solution

P Venugopalan, NU Aswathy Unnikrishnan

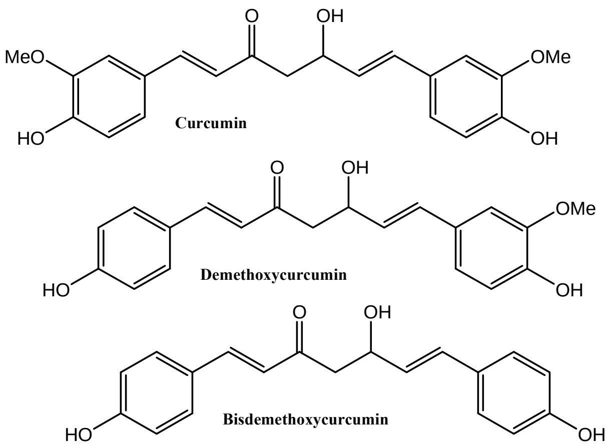
Abstract
The adsorption behaviour of turmeric with respect to Pb^{2+} has been studied in order to consider its application to the removal of Pb^{2+} from lead contaminated water samples. The batch method was employed and adsorption parameters were determined using both Langmuir and Freundlich isotherms. The results showed that turmeric is a potent adsorbent to remove lead (II) species from lead contaminated water samples.

Keywords: Curcuminoids, turmeric, sorbent, lead (II), Langmuir isotherm, Freundlich isotherm

1. Introduction

Contamination of water with lead (II) ions is a large environmental concern associated with the increasing of industrial processes which discharge aqueous effluents containing lead (II) ions. Lead (II) ions are not biodegradable and tend accumulate in living organisms, causing various health problems [1-4]. Classically, "lead poisoning" or "lead intoxication" has been defined as exposure to high levels of lead typically associated with severe health effects. Poisoning is a pattern of symptoms that occur with toxic effects from mid to high levels of exposure; toxicity is a wider spectrum of effects, including subclinical ones (those that do not cause symptoms). However, professionals often use "lead poisoning" and "lead toxicity" interchangeably, and official sources do not always restrict the use of "lead poisoning" to refer only to symptomatic effects of lead. The amount of lead in the blood and tissues, as well as the time course of exposure, determines toxicity. Lead poisoning may be acute (from intense exposure of short duration) or chronic (from repeat low-level exposure over a prolonged period), but the latter is much more common. Diagnosis and treatment of lead exposure are based on blood lead level (the amount of lead in the blood), measured in micrograms of lead per decilitre of blood (μg/dL).The World Health Organization state that a blood lead level of 10 ug/dL or above is a cause for concern; however, lead may impair development and have harmful health effects even at lower levels, and there is no known safe exposure level. Authorities such as the American Academy of Paediatrics define lead poisoning as lead levels in blood higher than 10 μg/dL [2, 3]. Lead form variety of compounds and exists in the environment in various forms. Features of poisoning differ depending on whether the agent is an organic compound (one that contains carbon), or an inorganic one. Organic lead poisoning is now very rare, because countries across the world have phased out the use of organic lead compounds as gasoline additives, but such compounds are still used in industrial sector. Organic lead compounds, which cross the skin and respiratory tract easily, affect the central nervous system predominantly. There are many conventional processes for the removal of lead and the different heavy metals from industrial waste water steams such as precipitation, coagulation, ion exchange etc. [5-8]. These processes have many disadvantages such as incomplete removal, high energy and reagents costs and disposal of toxic sludge [9-13]. Active research has produced a wide range of methods such as adsorption ion exchange, electro deposition, chemical precipitation, coagulation, solvent extraction and complexing. Among the several methods described, adsorption is the preferred method, due to its high efficiency and easy handling, for removing heavy metal ions [14-17]. Adsorption of Pb (II) ions have been studied by a variety of materials such as activated charcoal, polymeric synthetic resins, clays, oxide solids. It appears to be an important means of controlling the Pb (II) concentration in water and waste water. Lead is known to form a stable complex with crude turmeric extract by complexing with curcuminoids, the active component in turmeric [18, 19]. In this communication we describe an efficient method for removing lead (II) ions from water samples using crude turmeric extract as adsorbent. Results with activated carbon have been included for a comparison.

Turmeric contains a wide variety of phylochemicals. The compounds responsible for the yellow colour of the rhizome are curcumin [1, 7-bis-(4-hydroxy-3-methoxyphenyl)-1, 6-hept- adien-3,5-dione], demethoxycurcumin and bisdemethoxy- curcumin (curcuminoids). The β-diketo moiety of curcumin- oids undergoes keto-enol tautomerism. Crystal studies have shown that the symmetric structure of curcumin leads to a statistically even distribution of the enol proton between the two oxygen atoms. The strong chelating ability of β-diketones has been widely investigated towards a great number of metal ions. In such conditions the curcumin molecule should bind with species which have a positive or partially positive charge, for example, a transition metal ion [18].



2. Experimental

The adsorbents used in this study were activated charcoal and turmeric powder. Turmeric rhizomes were collected from the local market, washed thoroughly, dried in an oven at 80 °C for 24 h, ground using a laboratory mill, sieved to 0.5–0.8 mm, and rinsed using 0.1 N HCl. Then the pH was adjusted with 0.1 N HCl at values (6–7). Finally, the powder so obtained was dried and stored in an oven at 80 °C till it reached constant density and humidity [20]. Activated charcoal was prepared by heating, for two hours in an oven, to remove any volatile matter in it. This was then stored in a desiccator over anhydrous $CaCl_2$ Analytical grade lead nitrate procured from E. Merck was used to prepare stock solution of lead for the studies. Concentration lead was measured using AAS (Perkin–Elmer 3110).

For adsorption studies batch experiments were carried out using the above two adsorbents [20, 21]. About 0.1g to 1g of adsorbents was accurately weighed using electronic balance and transferred to different stoppered bottles containing 50 ml of stock solution. These bottles were shaken well by means of a mechanical shaker for about 1 hour. Kept it in a water bath for about 30 minutes to attain equilibrium, filtered the solution through a Whatmann No.1 filter paper. Then a known volume, 1-2 ml of filtrate was used to estimate the concentration of lead. Batch experiments were also done at different temperatures 30, 40, 50, and 60^{0}C to find effect of temperature on adsorption.

The amount of metal ions adsorbed by the adsorbent was evaluated using equation (1):

$$Q_t = (C_0-C_t)\ V/w \qquad (1)$$

The mass balance equation [22] was used to determine the adsorption capacity (Q_e) from equation (2):

$$Qe = (C_0-C_e)\ V/w \qquad (2)$$

Where, C_o and C_t are the initial and final concentrations of lead (II) ions present in the sample before and after adsorption, for a period of time t (mg/L) respectively: C_e represent the concentrations of heavy metals in wastewater (mg/L) when equilibrium was attained: V (mL) is the volume of sample of water and w represent the mass (g) of the adsorbent used. The percentage of metal ions removed [23] was obtained from equation (3):

$$R\ \% = (C_0-C_t) \times 100/ C_0 \qquad (3)$$

Where (R %) is the ratio of difference in metal concentration before and after adsorption. Effect of Contact Time: The effect of contact time on removal of lead (II) ions was studied for a period of 120 min. 0.2 g of the adsorbent was added to different conical flask containing 50 mL of stock solution, the flask was closed and placed in a rotary shaker, and agitated at 150 rotation per minute (rpm), for each of the different contact times chosen (20, 40, 60, 80,100 and120 minute). The content of each flask was filtered and analyzed after each agitation time [23].

The effect of adsorbent dosage was studied by adding different mass of adsorbent (0.2-2g) into different conical flasks containing 50 mL of stock solution, corked and agitated in a shaker for 1 h at a speed of 150 rotations per minute (rpm) at a room temperature of 28 °C. The content of each flask was then filtered and analyzed after the agitation time [24].

The effect of pH on adsorption on metal ions was studied over a pH range of 2-12. For this particular study, 50 mL of stock solution was measured into different 250 mL conical flask and 1 g of the adsorbent (optimum value), was added and agitated at 150 rpm for one hour. The pH was adjusted from 2-7. The Whatman filter paper was used to filter the mixture and the filtrate analyzed to determine the concentrations of lead (II) ions. Shaking speed was varied from 150 to 350 rpm, to study the effect of shaking speed on adsorption of metal ion. 1 g of the adsorbents was added to different conical flask containing 50 mL of sample, corked and agitated in a shaker for a period of 1hr at room temperature of 28 °C. The content of each flask was then filtered and analyzed after the agitation time [25].

Kinetic Analysis: By analyzing the adsorptive uptake of lead (II) ions from sample at different time intervals, the kinetics of adsorption was studied. The pseudo-first-order and pseudo second order model equations are fitted to model the kinetics of heavy metals adsorption onto activated carbon [23]. The linearity of each model when plotted indicates whether the model suitably described the adsorption process or not. The general expression for pseudo-first-order equation model is shown in equation (4) and (5):

$$dQ_t/dt = k_1\ (Q_e-Q_t) \qquad (4)$$

The sorption capacities at equilibrium and at time t, are represented by Q_e and Q_t respectively (mg/g) and k_1 is the pseudo-first order sorption rate constant (g/mg/min). Applying boundary conditions after integration, from t = 0 to t = t and Q_t = 0 to Q_t = Q_t, the integrated form of equation becomes:

$$\log (Q_e-Q_t) = \log Q_e-(k_1/2.303)\ Q_t \quad (5)$$

The pseudo-second order chemisorption kinetic rate equation[24] is expressed as shown in equation (6):

$$1/ Q_t= 1/k_2\ Q_e^2+ t / Q_e \quad (6)$$

The sorption capacities at equilibrium and at time t, are represented by Q_e and Q_t(mg/g) respectively and k_2 is the rate constant of the pseudo-second order sorption (g/mg/min).

3. Results and Discussion

In the present work, we have examined the efficiency of natural turmeric powder and activated charcoal to remove lead (II) ions by adsorption, from aqueous solution under various conditions. The experimental data were analyzed using Langmuir and Freundlich isotherm and adsorption parameters that are characteristics of an adsorbent were determined [20, 21]. The Freundlich adsorption isotherm, one of the most widely used mathematical descriptions, gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich isotherm is defined as:

$$Q_e= k\ Ce^{1/n} \quad (7)$$

In the linearized form, above equation becomes:

$$\log Q_e = \log k + (1/n) \log C_e \quad (8)$$

Where C_e is the equilibrium concentration and Q_e is the amount of adsorbate adsorbed per unit mass of adsorbent. ''k'' is a parameter related to the temperature and ''n'' is a characteristic constant for the adsorption system under study, The plots of log Q_e against log Ce are shown in Fig. 1a-1b; the values of ''n'' between 2 and 10 show good adsorption [21]. The Langmuir equation is based on the assumptions that maximum adsorption corresponds to a saturated mono-layer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface [21].
The Langmuir isotherm is defined as:

$$Q_e= (bQ_mC_e) / (1 +bC_e) \quad (9)$$

In the linearized form, the above equation becomes:

$$C_e/Q_e = (C_e/Q_m) + (1/bQ_m) \quad (10)$$

Where Q_m and b are Langmuir constants related to the adsorption capacity, and sorption energy, respectively, C_e is the equilibrium concentration in mg/L, and Q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). The plots of C_e/Q_e against C_e are shown in Fig. 2a-2b. The linear fit is fairly good and enables the applicability of the Langmuir model. The Langmuir isotherm constants are listed in Table 1.It is found that experimental data were better fitted to the Langmuir equation than to the Freundlich equation, and therefore it is more suitable for the analysis of kinetics. The correlation coefficients R_L (Langmuir) and R_F (Freundlich) calculated for the linear ranges are also included in Table 1.
The effect of temperature on removal of lead from aqueous solution was found to decrease with increase in temperature. Thermodynamic parameter for adsorption of lead ions by turmeric powder such as ΔH^0, ΔG^0 and ΔS^0 were calculated from Langmuir parameter as per this equations,

$$\ln k=A-\Delta H^0/RT \quad (11)$$
$$\ln k= - \Delta G^0/RT \quad (12)$$

$$\Delta S^0 = \frac{(\Delta H^0 - \Delta G^0)}{T} \quad (12)$$

According to equation (11) the mean value of the enthalpy change due to the adsorption of lead ions by curcumin over the temperature range can be determined graphically by the linear plotting of ln k against 1/T using the least square analysis (Fig.3).
The mean enthalpy change can be determined from the slope of the straight line. The variation of Gibbs free energy and entropy change with temperature can be calculated using equation (12) and (13), respectively. The results are given in Table.2.An important result can be obtained from above table is that; Gibbs free energy (ΔG^0) is small and negative, with its value becomes large negative with increasing temperature. This indicates that the adsorption processes of lead ions by curcumin decreases by increasing temperature. The values of entropy change (ΔS^0) are positive and remain constant with temperature. This gives evidence that structural changes in lead ions and curcumin occur during the adsorption process. The negative value of enthalpy shows the exothermic nature of the adsorption process of lead ions by curcumin. The parameter Q_m, adsorption capacity, the Q_e value and percentage of removal was found to be higher for turmeric, suggesting that retention capacity of turmeric is higher for lead (II).When turmeric was placed in lead solution, in addition to normal adsorption of lead ions on the surface sites of the turmeric powder, ion exchange with metal ions using the protons of curcuminoids.
The relationship between contact time and the percentage removal of lead ions with activated charcoal and turmeric powder in Fig.4. The effect of contact time was studied at a room temperature of 28 ºC, at intervals of 10 min. The removal of metal ions increased as contact time increases. The percentage metal ions removal approached 100% within 50 min with turmeric powder, where as it took 60 min in the case of activated charcoal. The availability and accessibility of adsorption site is controlled by adsorbent dosage. Adsorbent dosage was varied from 0.2 g to 2 g, under the specific conditions (initial pH of 6, contact time of 50 min, 150 rpm shaking speed and at room temperature of 28 ºC). The results are given in Fig.5. The pH of the sample of water is one of the important factors governing the adsorption of the metal ions. The effect of pH was studied from a range of 2 to 7 under the precise conditions (at optimum contact time of 50 min, 150 rpm shaking speed, with 1 g of the adsorbents used, and at a room temperature of 28 ºC). From Fig.6, at pH 6, maximum removal was obtained for activated charcoal while 100% removal of Pb (II) ion was achieved even at a low pH of 4 for turmeric. The effect of shaking speed was investigated under the specified conditions (at optimum contact time of 50 min, 150 rpm shaking speed, with 1 g of the adsorbents used, at pH = 4 or 6 and at a room temperature of 28 ºC) with increase in shaking speed from 150 to 350 rpm is shown in Fig.7. With increase in shaking speed, the percentage removal of metal ions also increases. was due to the fact that, increase in stirring rate enhanced the metal ions diffusion to the surface

of the adsorbent; and also caused reduction in the film boundary layer around the adsorbent.
It is found that pseudo-second order reaction model yield very good straight line (Fig. 8) compared to the pseudo-first-order reaction model, which was significantly scattered (nonlinear).

In chemisorption, the heavy metals stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface.

Table 1: Langmuir and Freundlich parameters for the adsorption of lead (II) from aqueous solutions by various adsorbents.

Adsorbent	Langmuir parameters		Correlation coefficient R_L	Freundlich parameters		Correlation Coefficient R_F
	B	Q_m		k	n	
Turmeric Powder	8.42	0.2767	0.9525	3.846	3.678	0.9568
Charcoal	6.07	0.4287	0.9825	3.248	3.345	0.9845

Table 2: The thermodynamic parameters for the adsorption of Lead ions on curcuminoids

Temperature Kelvin	ΔH^0 kJ/mol Mean value	ΔG^0 kJ/mol	ΔS^0 J/mol/ K
303	-5.546	-13.630	26.67
313	-5.546	-13.883	26.63
323	-5.546	-14.156	26.65
333	-5.546	-14.429	26.67

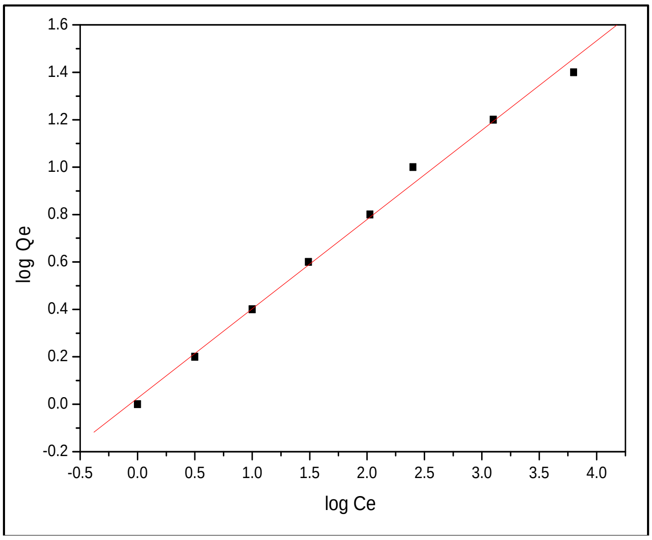


Fig 1a: Langmuir isotherm for adsorption of Pb (II) from aqueous medium using charcoal

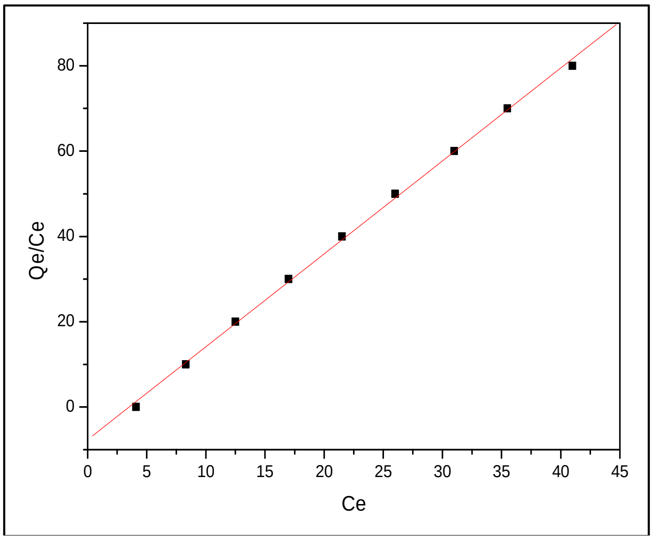


Fig 2a: Freundlich isotherm for adsorption of Pb (II) from aqueous medium using charcoal

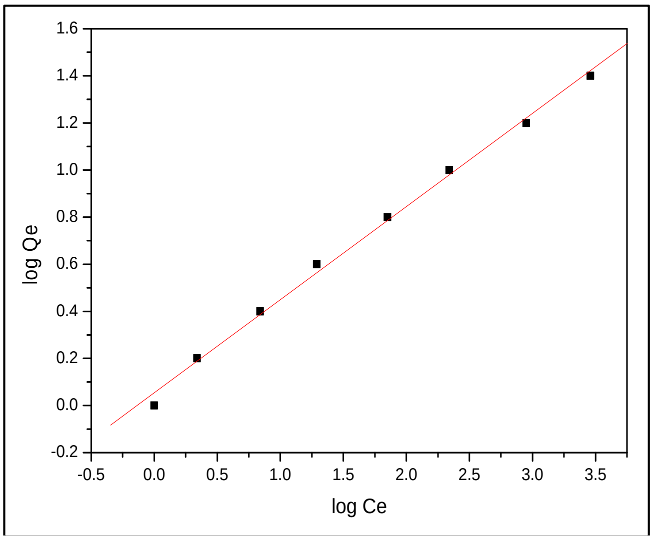


Fig 1b: Langmuir isotherm for adsorption of Pb (II) from aqueous medium using turmeric powder

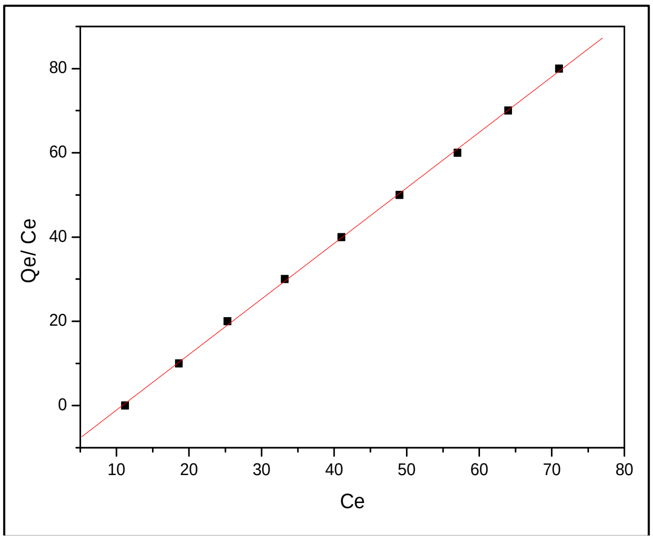


Fig 2b: Freundlich isotherm for adsorption of Pb (II) from aqueous medium using turmeric powder

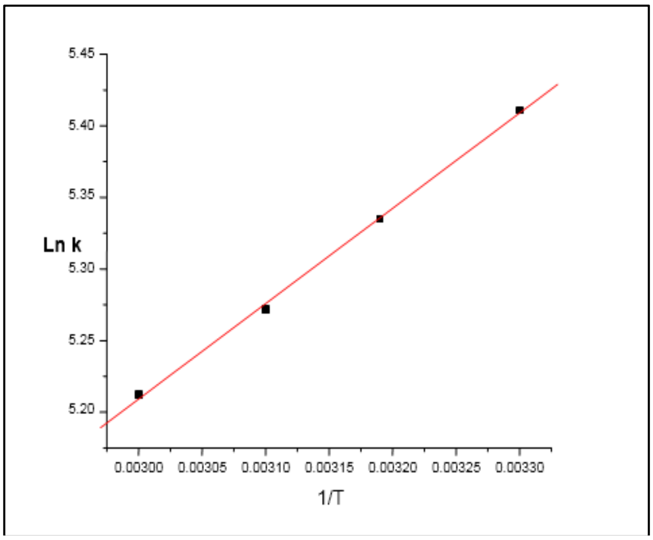


Fig 3: plot of ln k against 1/T

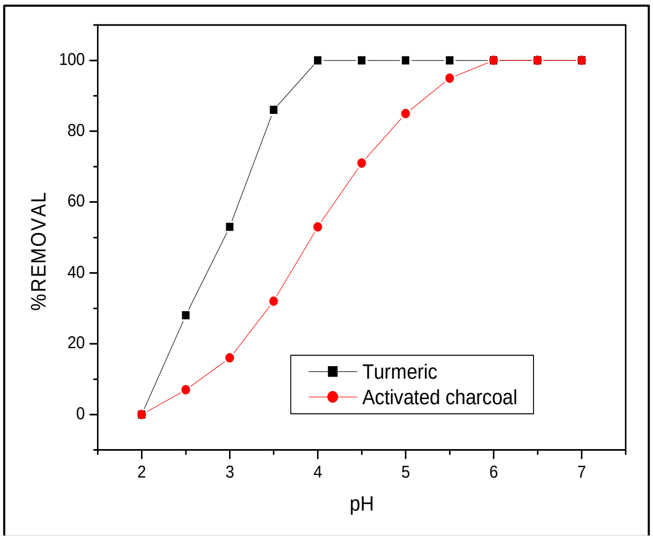


Fig 6: % Removal of lead with pH

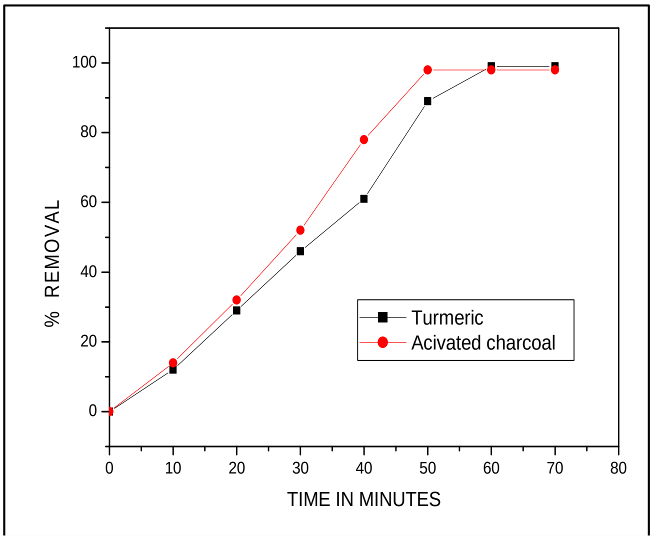


Fig 4: % Removal of lead with contact time

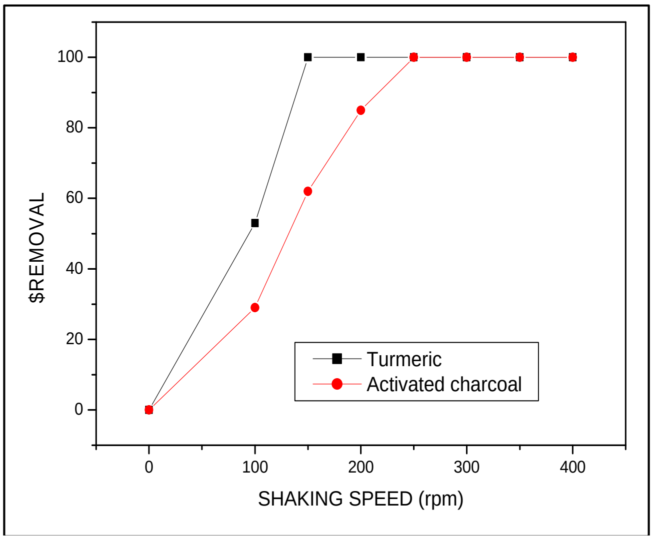


Fig 7: % Removal of lead with shaking speed

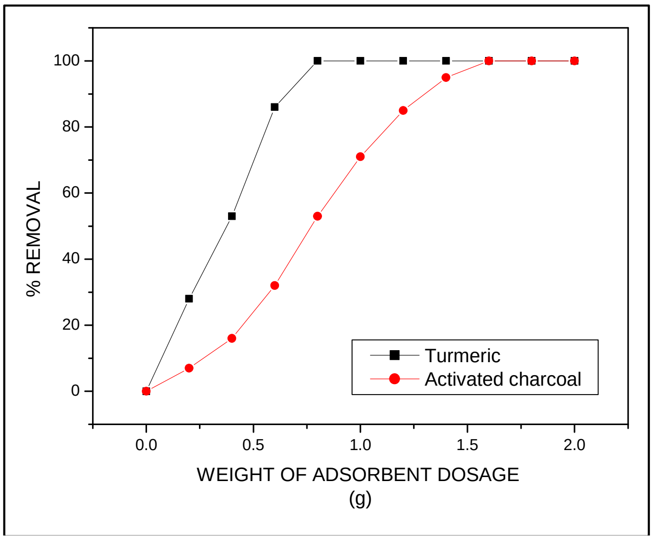


Fig 5: % Removal of lead with adsorbent dosage

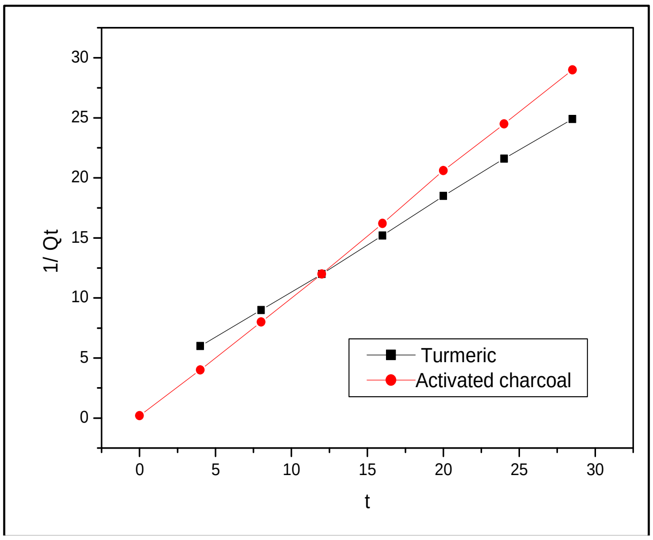


Fig 8: Pseudo second order reaction model for adsorption

4. Conclusion

The use of turmeric as a natural adsorbent for the removal of the lead (II) ions from aqueous solution was established. Langmuir and Freundlich adsorption isotherms were used to explain the adsorption process. The linear plots obtained are indicative of the applicability of Langmuir adsorption isotherm there by favouring the formation of monolayer coverage on the surface of the adsorbent. The uptake of lead is greater for turmeric while comparing with activated charcoal.

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