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ARTICLE



Equilibrium, kinetics and thermodynamics of Pb(II) ions from aqueous solution by adsorption onto chitosan-dolomite composite beads

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ABSTRACT

This paper aims to investigate the adsorption process of a new composite adsorbent prepared from chitosan (Ch) and dolomite (Do) for removal of lead ions from aqueous solutions. The adsorption process of Pb²⁺ ions onto Ch-Do composite adsorbent as initial Pb²⁺ concentration, solution pH, temperature, contact time and desorption was investigated. From the results, it has been observed that the highest removal efficiency is approximately 89% at contact time of 6 h, initial Pb²⁺ concentration of 500 mg L⁻¹, adsorbent dosage of 100 mg and agitation speed of 150 rpm at pH 4.0. Langmuir isotherm has a better fit with the experimental isotherm data ($R^2 = 0.920$). The maximum Pb²⁺ adsorption capacity from the Langmuir model was found as 0.332 mol kg⁻¹ at 25°C. Also, it performs pseudo-second-order superior performance in kinetic behaviour compared to other used kinetic models ($R^2 = 0.904$). Thermodynamic parameters showed the Pb²⁺ adsorption onto Ch-Do was endothermic, spontaneous and possible. The desorption studies have shown that Ch-Do composite adsorbent has a good adsorption/desorption performance for Pb²⁺ ions.

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KEYWORDS

Chitosan; dolomite; composite; adsorption; Pb²⁺

1. Introduction

The heavy metal pollutant in the environment has a harmful effect due to their toxic nature towards the ecosystem and humans [1,2]. Nowadays, the removal of heavy metal pollutions from wastewater is very important [3–5]. Among these heavy metals, lead is the most common metal in the toxic heavy metals on the earth that has negative effects on the environment. Lead is an inhibitor of metabolic poison and enzyme, can damage the central nervous system and lead can accumulate in the bones, brain, kidney and muscles in human [6,7]. Therefore, it is very important lead removal from wastewater. Lead is widely used in many industrial applications. It is mainly used in metal coating industry, accumulator, manufacturing, printing pigments, photographic materials and mining activities and is found in their wastewater. Several methods have been suggested to lead removal from wastewaters in the environment. These methods include flocculation, coagulation, electrochemical reduction, chemical precipitation, neutralisation, ion exchange, complexation and adsorption [8,9]. The adsorption

method in the removal of heavy metal ions from wastewater has advantages such as low cost, high selectivity, simplicity, efficiency, environmental friendliness and ease of application [10,11]. In order for the adsorption method to be applied more effectively, it is of special importance that the material chosen as adsorbent is economical, easily available, easily recycled and non-toxic [12]. For this purpose, the use of cheap, non-toxic, abundant in nature, low-cost adsorbents has become widespread in recent years. In the removal of heavy metal ions from wastewater; bentonite [13,14], zeolite [15], diatomite [16], vermiculite [17], dolomite [18] and natural polymers such as chitosan [19] and lignin [20] are commonly used adsorbents. Composite adsorbents [21–24] which were prepared from materials such as natural minerals, natural and synthetic polymers are the most studied ones among the adsorbents in recent years [25,26]. Composite materials come into prominence as an adsorbent by combining the properties of the materials in interest [27–29]. Studies in recent, especially composite materials are widely used in the removal of heavy metal ions from aqueous solutions.

Dolomite is a type of mineral in the combination of the double carbonate compound of calcium and magnesium. The chemical formula of dolomite is $\text{CaMg}(\text{CO}_3)_2$ [30]. Dolomite is used in many sectors glass, plastic, paint, leather, ceramic, iron and steel industry, fertiliser, brick, cement, filling, chemistry, refractory, construction and agriculture. Additionally, dolomite is used as an adsorbent in heavy metal removal [31].

Chitosan contains essential amino and hydroxyl groups to binding heavy metal ions. Chitosan is a natural polymer that is abundant in nature, obtained by deacetylation of the chitin. Chitosan is insoluble in water, organic solvents, neutral and alkaline pH, while it dissolves in dilute organic acid solutions ($\text{pH} < 6$) such as acetic acid, formic acid, lactic acid [32,33]. Chitosan has antibacterial and antifungal effects. Chitosan is used in many sectors such as textile, cosmetics, medical materials and agricultural fields. In addition, it is used as an adsorbent after various modification processes in heavy metal removal [34].

In this study, for the first time, a chitosan-dolomite composite was synthesised using chitosan biopolymer and dolomite mineral. Therefore, practical use for chitosan was provided a useful, low cost, water-insoluble natural polymer/mineral adsorbent was created. The Ch-Do composite adsorbent was selected as a natural adsorbent due to its easy and economic preparation, effective, eco-friendly and cost-effective. To our present knowledge, this is the first report about the utilisation of Ch-Do composite beads for the adsorption of lead ions from aqueous solutions. This study shows the lead ions adsorption properties of a novel Ch-Do composite beads including isotherm, kinetic and thermodynamic studies. Also, the characterisation analyzes of this novel composite adsorbent was carried out in the current study.

2. Material and methods

2.1. Chemicals and apparatus

In this study, the natural dolomite was supplied from Akmin Mining (Ankara). Medium molecular weight chitosan (Sigma-Aldrich, Germany) was preferred. Epichlorohydrin (ECH) and sodium triphosphosphate (NaTPP) were obtained from Aldrich. $\text{Pb}(\text{NO}_3)_2$, 4-(2-pyridilazo) resorcinol (PAR) and other chemicals were achieved from Merk (Germany). Double-distilled water used in all dilutions and experiments. Spectrophotometric analysis was carried out by a UV-vis spectrophotometer (SHIMADZU, 160 A model, Japan). The surface of unloaded and Pb^{2+} loaded Ch-Do composite adsorbent were characterised by

FT-IR and SEM-EDX analysis. The FT-IR spectra were recorded on a Perkin Elmer 400 spectro-photometer. SEM images and EDX compositional data were obtained with a Leo 440 Computer Controlled Digital System.

2.2. Preparation of chitosan-dolomite composite beads

To prepare the Ch-Do composite, 2 g of Ch and Do was added in a 5% (v/v) acetic acid solution and mixture. Mixed in room conditions for 2 h. The mixture was left overnight. The next day, 4.0 mL the cross-linking agent, ECH solution was added to the mixture and mixed. The mixture was then added dropwise to the 0.5 mol L⁻¹ the cross-linking agent, NaTPP solution and composite material was formed [34]. The synthesised composite was precipitated and washed three times with double-distilled water, then the composite was dried in an oven at 40°C, ground and stored in closed containers for later use. Schematic illustration for the synthesis of Ch-Do composite beads is presented in Figure 1.

2.3. Methods of analysis

The concentration of Pb²⁺ ions was determined by measuring UV-vis spectrophotometric method of the complex formed by PAR [34]. PAR was used as a complex-forming reagent for determination of Pb²⁺ in the supernatants. A solution of 3.5 × 10⁻³ mol L⁻¹ of PAR in 0.7 mol L⁻¹ of Tris/HCl at pH 8.0–9.0 was prepared. A 50 µL fraction of supernatant was added onto 3 mL of the reagent and the absorbance of the formed metal complex was measured at λ = 518.5 nm for Pb²⁺.

2.4. Batch adsorption procedure

Adsorption experiments were performed by using the batch method. Stock Pb²⁺ solution (1000 mg L⁻¹) was prepared using double distilled water. For the adsorption experiments, 100 mg of Ch-Do composite adsorbent was put into 10 mL of Pb²⁺ solution (500 mg L⁻¹). The adsorption was carried out at 25°C and both Ch-Do composite adsorbent and Pb²⁺ in polypropylene tubes of 10 mL were kept in a thermostatic water bath with constant agitation speed (140 rpm) for 24 h. The pH was adjusted with dilute HCl and NaOH solutions (each one, 0.1 and/or 1.0 mol L⁻¹). Batch experimental conditions are given in Table 1. Pb²⁺ ion concentration was determined by the absorbance measurement. % Adsorption and Q (mol kg⁻¹) were calculated with equation in Table 2.

2.5. Desorption experiments

Desorption studies were performed for adsorbent recovery and re-use in adsorption processes. In this study, dilute HCl, NaOH, HNO₃ and ethyl alcohol solutions (each one, 0.1 mol L⁻¹) were used for desorption of the Pb²⁺ ions from the surface of the Ch-Do. In order to determine the recovery property of the adsorbent, the experiments were repeated three times with the same adsorbent for the adsorbent/desorption cycle. At the end of the each experiment, the solutions were centrifuged at 5000 rpm for 10 min to ensure liquid-solid separation and the amount of Pb²⁺ ions in the equilibrium solution

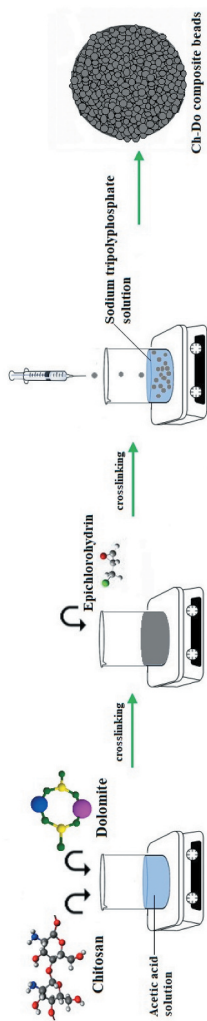


Figure 1. Schematic illustration for synthesis of Ch-Do composite beads.

Table 1. Batch experimental conditions for adsorption of Pb²⁺ onto Ch-Do composite adsorbent.

Aim of experiment	Solution pH	Initial Pb ²⁺ conc. (mg L ⁻¹)	Contact time (min)	Temperature (°C)
Effect of pH	1.0–5.0	500	1440	25
The effect of biosorbent dosage	4.0	500	1440	25
Effect of concentration	4.0	25–1000	1440	25
Effect of time	4.0	500	2–1440	25
Effect of temperature	4.0	500	1440	5, 25, 40
Desorption	4.0	500	1440	25

Table 2. Isotherm, kinetic and thermodynamic equations.

Model	Equation	Parameters
The adsorbed amount	$Q = \left[\frac{(C_i - C_e)V}{m} \right]$	Q _{ads}
% Adsorption	Adsorption% = $\left[\frac{(C_i - C_f)}{C_i} \right] \times 100$	Adsorption%
% Desorption	Desorption% = $\frac{Q_{des}}{Q_{ads}} \times 100$	Q _{des}
Isotherm	Equation	Parameters
Langmuir	$Q_e = \frac{X_L K_L C_e}{1 + K_L C_e}$	X _L , K _L
Freundlich	$Q_e = X_F C_e^\beta$	X _F , β
Dubinin-Raduskevich	$Q_e = X_{DR} e^{-K_{DR} \epsilon^2}$ $\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$ $E_{DR} = (2K_{DR})^{-0.5}$	X _{DR} , K _{DR} ε E _{DR}
Kinetic	Equation	Parameters
Pseudo first order	$Q_t = Q_e [1 - e^{-k_1 t}]$	k ₁ , Q _e
Pseudo second order	$Q_t = \frac{t}{\left[\frac{1}{k_2 Q_e^2} \right] + \left[\frac{t}{Q_e} \right]}$	k ₂ , Q _e
Intraparticle diffusion	$Q_t = k_i t^{0.5}$	k _i
Thermodynamics	Equation	Parameters
The distribution coefficients	$K_D = \frac{Q}{C_e}$	K _D
The free energy of adsorption	$\Delta G^0 = -RT \ln K_L$	ΔG ⁰
Van't Hoff	$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$	ΔH ⁰ , ΔS ⁰

C_i is the initial concentration of the bio-sorbent (mg L⁻¹), C_f is the equilibrium concentration (mg L⁻¹), m refers to the bio-sorbent mass (mg) and V is the solution volume (mL), Q_e: The adsorbed amounts at time t (mg g⁻¹), Q_{des}: desorbed amount of adsorbate (mol kg⁻¹), Q_{ads}: adsorbed amount of adsorbate (mol kg⁻¹), X_L: Langmuir adsorption equilibrium constant (L mg⁻¹), X_F: Freundlich constants, β; adsorbent surface heterogeneity, X_{DR}: DR constant related to the sorption energy (mol² K J⁻²), ε: Polanyi potential, R: Ideal gas constant (8.314 J mol⁻¹ K⁻¹), T: absolute temperature (298 K), E: Free energy change (kJ mol⁻¹), k₁ (min⁻¹), k₂ (mg g min⁻¹), and k_i (mg g min^{-0.5}), are the rate constants, H: Initial bio-sorption rate, K_D: The distribution coefficients, ΔG⁰: The free energy of adsorption (kJ mol⁻¹), ΔH⁰: The value of enthalpy changes (kJ mol⁻¹), ΔS⁰: The value of entropy changes (kJ mol⁻¹).

was determined by UV-vis spectrophotometric method. % Desorption was calculated with equation in Table 2.

3. Result and discussion

3.1. Adsorbent characterisation

FT-IR spectra analyses for the Ch-Do composite before and after adsorption of Pb²⁺ were undertaken and results are illustrated in Figure 2. When the Ch-Do spectrum was examined, it is observed that the absorption band at 3291–3147 cm⁻¹ is assigned to N-H and O-H

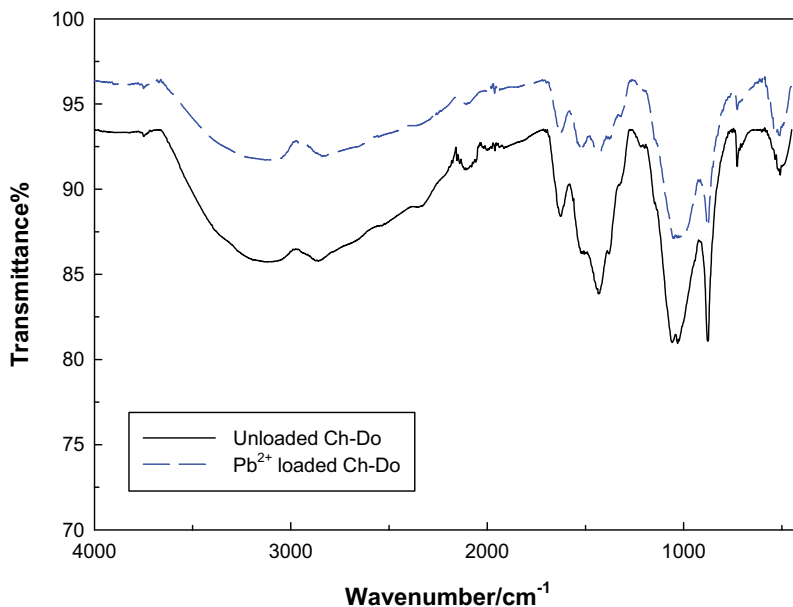


Figure 2. FT-IR spectra of Ch-Do before and after adsorption of Pb^{2+} . $\{[Pb^{2+}]_0:500 \text{ mg L}^{-1}$, adsorbent dosage:100 mg, natural pH:4.0, contact time:24 h, temperature:25 $^{\circ}$ C}.

stretching, the peak at 2873 cm^{-1} is corresponds to C-H symmetric and asymmetric stretching, 1623 cm^{-1} is assigned to C=O stretching of amide I, 1517 cm^{-1} is corresponds to the N-H bending of the primary amine, 1425 and 1364 cm^{-1} is assigned to the CH_2 bending and CH_3 symmetrical deformations, 1059 – 1036 cm^{-1} is assigned to C-O stretching, which are characteristic peaks for chitosan [35–37]. On the other hand, the Ch-Do spectrum was showed the main absorption bands (Ca, $CaCO_3$ and CaO) of dolomite at 3201 cm^{-1} , 1441 cm^{-1} , 869 cm^{-1} and 724 cm^{-1} [38–40]. Therefore, FT-IR spectra of Ch-Do composite indicated that the Ch-Do composite confirm hybrid material of chitosan and dolomite. After Pb^{2+} adsorbed Ch-Do exhibited FT-IR spectra with a visible decrease of peak intensities. This results indicated the surface complexation between Pb^{2+} with the functional groups of the Ch-Do surface.

In order to examine the morphology of before and after Pb^{2+} adsorbed Ch-Do, SEM and EDX analyses is used. The SEM photographs of before and after Pb^{2+} adsorbed Ch-Do composites are given in the Figure 3(a,b). The SEM photographs of the Ch-Do exhibited considerable difference after Pb^{2+} adsorbed Ch-Do, which is not clearly understood. Changes in SEM images obtained before/after Pb^{2+} adsorption on Ch-Do were considered as evidence for Pb^{2+} adsorption. The results of EDX analysis Figure 3(c,d) of the Ch-Do composite were: C: 30.5%; O: 50.6%; Mg: 1.7%; Ca: 4.4%; Si: 0.6%; P: 11.0%. On the other hand, Pb^{2+} adsorbed Ch-Do chemical analysis were as follows: C: 25.5%; O: 43.9%; Mg: 1.6%; Ca: 2.6%; Al: 0.5%; P: 11.3% and Pb: 14.6% as obtained using semi-quantitative EDX data. The Pb content in EDX spectra of Ch-Do is evidence of adsorption of Pb^{2+} onto Ch-Do.

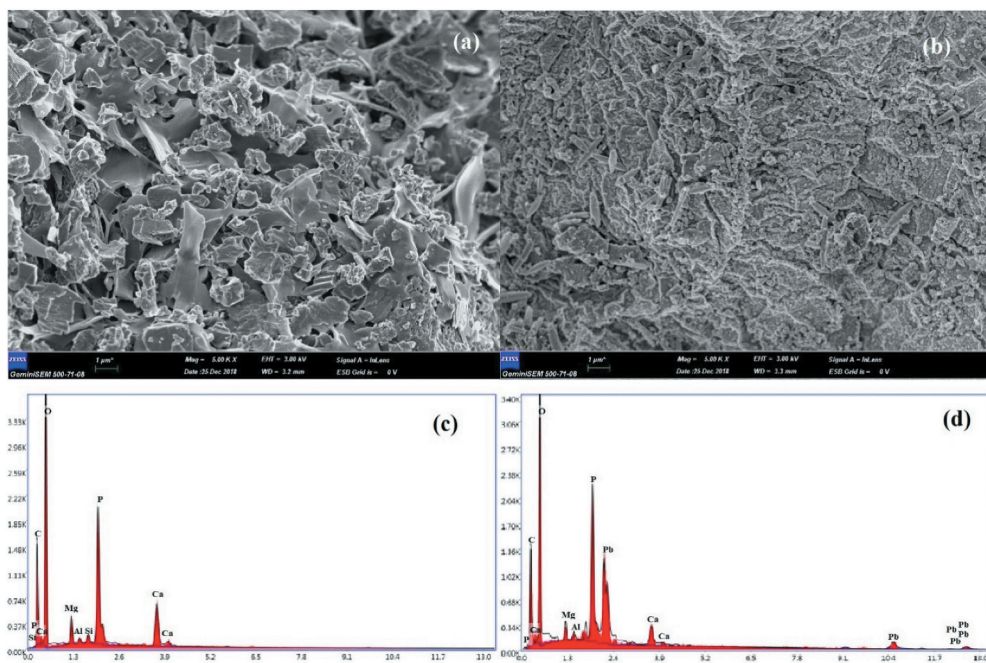
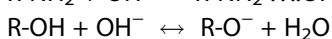
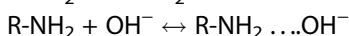
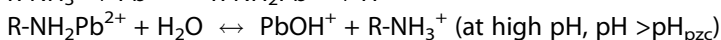
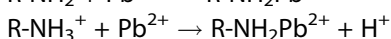
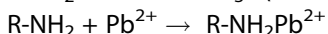
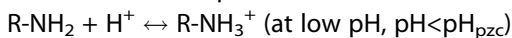


Figure 3. SEM photographs of Ch-Do before (a) and after (b) adsorption of Pb²⁺ and EDX results of Ch-Do before (c) and after (d) adsorption of Pb²⁺. {[Pb²⁺]₀:500 mg L⁻¹, adsorbent dosage:100 mg, natural pH:4.0, contact time:24 h, temperature:25°C}.

3.2. Determination of point of zero charge (pH_{pzc}) and effect of pH on adsorption

Surface charge of Ch-Do composite adsorbent is an important factor for affecting Pb²⁺ ions adsorption. In order to determine the PZC values of the Ch-Do composite adsorbent, 100 mg adsorbent was incubated for 24 h in pH solutions ranging from 1.0- to 12.0. The pH was adjusted with dilute KNO₃, HCl and NaOH solutions (each one, 0.1 and/or 1.0 mol L⁻¹). And then, the equilibrium pH values were measured. The determination of pH_{pzc} of the Ch-Do composite are illustrated in Figure 4. The surface charge of Ch-Do composite was found to be 5.52 [41].

The adsorption mechanism is related to the physicochemical interactions of the species in solution. The adsorption mechanism for Pb²⁺ ions of Ch-Do composite beads may be estimated that the adsorptive active centres for Pb²⁺ ions are at the amino groups and the hydroxyl groups in chitosan and the oxygen atoms in dolomite. According to this, the following chemical reactions may be suggested to explain for the adsorption of Pb²⁺ ions onto Ch-Do composite beads:



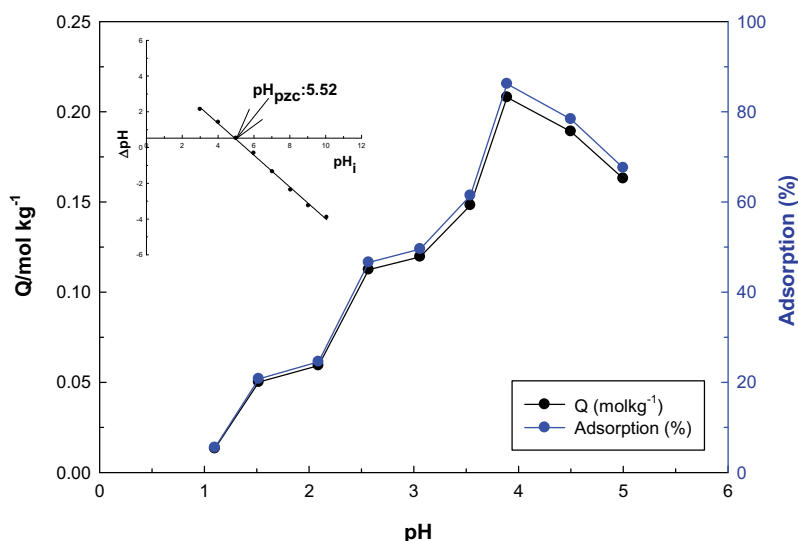


Figure 4. The effect of pH on adsorption of Pb^{2+} onto Ch-Do [$[\text{Pb}^{2+}]_0:500 \text{ mg L}^{-1}$, adsorbent dosage:100 mg, pH:1.0–5.0, contact time:24 h, temperature: 25°C] and pH_{pzc} plots of Ch-Do composite.

where R represents all other components except $-\text{NH}_2$ in the Ch-Do composite beads. At low pHs, more amino groups are protonated. At low pHs, the surface charge is positive ($\text{pH} < \text{pH}_{\text{pzc}}$), so H^+ and Pb^{2+} ions compete for adsorption to active centres of Ch-Do composite. The surface charge of Ch-Do composite will go negative with increasing pH. At high pHs, the surface charge is negative ($\text{pH} > \text{pH}_{\text{pzc}}$), and OH^- ions compete for adsorption to active centres and Pb^{2+} ions also is precipitated as hydroxide [42].

The results related to the effect of pH on the adsorption of Pb^{2+} ions onto Ch-Do composite are presented in Figure 4. The results showed that adsorption increased with increasing pH. According to the Figure 4, the percentage of the adsorption rate increased from 5% to 86% with increasing pH value from 1.0 to 4.0, respectively. Maximum adsorption rate was found as 86% at pH 4.0, which was the natural pH of the Pb^{2+} solution and was found to be the pH at which the adsorption was highest. Therefore, all adsorption experiments were performed at the natural pH of Pb^{2+} ion. The pH of the solution at pH 4.0 and above was not studied due to the precipitation of Pb^{2+} ions as hydroxides.

3.3. Adsorption isotherm models

Adsorption isotherms describe the adsorption behaviour of Pb^{2+} ions onto Ch-Do composite. Langmuir, Freundlich and Dubinin Radushkevich (D-R) isotherm models were used to specify the adsorption process, surface properties and adsorption mechanism of the Ch-Do composite [43,44].

The adsorption isotherms of Pb^{2+} onto Ch-Do composite were presented in Figure 5 and the adsorption isotherm parameters were presented in Table 3. The Pb^{2+} adsorption efficiency was high at low Pb^{2+} concentrations due to empty active centres on Ch-Do composite surface, whereas at high Pb^{2+} concentrations, the Pb^{2+} adsorption was

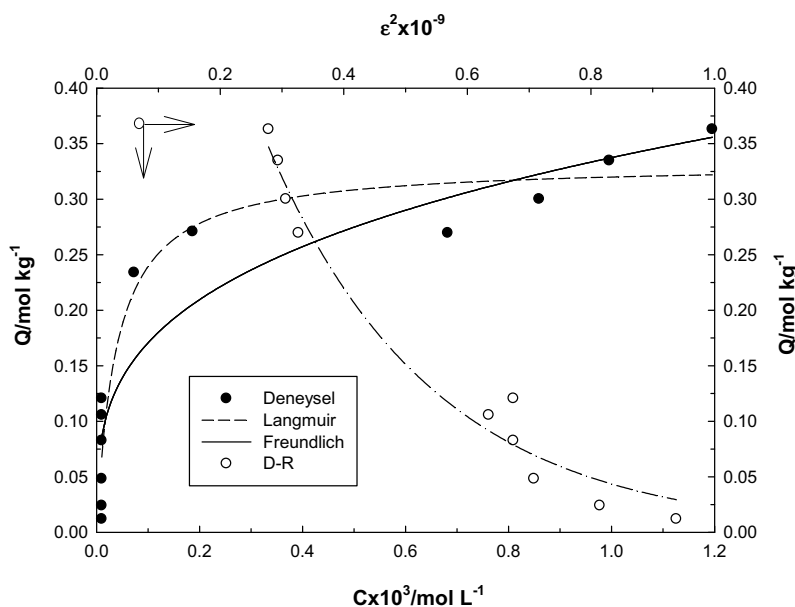


Figure 5. Experimentally obtained adsorption isotherms Pb^{2+} onto Ch-Do composite and their compatibility to Langmuir, Freundlich and D-R models $\{[\text{Pb}^{2+}]_0: 25\text{--}1000 \text{ mg L}^{-1}$, adsorbent dosage: 100 mg, natural pH: 4.0, contact time: 24 h, temperature: 25°C).

Table 3. Langmuir, Freundlich and Dubinin–Radushkevich isotherm models parameters.

Isotherm	Parameter	Value	R^2
Langmuir	X_L (mol kg^{-1})	0.332	0.920
	K_L (L mol^{-1})	8521	
Freundlich	X_F	2.61	0.864
	β	0.296	
D-R	X_{DR} (mol kg^{-1})	0.990	0.976
	$K_{DR} \times 10^9 / \text{mol}^2 \text{KJ}^{-2}$	3.74	
	$E_{DR} / \text{kJ mol}^{-1}$	11.6	

reduced due to almost all empty active centres on Ch-Do composite were filled. Langmuir isotherm model defines monolayer adsorption in adsorption on homogeneous surfaces [45]. The maximum adsorption capacity was found to be $0.332 \text{ mol kg}^{-1}$ from Langmuir isotherm model and Langmuir constant was found in 8521 L mol^{-1} . The Freundlich isotherm model describes that the process is multi-layer heterogeneous adsorption [46]. Freundlich adsorption capacity, X_F was found 2.61 and β surface heterogeneity was also found as 0.296. Since the β value was between 0 and 1, the adsorption of Pb^{2+} onto Ch-Do composite was favourable [47]. The determination coefficient R^2 values calculated from Langmuir and Freundlich isotherm models were compared and, it was observed that the adsorption process was more suitably described as Langmuir isotherm. For the determination of adsorption energy were used from Dubinin–Radushkevich isotherm equations. If the adsorption energy is $8 < E < 16 \text{ kJ mol}^{-1}$, the adsorption is chemically controlled and $E < 8 \text{ kJ mol}^{-1}$ indicates that the adsorption proceeds physically [48]. The adsorption energy for Pb^{2+} onto Ch-Do composite was found to be 11.6 kJ mol^{-1} reveals the adsorption proceeds chemically.

3.4. Effect of contact time on adsorption

Three kinetic models were used to describe the adsorption of Pb^{2+} ions from an aqueous solution, namely: the pseudo-first-order (PFO), pseudo-second-order (PSO) and intra-particle diffusion (IPD) kinetic models. Kinetic model equations were presented in Table 1. When the Figure 6 examined, it was observed that the first 20 min of Pb^{2+} adsorption was rapid and Pb^{2+} adsorption reached equilibrium within 360 min (6 h). When the correlation coefficients of the PFO and PSO kinetic models were compared, it was seen that the adsorption kinetics was better fit with the PSO kinetic model. At the same time, when the experimentally calculated Q_t values and the theoretically calculated Q_e values were examined (Table 4), the results of the PSO kinetic model were found to be closer to each other. The adsorption kinetics showed that the adsorption process better adapted to PSO kinetic. These results

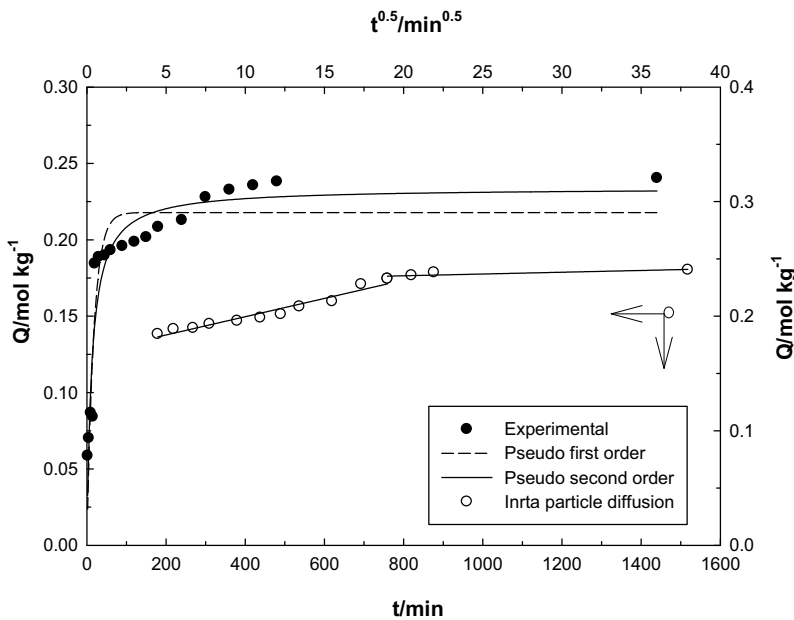


Figure 6. Compatibility of Pb^{2+} adsorption kinetics to pseudo-first order, pseudo-second order and intraparticle diffusion models ($[Pb^{2+}]_0: 500 \text{ mg L}^{-1}$, adsorbent dosage: 300 mg, natural pH: 4.0, contact time: 2–1440 min, temperature: 25°C).

Table 4. Pseudo first order, pseudo-second order and intraparticle diffusion kinetic models parameters.

Kinetic model	Parameter	Value	R^2
Pseudo first order	$Q_t/\text{mol kg}^{-1}$	0.240	0.876
	$Q_e/\text{mol kg}^{-1}$	0.218	
	$k_1 \times 10^3/\text{dk}^{-1}$	57.5	
	$H \times 10^3/\text{mol kg}^{-1} \text{ min}^{-1}$	12.5	
Pseudo second order	$Q_t/\text{mol kg}^{-1}$	0.240	0.904
	$Q_e/\text{mol kg}^{-1}$	0.234	
	$k_2 \times 10^3/\text{mol}^{-1} \text{ kg min}^{-1}$	0.304	
	$H \times 10^3/\text{mol kg}^{-1} \text{ min}^{-1}$	18.9	
Intra particle diffusion	$k_i \times 10^3/\text{mol kg}^{-1} \text{ min}^{-0.5}$	167	0.948

indicated that the adsorption process followed the PSO kinetic. Also, the IPD model has two linear components, that the adsorption process takes place primarily at the active centres on the adsorbent's surface, and that subsequent diffusion into the pores of the adsorbent is gradually occurred. According to these results, the adsorption of Pb^{2+} ions onto Ch-Do composite was controlled by chemisorption [49,50].

3.5. Effect of temperature on adsorption

Temperature is an important parameter for the adsorption process. In order to explain the thermodynamic behaviour of Pb^{2+} ions adsorption onto the Ch-Do composite, it was studied at temperatures of 5°C, 25°C, and 40°C and Figure 7 was obtained. In Figure 7 ($\ln K_D - 1/T$) the values of ΔH^0 and ΔS^0 were calculated from the slope of the graph and the cut-off, respectively. Adsorption enthalpy (ΔH^0 : 63.3 kJ mol^{-1}) indicated that the adsorption process was endothermic. Endothermic process cover the transferring of lead ions to the surface of solid. It also involves other stages such as dehydration, dissociation, complex forming and transferring on surface. On account of, all process needs heat in order to make start adsorption process. Adsorption entropy change (ΔS^0) was calculated as 266 $\text{J mol}^{-1} \text{K}^{-1}$. A positive entropy change indicated that the irregularity of the liquid/solid interface increases. Dissociation of water molecules from hydrated lead ions causes an increase at entropy. During the adsorption of Pb^{2+} onto Ch-Do composite increased in the randomness of the system. Gibbs energy change values were found as $-10.1 \text{ kJ mol}^{-1}$, $-15.5 \text{ kJ mol}^{-1}$ and $-19.4 \text{ kJ mol}^{-1}$ at 5°C, 25°C, and 40°C, respectively. The negative Gibbs energy values indicated that it increased the tendency to spontaneously with increasing temperature.

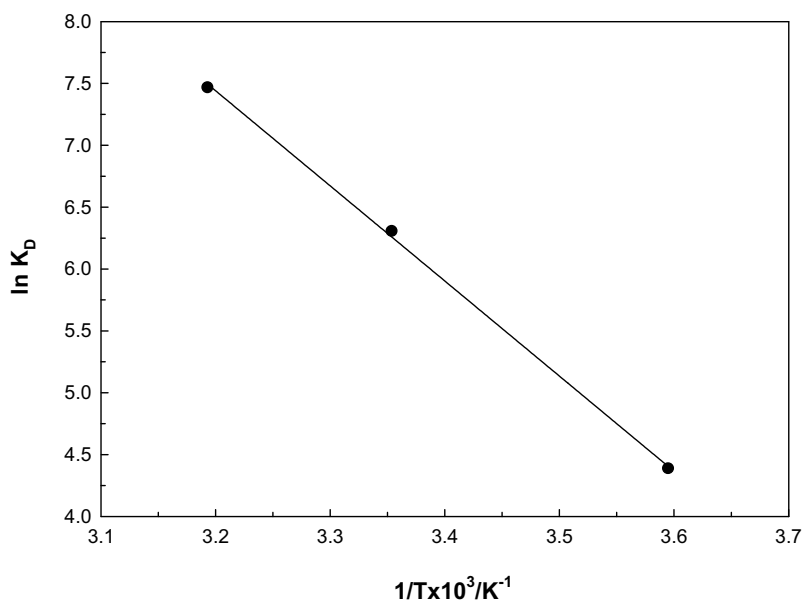


Figure 7. The effect of temperature on the adsorption. $\{[\text{Pb}^{2+}]_0\}$: 500 mg L^{-1} , adsorbent dosage: 100 mg, natural pH: 4.0, contact time: 24 h, temperature: 5°C, 25°C and 40°C.

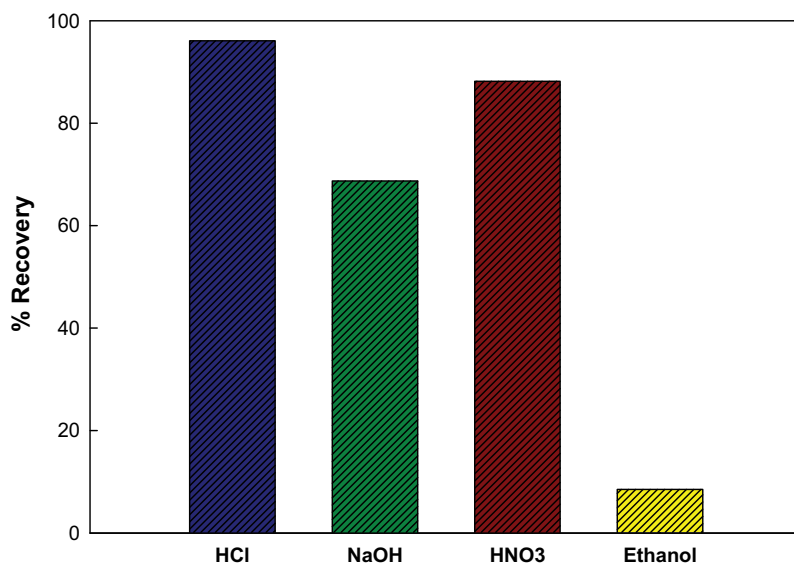


Figure 8. Recovery percent of various solvent for desorption of Pb^{2+} . $\{[Pb^{2+}]_0; 500 \text{ mg L}^{-1}$, adsorbent dosage: 100 mg, natural pH: 4.0, contact time: 24 h, temperature: 25°C}.

3.6. Desorption

Desorption investigated for Pb^{2+} ions onto Ch-Do composite. The obtained Pb^{2+} removal efficiency for three cycle is plotted in Figure 8. The percentage of Pb^{2+} desorbed for HCl, NaOH, HNO_3 and Ethyl alcohol were; 98%, 78%, 89%, and 1.5%, respectively. The maximum recovery percentage for Pb^{2+} ions onto Ch-Do composite was achieved with HCl. The minimum recovery percentage for Pb^{2+} ions onto Ch-D composite was achieved with Ethyl alcohol. Acidic solvents can easily desorb the adsorbed ions. Reusability studies showed that there were electrostatic interactions between Pb^{2+} ions and Ch-Do composite [51]. Due to Ch-Do composite has good reusability and high adsorption capacity, it can be used as a potential adsorbent in practical applications for removing of lead pollutants from wastewater.

3.7. Comparison with literature

In the literature, chitosan-based adsorbents with a wide range of adsorption capacities for Pb^{2+} have been studied. The maximum adsorption capacity obtained from the Langmuir model was used for the comparison of different chitosan composite adsorbents. As can be seen in Table 5, the maximum adsorption capacity of chitosan-dolomite composite

Table 5. Comparison of the adsorption capacities for adsorption Pb^{2+} onto chitosan-based adsorbents.

Adsorbent	Adsorption capacity/mol kg^{-1}	References
Chitosan/graphene oxide	0.543	[52]
Chitosan/sand	0.06	[53]
Chitosan/palygorskite	0.971	[54]
Chitosan saturated montmorillonite	0.347	[55]
Chitosan/graphene oxide	0.371	[56]
Chitosan/hydroxyapatite	0.06	[57]
Xanthate-modified magnetic chitosan	0.370	[58]
Chitosan/cellulose	0.13	[59]
Chitosan-GLA, chitosan-alginate	0.07;0.2	[60]
Chitosan/dolomite	0.332	This study

adsorbent ($0.332 \text{ mol kg}^{-1}$) exhibited better capacity values compared to most of the other chitosan-based adsorbents.

4. Conclusions

In this study, batch adsorption experiments were performed to remove Pb^{2+} from aqueous solution using Ch-Do composite. Optimal working parameters were found as pH of the solution: 4.0, adsorbent dosage: 100 mg, temperature: 25°C and contact time: 6 h. Under optimal conditions, the monolayer adsorption capacity was calculated as $0.332 \text{ mol kg}^{-1}$. The adsorption energy for Pb^{2+} onto Ch-Do composite was found to be $E_{\text{DR}}: 11.6 \text{ kJ mol}^{-1}$ reveals the adsorption proceeds chemically. The experimental kinetics were found that adsorption of Pb^{2+} onto Ch-Do well-described by the pseudo second-order rate kinetics. Thermodynamics parameters indicated that adsorption process was endothermic, possible and spontaneous. The recovery studies have shown that Ch-Do composite adsorbent has a good adsorption/desorption performance for ppm levels of Pb^{2+} . The new developed Ch-Do composite has very good properties such as high adsorption capacity for lead ions, high adsorption rate, and thermodynamically favourable, easy and economic preparation, environmental friendly, effective and cheap adsorbent and compatible with green chemistry concepts.

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Disclosure statement

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