



Lead (Pb) Sorption Kinetics by Clay Minerals: Bentonite and Zeolite

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ABSTRACT

Background: Heavy metal pollution chiefly lead (Pb) causes various environmental disequilibrium and health hazards. Immobilization of lead (Pb) using clay minerals is cost effective for metal remediation due to their higher surface area and negative charges.

Methods: This study was taken up to assess the Pb removal potentials of bentonite and zeolite from contaminated water and to study the effect of sorbent dosage, initial Pb²⁺ concentrations and incubation time intervals on Pb adsorption and desorption was studied.

Result: Zeolite was effective in immobilising Pb (78.0%) than bentonite (70.9%) which increased with increasing sorbent dosage and time intervals. The pseudo second-order kinetic model described the Pb adsorption precisely. Chemisorption was the dominant mechanism operating in aqueous solution system, hence, it could be concluded that zeolite can be utilized as an efficient sorbent for wastewater treatment.

Key words: Adsorption, Clay minerals, Desorption, Kinetic models, Lead.

INTRODUCTION

Water pollution emanating from heavy metal contamination has been considered to be a global concern in recent years (Beidokhti *et al.*, 2019; Tathe and Kolape, 2021). An increase in metallic substances in the water bodies particularly groundwater has been observed due to increased discharge of metals from industrial processes and urbanisation activities (Olukanni *et al.*, 2014; Silvy and Teenamol, 2019). The levels of heavy metals exceed permissible limits in the system pose risk and health hazards to human beings through their cyclic transfer (Lingamdinne *et al.*, 2018). The soil and waste water polluted with inorganic metal pollutants are difficult to treat as they are non-biodegradable and remain for longer period (Khan *et al.*, 2017). Out of various heavy metal pollutants, lead (Pb) ranks second, after As, on priority lists of Hazardous Substances of Agency for Toxic Substances and Disease Registry (ATSDR, 2015) and US Environmental Protection Agency (USEPA) owing to its widespread occurrence and potentially high ecotoxicity (Kushwaha *et al.*, 2018). The existence of >15 µg Pb²⁺ per litre in drinking water was found to be toxic to human beings (Khan *et al.*, 2017). The soluble Pb bioaccumulates in living organisms, causing toxic effects on terrestrial and aquatic biota through unintended ingestion of Pb by consuming contaminated water and crop produces (Hamid *et al.*, 2020). Ingestion of lead can cause anaemia, kidney malfunction, brain tissue damage and even death in human beings under extreme poisoning conditions (Mutter *et al.*, 2017).

Lead ions in aqueous solutions could be removed by various processes like ion exchange, adsorption, biosorption, precipitation, coagulation or electro-coagulation, cementation, osmosis and electro-dialysis (Arbabi, 2015) using various natural and synthetic materials. Most of the

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Pb removal techniques and materials are expensive and are not feasible for application in real life conditions on a larger scale. In this context, adsorption is a preferable method which could be adopted to remediate contaminated waters using low-cost materials as adsorbents (Salman *et al.*, 2017). Adsorption is a very efficient technique for metal contaminant removal and performance of the adsorbent is highly reliant on physicochemical properties of adsorbent, nature of contaminant and conditions of adsorption processes. To investigate the chemical adsorption rate, the rate-determining step in adsorption process, adsorbent material, effect of pH and time, chemical kinetic models were

employed to describe the reactions (Ray *et al.*, 2020) which permits to optimize the mechanism of adsorption pathways, to express the dependence of adsorbent surface properties, determine adsorbent capacities and design the adsorption systems effectively (Largitte and Pasquier, 2016). Adsorption efficiency is generally influenced by various factors like adsorbent dosage, initial metal concentration, contact time, particle size and pH of solution (Karri *et al.*, 2017). Thus, there is a need to recognise and investigate efficient, low-priced and readily available adsorbents (Karri *et al.*, 2017) to know the mechanisms of metal removal for choosing suitable sorbents under specific situations.

On the other hand, clay minerals have gained attention as effective and cheap sorbing and immobilizing materials for Pb because of their high net negative charge, cation exchange capacity, porosity, surface area, affinity towards Pb, lower cost, strong adsorption capacity, wider acceptability and easier availability (Melichova and Handzusova, 2013). Bentonite, a 2:1 clay mineral with two Si tetrahedral sheets sandwiching an Al octahedral sheet (Guerra *et al.*, 2013) and zeolites ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot n\text{H}_2\text{O}$), the three dimensional alkaline porous negatively charged alumino-silicates, neutralized by introducing exchangeable cations in structural sites. The negative charge arises due to the partial substitution of silicon (Si^{4+}) with aluminium (Al^{3+} , Hamidpour *et al.*, 2010; Sangeetha and Baskar, 2016; Akbar and Zahedi, 2016). These clay minerals are capable of removing Pb from aqueous solution without emitting any toxic substances into the environment (Guerra *et al.*, 2013). Thus, the study aims to investigate and compare the adsorption rate of bentonite and zeolite at varying contact time, initial Pb concentrations and sorbent doses. The data is also fitted in different kinetic models and kinetic parameters were computed to choose the best model to describe Pb removal.

MATERIALS AND METHODS

Pb standards and sorbents

The Pb standards were prepared using analytical grade lead nitrate ($\text{Pb}(\text{NO}_3)_2$) salt and using the 2000 mg l^{-1} stock solution, different Pb concentrations viz., 100, 250, 500, 1000 and 1500 mg l^{-1} were prepared. Bentonite and zeolite clay

minerals were used as sorbents which were of analytical grade purchased from M/s. Sigma Aldrich, Bangalore.

Batch sorption experiments

Batch sorption experiments were performed at room temperature with various sorbents applied at three different doses (1, 2.5 and 5 g) to the solutions having varied initial Pb^{2+} concentrations (100, 250, 500, 1000, 1500 and 2000 mg l^{-1}) at successive time intervals (24, 48, 72, 96 and 120 hrs). The experiment was conducted in duplicates with a blank simultaneously to quantify the amount of Pb adsorbed and desorbed by the sorbents.

Lead adsorption studies

Bentonite and zeolite clay minerals as sorbents was weighed and transferred into 50 ml centrifuge tubes to which 25 ml of Pb^{2+} solution was added at different concentrations. The centrifuge tubes were shaken on a mechanical shaker for the postulated time intervals of 24, 48, 72, 96 and 120 hours. After the stipulated time, tubes were centrifuged for 3 minutes at 5000 rpm and the supernatant was filtered using Whatman No.42 filter paper and stored in refrigerated conditions for further analysis. The Pb^{2+} concentration was determined in the filtrate at different time period using an atomic absorption spectrophotometer (Model: GBC AvantaPM). The amount of Pb^{2+} adsorbed (q_e , mg g^{-1}) was calculated (Ray *et al.*, 2020) according to equation (1)

$$q_t = V_a \times \frac{C_o - C_f}{m} \quad \dots(1)$$

Where:

C_o and C_f = Concentrations of Pb^{2+} (mg l^{-1}) in the initial and final solutions, respectively.

V = Volume of Pb^{2+} solutions added (25 ml).

'm' = Mass of sorbents (g).

The adsorption rate (AR, %) was calculated as below.

$$\text{AR (\%)} = \frac{C_o - C_f}{C_o} \times 100 \quad \dots(2)$$

Kinetic models

Lead adsorption data acquired from the investigation was fitted into zero, first, second order kinetics, intraparticle

Table 1: Details of the models used and their constants.

Models	Equations	Kinetic constants	References
Zero-order kinetic	: $q_t = q_0 - k_0 t$	k_0 : zero order rate constant, $\text{mg kg}^{-1} \text{min}^{-1}$	Firoz <i>et al.</i> (2022)
First order kinetic	: $q_t = q_0 \cdot e^{-k_1 t}$	k_1 : first-order rate constant, min^{-1}	Ray <i>et al.</i> (2020)
Second order kinetic	: $1/q_t = 1/q_0 - k_2 t$	k_2 : second-order rate constant, min^{-1}	Ray <i>et al.</i> (2020)
Intraparticle diffusion	: $q_t = q_0 + k_p t^{1/2}$	k_p : diffusion rate constant, $\text{mg}^{0.5} \text{kg}^{0.5}$	Morris and Weber (1962)
Power function	: $q_t = \alpha t^\beta$	α : initial rate of sorption (mg kg^{-1}) β : release rate constants, (mg kg^{-1}) ⁻¹	Aharoni <i>et al.</i> (1991)
Pseudo-second order kinetic	: $t/q_t = 1/h + t/q_e$	$h = k_q^2 h$: initial sorption rate, mg (g min)^{-1} k_2 : rate constant of pseudo-second order	Ho and McKay (1999)

where ' q_0 ' and ' q_t ' are the quantity of Pb^{2+} (mg kg^{-1}) at time t (minutes) and k_0 , k_1 and k_2 are the release constants of Pb^{2+} as per zero, first and second order kinetic equations, respectively. The best fitting model was chosen by considering the coefficient of determination (R^2).

diffusion model, power function and pseudo-second order kinetic models. The details of the models used and their constants are furnished in Table 1.

Statistical analysis

All the statistical analysis was carried out using SPSS software. A simple variance analysis was done (ANOVA) for factorial completely randomized block design with threefactorial arrangement (Pb^{2+} concentration, sorbent dose and incubation interval) and two replications. The least significance test was used to detect the differences between the means at $p < 0.005$. Simple correlation between various factors were performed using the procedure described by Snedecore and Cochran (1967) with the help of SPSS software.

RESULTS AND DISCUSSION

Lead (Pb^{2+}) adsorption

Effect of Pb concentrations

The effect of initial Pb^{2+} concentrations of the solution on Pb adsorption rate was investigated and depicted in Fig 1a. The removal of Pb^{2+} relied on the initial Pb concentration which varied from 88.1 to 46.7% for bentonite and 87.7 to 61.8% for zeolite. At lesser Pb^{2+} concentrations, no much variation was noted and remains the same for bentonite (88.1%) and zeolite (87.7%) but with increasing Pb^{2+}

concentrations, zeolite (61.8%) exhibited superior adsorption rates. The adsorption rate was higher in zeolite at 100 to 1000 mg l^{-1} (87.7 to 79.7%) but decreased steeply from 79.7 to 61.8% when the initial Pb concentration in the solution increased from 1000 to 2000 mg l^{-1} however in bentonite the rate of Pb removal dropped linearly. The adsorption rates declined for both the sorbents with increasing Pb^{2+} concentrations since the sorbent surfaces were loaded with Pb ions *viz.*, loading effect (Keles *et al.*, 2010) where the fraction of available surfaces for Pb^{2+} adsorption was higher at lower concentrations than that of higher concentrations (Elboughdiri, 2020). At lower concentrations, more active sites would be available on the adsorbent to adsorb the Pb ions resulting in higher adsorption rates (Melichova and Hromada, 2013; Glatstein and Francisca, 2015). However, at higher concentrations, the active sites would be saturated with adsorbed Pb ions resulting in more Pb ions left un-adsorbed in the solution (Pawar *et al.*, 2016; Hussain and Ali, 2021).

Effect of incubation intervals

The Pb^{2+} adsorption rate by the sorbents were studied at different incubation time intervals (Fig 1b) and a linear increase in the adsorption rate was discovered with the advancement of time in both the sorbents. The adsorption rate increased from 0 to 63.2% for bentonite and 72.9% for zeolite within 24 hours of incubation. This higher adsorption

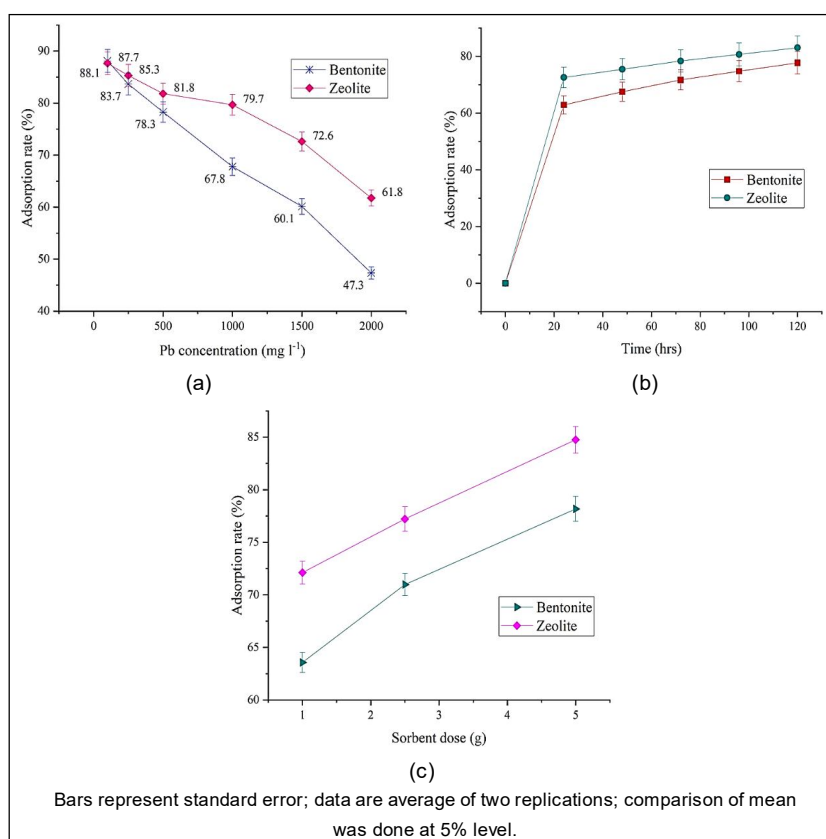


Fig 1: Adsorption rate (%) by clay minerals as influenced by (a) Initial Pb concentrations (b) Time (c) Sorbent doses.

rate might be ascribed to the accessibility of enormous active vacant sorption sites existing on the clay minerals initially and an enhanced concentration gradient between the solute in bulk solution and the solute near sorbent surfaces (Hamidpour *et al.*, 2010; Pawar *et al.*, 2016) resulting in faster ion exchange. It was then saturated with the passage of time (Zhang *et al.*, 2016; Hussain and Ali, 2021) resulting in a slow and steady growth in the adsorption rate (63.2 to 77.3% for bentonite and 72.9 to 82.5% for zeolite from 24 to 120 hrs).

Effect of sorbent dose

The effect of sorbent dosage on the removal of lead ions at various contact time intervals was investigated with different adsorbent dosage (1.0-5.0 g 25 ml⁻¹) and the outcomes were depicted in Fig 1c. Higher adsorption rates were noticed with increasing sorbent dosage irrespective of type of sorbent studied. The Pb²⁺ adsorption rate varied from 63.5 to 78.2% in bentonite and 70.4 to 86.5% in zeolite clay minerals with the increasing sorbent doses from 1 to 5g owing to the increase in number of adsorption sites (Elboughdiri, 2020; Keles *et al.*, 2010). The absorption of Pb ions increases with the quantity of bentonite and zeolite added because of the accessibility of greater surface area and greater number of ex-changeable sites in clay structure

at a time when the initial metal concentration is constant, resulting in higher Pb²⁺ removal efficiency (Melichova and Hromada, 2013; Zhang *et al.*, 2016 and Elboughdiri, 2020). Similar findings were reported by Hamidpour *et al.* (2010); Pawar *et al.* (2016) and Hussain and Ali (2021).

Adsorption kinetics

The kinetics of Pb sorption in solid-metal ions system reflects the rate of Pb sorption on sorbents and the time required to reach equilibrium, which is crucial for the understanding of sorption process and sorbent performance. The adsorption data thus obtained was fitted into various kinetic models and the results have been reported in Table 2 and 3.

The higher coefficient of determination ($R^2 = 0.999^{**}$), represented the validity of pseudo-second order model for lead sorption by both the sorbents followed by intraparticle diffusion and power function model. According to pseudo second order kinetics, rate-determining step in Pb²⁺ sorption was chemical sorption (Dragan *et al.*, 2010). A linear variation in amount of Pb sorbed per unit time (t/q_t) at time (t) for both bentonite and zeolite at different initial Pb²⁺ concentrations was explained in Fig 2. The initial sorption rate 'h', pseudo-second-order rate constant 'k', amount of Pb²⁺ adsorbed at equilibrium 'q_e' acquired from

Table 2: Kinetic parameters computed using various models for bentonite clay to describe Pb sorption in aqueous solution.

Kinetic parameters	Pb concentration (mg l ⁻¹)					
	100	250	500	1000	1500	2000
Zero order kinetics						
Initial amount of Pb adsorbed (q ₀) mg g ⁻¹	1.00	2.52	4.14	6.57	8.17	7.97
Rate of Pb adsorption (K ₀ * 10 ²) mg g ⁻¹ S ⁻¹	0.16	0.24	0.82	2.22	3.83	4.76
R ²	0.916	0.954	0.906	0.906	0.955	0.997
First order kinetics						
Initial amount of Pb adsorbed (q ₀) mg g ⁻¹	1.00	2.52	4.16	6.65	8.38	8.31
Rate of adsorption (K _f * 10 ³) mg g ⁻¹ S ⁻¹	1.45	0.90	1.76	2.79	3.59	4.25
R ²	0.910	0.957	0.887	0.885	0.938	0.986
Second order kinetics						
Initial amount of Pb adsorbed (q ₀) mg g ⁻¹	1.00	2.53	4.17	6.71	8.52	8.53
Rate of adsorption (K * 10 ⁴) mg g ⁻¹ S ⁻¹	3.20	3.33	3.78	3.53	3.39	3.83
R ²	0.904	0.959	0.867	0.862	0.916	0.965
Intraparticle diffusion						
Initial adsorbed amount (q ₀) mg g ⁻¹	0.86	2.31	3.63	5.19	6.24	5.52
Diffusion rate constant (kp) mg ^{0.5} kg ^{0.5}	0.03	0.05	0.13	0.36	0.58	0.73
R ²	0.976	0.979	0.966	0.964	0.979	0.983
Power function						
Initial rate of sorption (α) mg kg ⁻¹	0.72	2.07	3.00	3.96	4.76	4.14
Release rate constants (β) (mg kg ⁻¹) ⁻¹	0.11	0.06	0.11	0.17	0.20	0.24
R ²	0.944	0.936	0.993	0.985	0.969	0.981
Pseudo second order kinetics						
Amount of Pb ²⁺ adsorbed at equilibrium (q _e) mg g ⁻¹	1.28	2.90	5.31	9.84	14.0	15.5
Initial sorption rate (h) mg g ⁻¹ min ⁻¹	10.1	7.51	2.76	0.87	0.45	0.32
Rate of sorption (k _{2,10⁻²}) g (mg min) ⁻¹	0.101	0.075	0.028	0.009	0.005	0.003
R ²	0.998	0.999	0.999	0.999	0.993	0.987

the pseudo second-order model was listed in Table 2 and 3. Increasing Pb^{2+} concentration decreased the initial Pb^{2+} sorption rate (h) from 10.1 to 0.32 $mg\ g^{-1}\ min^{-1}$ for bentonite and 12.9 to 0.35 $mg\ g^{-1}\ min^{-1}$ for zeolite as Pb^{2+} concentration increased from 100 to 2000 $mg\ l^{-1}$. The magnitude of Pb^{2+} adsorbed at equilibrium (q_e) augmented from 1.28 to 15.5 $mg\ g^{-1}$ for bentonite and 1.26 to 19.2 $mg\ g^{-1}$ for zeolite with increasing Pb^{2+} concentration. Comparing the two sorbents, the initial rate of Pb^{2+} sorption (h), rate constant (k) and equilibrium concentration (q_e) were

relatively higher for zeolite than bentonite. There was a decline in pseudo-second order rate constant (k) for the adsorption of Pb^{2+} on both bentonite and zeolite clays, as initial Pb^{2+} concentration was increased (Table 2 and 3). This shows that, time required for adsorption of Pb^{2+} to attain equilibrium is extended with increased initial Pb concentrations. The linearity of plots for the pseudo-second order model in Fig 2 indicates that, chemical reaction through exchange or sharing of electrons between sorbent and sorbate is the main rate-controlling step throughout

Table 3: Kinetic parameters computed using various models for zeolite clay to describe Pb sorption in aqueous solution.

Kinetic parameters	Pb concentration ($mg\ l^{-1}$)					
	100	250	500	1000	1500	2000
Initial amount of Pb adsorbed (q_0) $mg\ g^{-1}$	1.01	2.47	5.06	8.56	11.4	12.5
Rate of Pb adsorption ($K_0 * 10^2$) $mg\ g^{-1}\ S^{-1}$	0.10	0.26	0.40	1.90	2.89	3.43
R^2	0.836	0.976	0.963	0.971	0.971	0.974
First order kinetics						
Initial amount of Pb adsorbed (q_0) $mg\ g^{-1}$	1.01	2.47	5.06	8.62	11.5	12.7
Rate of adsorption ($K_f * 10^3$) $mg\ g^{-1}\ S^{-1}$	0.91	0.98	0.74	1.92	2.17	2.31
R^2	0.845	0.977	0.963	0.964	0.960	0.966
Second order kinetics						
Initial amount of Pb adsorbed (q_0) $mg\ g^{-1}$	1.01	2.48	5.07	8.67	11.6	12.8
Rate of adsorption ($K * 10^4$) $mg\ g^{-1}\ S^{-1}$	8.38	3.69	1.39	1.96	1.64	1.56
R^2	0.854	0.978	0.962	0.956	0.947	0.956
Intraparticle diffusion						
Initial adsorbed amount (q_0) $mg\ g^{-1}$	0.91	2.10	4.66	7.44	9.65	9.47
Diffusion rate constant (k_p) $mg^{-0.5}\ kg^{0.5}$	0.03	0.07	0.08	0.30	0.46	0.72
R^2	0.999	0.963	0.947	0.980	0.995	0.963
Power function						
Initial rate of sorption (α) $mg\ kg^{-1}$	0.78	1.79	4.25	6.16	7.81	7.48
Release rate constants (β) ($mg\ kg^{-1}$) $^{-1}$	0.09	0.09	0.05	0.11	0.13	0.17
R^2	0.994	0.923	0.881	0.959	0.987	0.920
Pseudo second order kinetics						
Amount of Pb^{2+} adsorbed at equilibrium (q_e) $mg\ g^{-1}$	1.26	2.98	5.67	11.4	15.7	19.2
Initial sorption rate (h) $mg\ g^{-1}\ min^{-1}$	12.9	4.67	4.37	1.06	0.69	0.35
Rate of sorption ($k_{2*10^{-2}}$) $g\ (mg\ min)^{-1}$	0.129	0.047	0.044	0.011	0.007	0.004
R^2	0.999	0.997	0.999	0.998	0.998	0.989

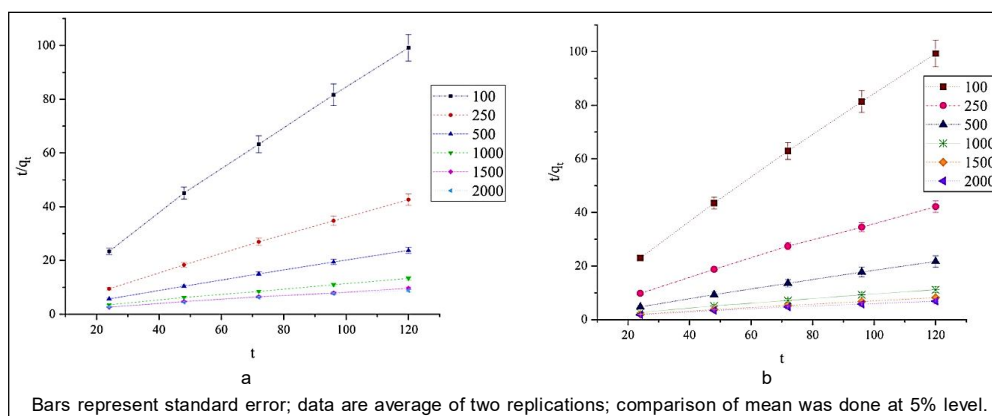


Fig 2: Kinetics of Pb adsorption by pseudo-second order model from clay minerals (a) Bentonite (b) Zeolite.

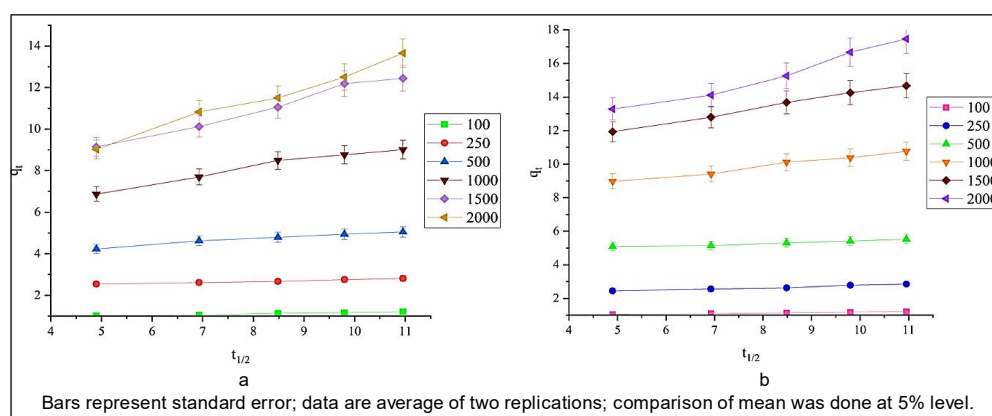


Fig 3: Kinetics of Pb adsorption by intraparticle diffusion model from clay minerals (a) Bentonite (b) Zeolite.

the adsorption process (Vadivelan *et al.*, 2005) and the mechanism follows a pseudo-second order reaction scheme. These outcomes are in harmony with the interpretations of Kragovic *et al.* (2012); Guerra *et al.* (2013) and Pawar *et al.* (2016).

The intraparticle diffusion model also showed good correlation with higher R^2 values for both the sorbents ranging from 0.964** to 0.983** for bentonite and 0.947** to 0.999** for zeolite indicating that this model could also describe the adsorption process in a better way. Here in addition to chemisorption, physisorption also contributed for the Pb adsorption onto the sorbents. However, the R^2 values for bentonite was slightly higher than zeolite. The diffusion rate constant escalated from 0.03 to 0.73 $\text{mg}^{-0.5} \text{kg}^{0.5}$ for bentonite and 0.73 to 0.72 $\text{mg}^{-0.5} \text{kg}^{0.5}$ for zeolite with increasing initial Pb concentrations depicting higher diffusion of Pb ions into the surface of sorbents when the concentration gradient is enhanced. However, the plot of ' q_t ' versus ' $t_{1/2}$ ' (Fig 3) showed a deviation from origin for the exclusion of Pb^{2+} . This result might be ascribed to the difference in mass transfer at the beginning and completion of sorption process (Pawar *et al.*, 2016). These results are in line with the inferences reported by Katsou *et al.* (2011) and Javanbakht *et al.* (2019).

CONCLUSION

This study demonstrates that both bentonite and zeolite clay minerals as sorbents showed higher Pb^{2+} sorption from aqueous solutions. However, zeolite possess higher Pb removal efficiency than bentonite clay with lesser desorption of adsorbed Pb^{2+} . The adsorption rate increased with increasing sorbent dose and at successive time intervals for both the sorbents. The different models tested for sorbent-metal ion interactions, showed that pseudo second order model explained the Pb^{2+} adsorption mechanism viz., chemisorption followed by intraparticle diffusion model. Chemisorption is the main rate limiting step in Pb^{2+} sorption and desorption was highly influenced by the net negative charges of the sorbents used. Hence it could be concluded that, zeolite is the effective sorbent used for removing Pb^{2+}

from the aqueous systems and pseudo second order model best describes the Pb^{2+} sorption than other models.

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Conflict of interest

The authors do not have any conflict of interest to declare.

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