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Adsorption characteristics of Pb(II) ions onto wasted iron ore tailing with phosphorus used as natural adsorbent from aqueous solution

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ABSTRACT

Iron ore tailing with phosphorus (IOTP), as industrial solid waste was used to remove Pb(II) ion from aqueous solution. Factors influencing the adsorption process were analyzed, and the related adsorption mechanism was discussed. The results indicate that the adsorption of Pb(II) ion onto IOTP is strongly dependent with pH value of the solution. An optimum adsorption capability is achieved at pH = 6.0. Complexation acts the vital mechanism for Pb (II) ion removal when pH varies from 1.5 to 7.0. While chemical precipitation plays an important role with pH rising beyond 7.0. Kinetic studies show that the removal of Pb(II) ion by IOTP is rapid with the removal capacity over 95% in 30 min. Adsorption kinetics follow the pseudo-second-order model. Langmuir and Freundlich isothermals are used to simulate equilibrium adsorption data, and it fits well with Langmuir isothermal model. The maximum capacity of adsorption is found to be 17.03 mg/g at 60°C. Thermodynamic study reveals that Pb (II) ion adsorption is spontaneous and endothermic. IOTP is a promising material for Pb (II) ion removal in wastewater treatment, due to the possession of both low cost and high adsorption capability.

Keywords: Iron ore tailing with phosphorus (IOTP); Pb(II) ion removal; Adsorption; Isotherm; Kinetics; Thermodynamic

1. Introduction

With the increasing emission of heavy metals (Pb, Cd, Hg, Cr, As, etc.) into environments, water pollution by heavy metals has become a serious issue nowadays. Among all the heavy metals, lead is one of the most toxic pollutants released into the environment, and it can be found in the effluents of battery manufacturing, metal smelting, alloys formation, mining and pigments industries [1–3]. Pb is easily concentrated by the food chain, which threatens human health [4]. The presence of Pb(II) ion at low concentrations in drinking water may cause human diseases like hepatitis, anemia, nervous diseases, nephrite syndrome, kidney failure, etc. Therefore, the removal of Pb(II) ion becomes an extremely urgent mission in the worldwide.

Up to now, there are lots of methods for Pb(II) ion removal, such as ion exchange, chemical precipitation, membrane filtration, flocculation, coagulation and adsorption. In these methods, adsorption is a promising technique of wastewater treatment, particularly for wastewater with low Pb(II) ion concentrations. Activated carbon is a conventional adsorbent for the removal of heavy metal ions from aqueous solutions, but due to high maintenance cost this adsorbent does not suit the needs of developing countries [5]. A great attention has been paid to low-cost adsorbents over past years, such as kaolinitic clay [6], blast furnace sludge [7], peat [8], palygorskite clay [9], keratin waste [10] and other materials [11–15]. The major advantages of using these materials or by-products for Pb(II) ion wastewater

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treatment are low cost, environmental friendliness, chemical stability (low solubility) and easy accessibility.

Iron ore tailing with phosphorus (IOTP) is an industrial solid waste derived from mining high phosphorus iron ores. IOTP is becoming an important problem in the world as a result of the fact that it not only cause landslide and dust pollution, but also occupy the land resources. For these reasons, their treatment and recycling are becoming an important problem for many provinces and regions of China. The main chemical components of IOTP are metal oxides (hematite), quartz, dolomite and the IOTP is characterized by low cost and high efficiency with regard to the removal of Pb(II) ion, phosphate ion and Cd(II) ion from wastewater [16–19]. In our previous paper [16], IOTP was employed as adsorbent for the Pb(II) ion removal from wastewater, and the effects of initial Pb(II) ion concentration, reaction time, reaction temperature and adsorbent dosage on the Pb(II) ion removal efficiency were investigated. The results showed that the Pb(II) ion removal efficiency exceeds 99% at ambient temperature under the optimized adsorption conditions, and the Pb(II) ion concentration of the treated wastewater completely meets with the requirement of national discharge standards of lead and zinc industrial pollutants (GB 25466-2010) (TPb (total Pb) = 0.5 mg/L) in China. It is well recognized that IOTP is an effective and low-cost adsorbent for Pb(II) ion adsorption. However, related studies of adsorption mechanism of IOTP, such as the isotherm, kinetic and thermodynamic adsorption of Pb(II) ion by IOTP minerals still remain an unexplored field. It is of great importance to study the adsorption mechanism of Pb(II) ion by IOTP to elucidate the absorption behaviour and reaction processes, and to optimize adsorption conditions in practice.

In present study emphasis is put on investigating Pb(II) ion adsorption isotherm, kinetics and thermodynamics on IOTP. Several kinetic models (including pseudo-first-order model, pseudo-second-order model, intra-particle diffusion model, and Elovich model) are used to fit the kinetic experimental data. Corresponding kinetic parameters are then calculated. The isotherm models of Freundlich and Langmuir equations are applied to evaluate the adsorption equilibrium.

2. Materials and methods

2.1. Materials

IOTP used in this study was obtained from Wushan, Chongqing, China, and its chemical composition is summarized in Table 1. The ores were crushed and sieved to obtain the adsorbent with particle size less than 0.147 mm. A stock solution of 1000 mg /L was prepared by dissolving a certain amount of chemically pure $Pb(NO_3)_2$ in deionized water. Pb(II) ion solutions in different concentrations were prepared by diluting the stock Pb(II) ion solution with deionized water. An appropriate volume of 0.1 mol/L HCl and NaOH was used to adjust the pH of the solution.

2.2. Adsorption experiments

Adsorption experiments were set up with the following procedures. First, a defined volume of Pb(II) ion stock solution was diluted to the required concentration by adding deionized water in 150 mL glass round-bottom flasks immersed in a thermostatic shaker bath. The pH value of the solution was then adjusted to the designed value and a defined amount of adsorbent was added. The mixture was stirred at 260 rpm for a fixed time scale, using a potentiometer to monitor the stirring speed. Liquid samples were collected at various time intervals and filtering process was applied to separate solid from liquid, then the filtrate was ready for Pb(II) ion analysis.

Table 1
Multielement chemical composition of IOTP (wt.%)

Component	wt.%
TFe*	25.49
SiO_2	16.13
CaO	20.76
MgO	7.99
Al_2O_3	5.55
MnO	0.36
V_2O_5	0.10
K_2O	0.25
Na_2O	0.06
P	1.26
F	0.77
S	0.04
IL**	10.11

* TFe is the total Fe in IOTP, which is consisted of Fe existed in Fe_2O_3 and ($FePO_4$).
** IL. is the loss of ignition, which is mainly caused by the decomposition of dolomite ($CaMg(CO_3)_2$).

The influence of initial pH value (varying from 1.5 to 12) on Pb(II) ion adsorption was examined under a constant IOTP dosage of 50 g/L, with a fixed initial Pb(II) ion concentration of 50 mg/L, and adsorption experiments were conducted at 25°C for 60 min.

Pb(II) ion adsorption kinetics were evaluated, with different initial Pb(II) ion concentrations (10, 40, 50, 60 and 100 mg/L) as well as various adsorption times (10, 30, 40, 50, 60 and 70 min) at 30°C, and the initial pH and IOTP dosage were fixed to 6.0 and 50 g/L, respectively.

The effect of adsorption temperature on Pb(II) ion removal and Pb(II) ion adsorption isotherms tests were studied at four different temperatures (30, 40, 50 and 60°C) for 30 min with fixed IOTP dosage of 50 g/L and pH value of 6.0, and the initial Pb(II) ion concentration varied from 10 to 100 mg/L.

2.3. Theoretical basis

In order to investigate the potential rate-controlling step of the Pb(II) ion adsorption process, several kinetics models including Elovich model, pseudo-first-order model, intra-particle diffusion model and pseudo-second-order model were employed to evaluate Pb(II) ion adsorption kinetics performance. The following Eqs. (1)–(5) were applied for describing the four kinetics models, respectively

[20–23]:

Elovich model: $Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$ (1)

Pseudo-first-order model: $Q_t = Q_e(1 - e^{-k_1 t})$ (2)

The linear equation of Eq. (2) model is as follows:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{3}$$

Intra-particle diffusion model: $Q_t = c + k_m t^{1/2}$ (4)

Pseudo-second-order model: $\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$ (5)

where t is the contact time of adsorption experiment (min); Q_e (mg/g) and Q_t (mg/g) are the adsorption capacity at equilibrium and a certain time t, respectively; α is the initial adsorption rate constant (mg/(g·min)) and the parameter β (g/mg) is related to the extent of surface coverage and activation energy for chemisorption; k_1 (min^{-1}) is the rate constant of the pseudo-first order model; k_m ($\text{mg/(g·min}^{0.5}\text{)}$) is the rate constant of the intra-particle diffusion model and c is obtained from the intercept; k_2 (g/(mg·min)) is the rate constant of the pseudo-second order model; the initial adsorption rate is $k_2 Q_e^2$ (mg/(g·min)).

Adsorption isotherms data were evaluated using the Langmuir and Freundlich models. The linear equations of these two experiential models are expressed in Eqs. (6) and (7), respectively [24,25]:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}} \tag{6}$$

$$\lg Q_e = \lg k + \frac{\lg C_e}{n} \tag{7}$$

where C_e is the equilibrium concentration of Pb(II) ion in the solution (mg/L), Q_e is the Pb(II) ion concentration in the solid adsorbent (mg/g), $C_{\max}$ is the maximum adsorption capacity (mg/g), k is a constant related to the adsorption capacity ($\text{mg}^{1-1/n}\text{L}^{1/n}\text{/g}$); b is a constant related to the energy of adsorption (L/mg), n is a constant related to the energy of adsorption.

The removal efficiency (w) and removal capacity of Pb(II) (Q_e) was calculated as follows:

$$w(\%) = \frac{C_o - C_e}{C_e} \times 100 \tag{8}$$

$$Q_e = \frac{(C_o - C_e)V}{m} \tag{9}$$

where C_0 and C_e are the initial and equilibrium concentrations of Pb(II) (mg/L), respectively. V is the volume of Pb(II) solution (L) and m is the mass of the adsorbent (g).

A further analysis of the Langmuir equation can be expressed by a dimensionless constant called equilibrium parameter R_0 [26].

$$R_0 = \frac{1}{1 + bC_o} \tag{10}$$

where b is the Langmuir constant and C_0 is the initial Pb(II) ion concentration (mg/g), R_0 values indicate the type of isotherm process whether it is irreversible adsorption ($R_0 = 0$), favorable adsorption ($0 < R_0 < 1$), linear adsorption ($R_0 = 1$) and unfavorable adsorption ($R_0 > 1$).

The change of Gibbs free energy ($\Delta G°$) is obtained using following relationship:

$$\Delta G^o = -RT\ln K \tag{11}$$

where R is the gas constant, K is the equilibrium constant which is numerically approximated the Langmuir constant b (L/mol) [27], and T (K) is the temperature.

Thermodynamic parameters enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) are evaluated by the following equation [28]:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{12}$$

$\Delta H°$ and $\Delta S°$ can be determined from the intercept and slope of $\Delta G°$ against T.

2.4. Characterization methods

The pH value of the aqueous solution was measured by pH meter (METTLER-TOLED). To follow the adsorption of Pb(II) ion by IOTP, the Pb(II) ion concentration of all samples including wastewater was analyzed by flame atomic absorption spectrophotometry method (TAS-986, Beijing Puxi Science and Technology Instrument Co., Ltd. China). The Pb(II) ion removal efficiency was calculated from the difference between the initial concentration (C_o) and the equilibrium one (C_e) using Eqs. (8), and the Pb(II) ion adsorption capacity was calculated by using the aforementioned Eq. (9). Fourier Transform infrared spectroscopy (FTIR) spectra of IOTP before and after adsorption were collected on a Nicolet 5DXC FTIR spectrophotometer (Nicolet Co., USA) using the transmission model (2 mg sample/100 mg spectral grade KBr). All IR measurements were implemented at room temperature. Phase analysis of IOTP was examined by X-ray diffraction (XRD) (Model D/max 2500 PC, Rigaku, Japan) with Cu Ka radiation. Microstructure of IOTP was observed by scanning electron microscopy (SEM) (Model JSM-7800F, JEOL, Japan). The particle size distribution and specific surface area of IOTP were characterized using nitrogen adsorption BET method by laser diffraction particle size analyzer (LDPSA) (Model MS 2000, Malvern, USA).

3. Results and discussion

3.1. Characteristics of IOTP

The X-ray diffraction pattern (Fig. 1) indicates that the crystalline phases in IOTP are mainly comprised of hematite (Fe_2O_3), dolomite ($CaMg(CO_3)_2$) and quartz (SiO_2). In addition, minor amount of fluorapatite ($Ca_5(PO_4)_3F$), rodolicoite ($FePO_4$) and calcium phosphate ($CaPO_4$) are presented in IOTP. Fig. 2 presents the typical SEM images of IOTP powders after being crushed and screened. It can be seen that the IOTP show notable non-uniformity in particle size. Besides, numerous fine IOTP particles are aggregated on the surface of coarse IOTP particle, resulting in a porous structure and rough surface. The powder has an average particle size of 20.9 μm and specific surface area of 1.12 m^2/g. The specific surface area of IOTP in present paper is slightly larger than that of other industrial wastes used for Pb(II) ion removal in previous paper [29]. In addition, particle size analysis (Fig. 3) shows a broad distribution of particle size i.e. 1.86% less than 1 μm, 95.78% between 1 and 100 μm and 2.36% more than 100 μm.

3.2. Influence of initial pH value on Pb(II) ion adsorption and FTIR analysis

pH value of aqueous solution is considered to be an important factor for the removal of Pb(II) ion. Fig. 4 shows the influence of initial pH value on the Pb(II) ion adsorption with the pH value varying from 1.5 to 12.0. The Pb(II) ion adsorption capacity escalates rapidly from 4.46 mg/g to 9.83 mg/g with the pH value increasing from 1.5 to 3.0. However, when the initial pH value ranged at 3.0–8.0, pH value has a weak influence on the Pb(II) ion adsorption capacity (keeps within 9.72–9.99 mg/g). Maximum adsorp-

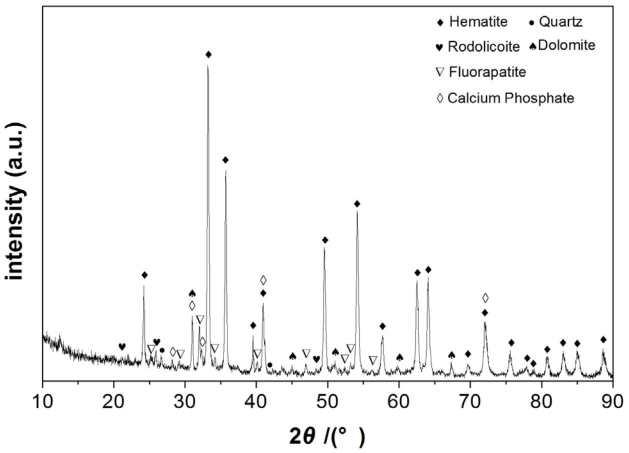

Fig. 1. XRD pattern of IOTP.

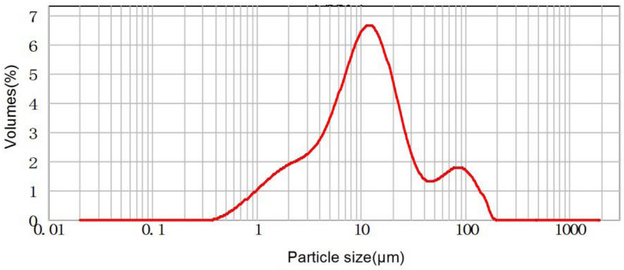

Fig. 3. Particle size distribution of IOTP.

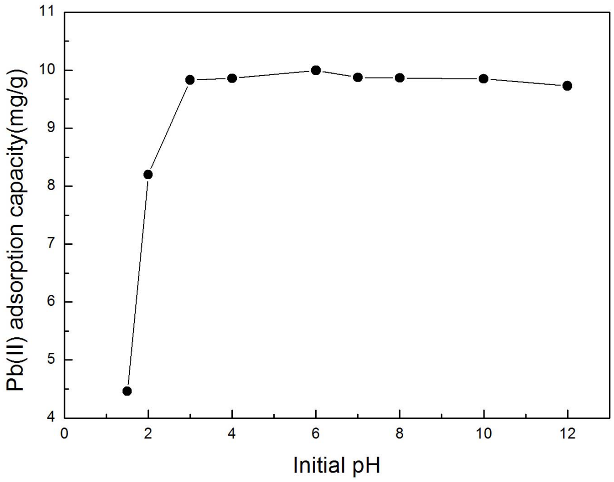

Fig. 4. Effect of pH on Pb(II) ion adsorption on IOTP, where the initial Pb(II) ion concentration, IOTP dosage, adsorption temperature and adsorption time were fixed to 50 mg/L, 50 g/L, 25°C and 60 min, respectively.

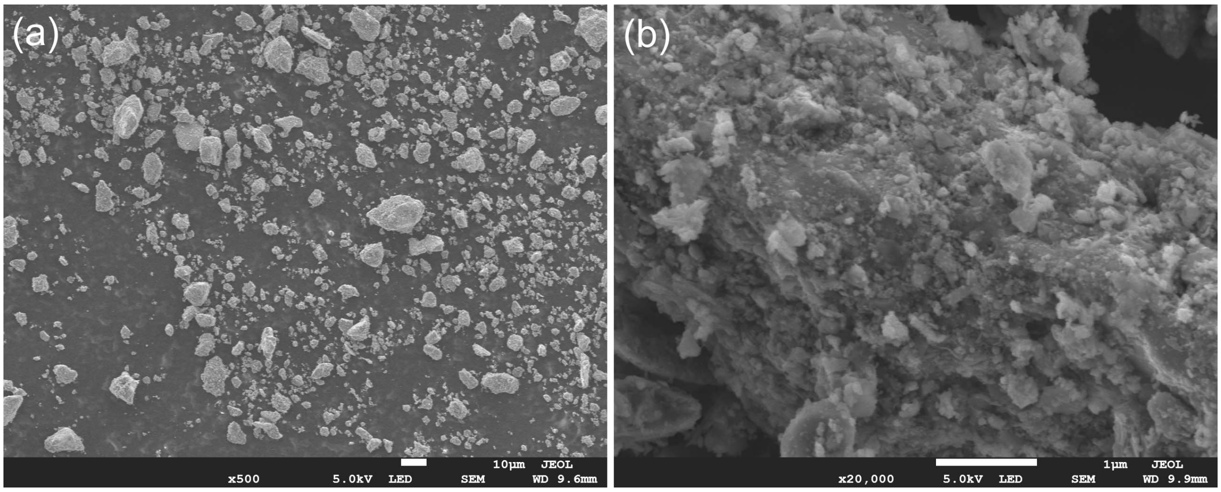

Fig. 2. SEM micrographs of IOTP at different magnifications (a) 500× and (b) 20000×.

tion capacity of 9.99 mg/g was obtained at pH 6.0. Whereas, when the initial pH value is above 6.0, the Pb(II) ion adsorption capacity decreases slightly with increasing pH.

The strong influence of pH value on the Pb(II) ion adsorption capacity can be attributed to the fact that pH determines the nature of the Pb(II) ion species as well as hydrolysis products on IOTP surface. Based on the previous work [30], Pb(II) in the solution could exist in several forms at various pH. With the pH increasing, the main form of Pb(II) in the solution transforms as the following sequence: Pb^{2+}, Pb(OH)$^{+}$, Pb(OH)$_2^{0}$ and Pb(OH)$_3^{-}$.

At low pH (<3.0), the main form of Pb(II) is Pb^{2+}, meanwhile, the high concentration of H$^+$ gives rise to the combination of adsorbent with hydronium ions. The protonation of adsorbent causes the rejection of Pb^{2+}, therefore, leads to competition and repulsion between H$^+$ and Pb(II) ions for active sites on the surface of adsorbent [31,32]. When the pH within the range of 3.0–7.0, most of the active sites were occupied, H$^+$ ions were less available. Then, more Pb (II) ions can get access to adsorption sites, and the hydroxy complexes absorption will be favored. Thereby, the improved adsorption capability will be attained. Whereas, Pb (II) would exist in the form of Pb(OH)$_2$ in alkaline condition as the pH escalating above 7.0.

Metal sorption is well correlated to the specific surface of the adsorbent [33]. As mentioned above, IOTP has high amount of hematite, dolomite and quartz. Surfaces of oxide and dolomite in aqueous suspension usually coordinate water molecules [18,34], hence IOTP surfaces will be covered by surface hydroxyl groups. The functional groups play an important role in the adsorption of Pb(II) ion onto the IOTP. To clarify the adsorption mechanisms of Pb(II) ion on the IOTP, the FTIR spectra (Fig. 5) of IOTP samples before and after adsorption were analyzed. The adsorption experiment was carried out in Pb(NO$_3$)$_2$ solution at 30 °C for 30 min, with initial Pb(II) ion concentration 50 mg /L, IOTP dosage 50 g/L, pH 3.0 and stirring speed of 260 rpm. Two valleys at 3455 cm^{-1} and 1635 cm^{-1} are observed in Fig. 5, which arise from the bending and stretching vibrations of H-O-H (physisorbed water molecule) [18,35]. The bands at 1100, 1034, 913 and 800 cm^{-1} could be attributed to the stretching mode of multicentered hydroxyl group S-OH (where S represents a central ion of the mineral surface) [36]. After IOTP reacting with Pb(II) ion solution, the S-OH bands at the four valleys (1100, 1034, 913 and 800 cm^{-1}) are all completely disappeared, while two new valleys appear at 1022 and 884 cm^{-1}. The new bands could be primarily involved in the formation of inner-sphere surface complex (S-O-Pb) between Pb(II) ion and adsorbent. This indicates that the surface hydroxyl groups (S-OH) are exchanged by the adsorbed Pb(II) ion. Fig. 6 illustrates the proposed mechanism for Pb (II) ion adsorption process, leads to the conclusion that Pb (II) ion adsorption at pH 3.0 would occur at the aqueous Pb(II) ion/IOTP interface. It is also implies that the replacement of surface hydroxyl groups by the Pb(II) ions (complexation) is the predominant adsorption mechanism.

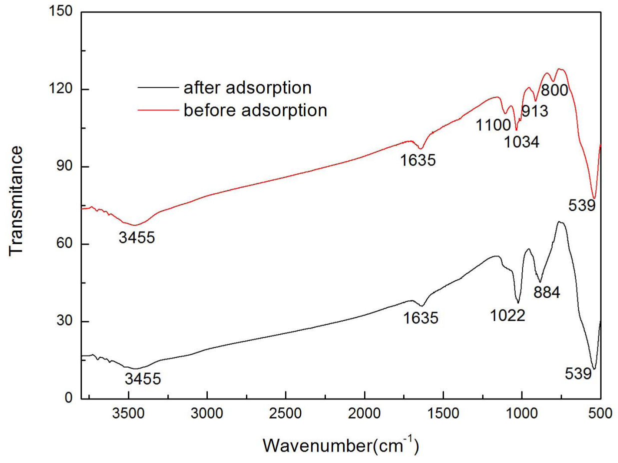

Fig. 5. FTIR spectra of IOTP samples before and after Pb(II) ion adsorption; the adsorption experiments were carried out at 30°C, and the pH value, the initial Pb(II) ion concentration, IOTP dosage, and adsorption time were fixed to 3.0, 50 mg/L, 50 g/L, and 60 min, respectively.

3.4. Pb(II) ion adsorption kinetics

The results of Pb (II) ion adsorption kinetics with different initial Pb (II) ion concentrations in Fig. 7 shows adsorp-

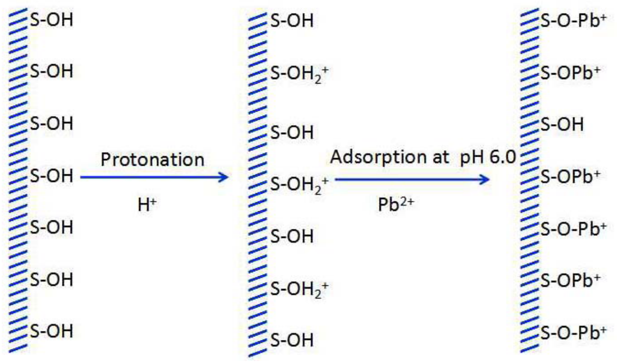

Fig. 6. Schematic diagram of the major mechanism for adsorption of Pb(II) ion onto the surface of IOTP.

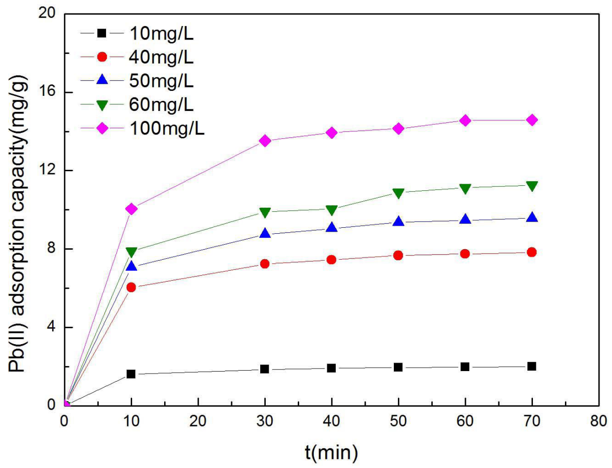

Fig. 7. The variation of adsorption capacity of IOTP with adsorption time at various initial Pb(II) ion concentrations, where the initial pH, IOTP dosage, and adsorption temperature were fixed to 6.0, 50 g/L and 30°C, respectively.

tion is very fast initially and the removal capacity over 95% is recorded within 30 min. Whereas, the adsorption capacity slows with the prolonged reaction time. Ample adsorption sites and the higher solute concentration gradient may account for the observed rapid adsorption during incipient stage. With the reaction further progressed, the availability of adsorption sites and the Pb(II) ion concentration are reduced, thus decreasing Pb(II) ion uptake rate.

In order to investigate the mechanisms of Pb(II) ion adsorption process, the linearized equations of Elovich model, intra-particle diffusion model, pseudo-first-order model and pseudo-second-order model kinetic models are adopted to fit experimental results, and the fitted plots are shown in Figs. 8a–d. In addition, the corresponding rate constants, and the correlation coefficient (R^2) are listed in Table 2. Compared with the Elovich model, intra-particle diffusion model and pseudo-first-order model, the pseudo-second-order model agrees well with the experimental data. Moreover, the correlation coefficients (R^2) of pseudo-second-order model in all different initial Pb(II) ion concentrations are all above 0.99, which are higher than those of the above three models. These results indicate that the adsorption system studied satisfied the pseudo-second-order kinetic model. Also this suggests the Pb(II) ion uptake process is due to chemisorption, which implies the chemical sorption reaction is the rate-limiting step [37], and the adsorption capacity is proportional to the amount of active sites [38]. Similar phenomena have been observed in the adsorption of Pb(II) ion on microbial flocculant GA1 [2], copper oxide nanostructures [3], sulphonated biomass (S-III) of Cicer arietinum [39] and activated carbon prepared from Polygonum orientale Linn [40].

3.5. Pb(II) ion isotherm adsorption

The results of Pb(II) ion adsorption isotherm experiments at 30, 40, 50 and 60 °C are shown in Fig. 9. The adsorption capacity obviously increases with the temperature rising from 30 to 60°C. The observed enhancement in the adsorption capacity with an increasing of the temperature indicates that the adsorption process is endothermic in nature. Therefore, the higher temperature favors more efficient Pb(II) ion removal by adsorption onto IOTP.

The interaction and distribution of Pb(II) ions on the surface of adsorbent can be explained by adsorption isotherm study [41,42]. In order to further investigate the behavior of Pb(II) ion adsorption on IOTP, the isotherm data from Fig. 9

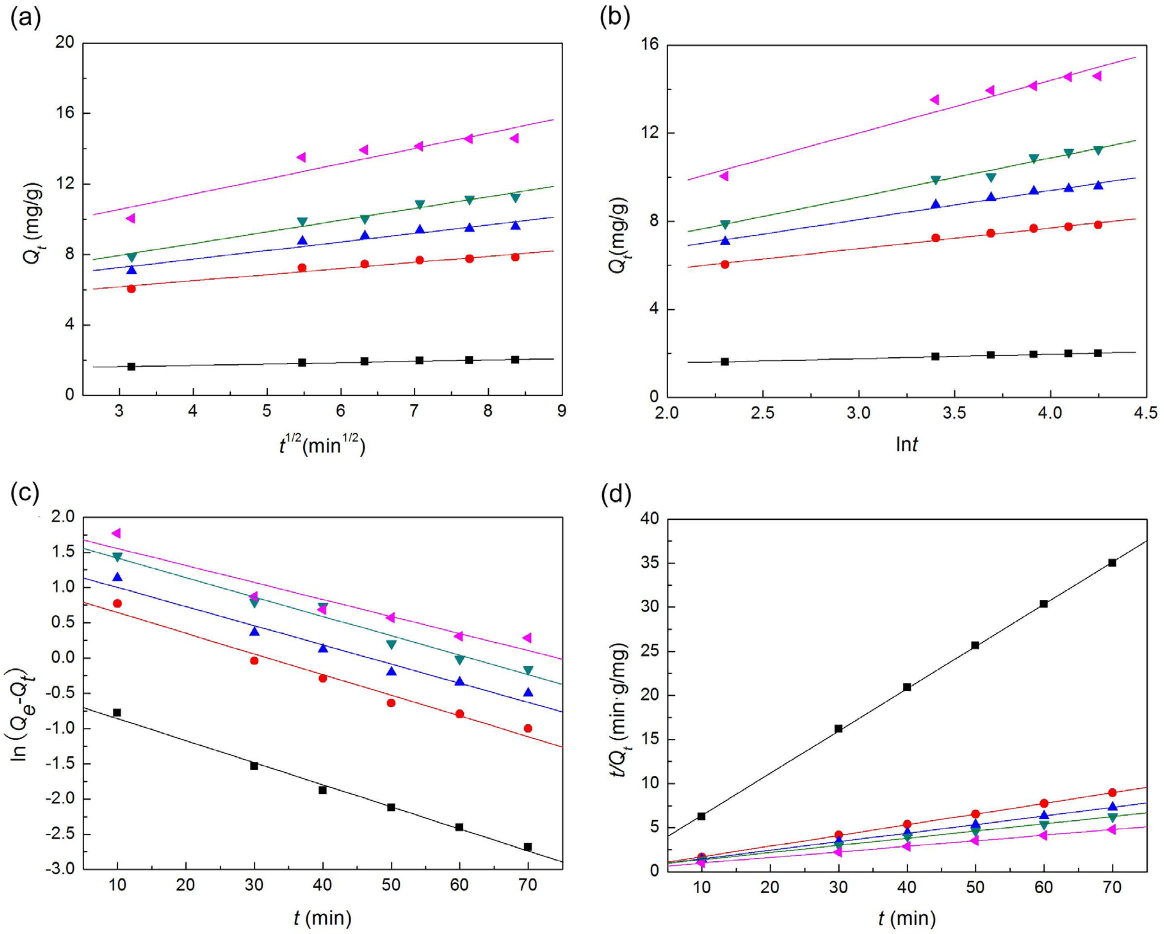

Fig. 8. Linearized form plots of different kinetic models for Pb(II) ion adsorption on IOTP. (a) intra-particle diffusion model; (b) Elovich model; (c) pseudo-first-order model; (d) pseudo-second-order model; the adsorption experiments were carried out with fixing the initial pH, IOTP dosage, and adsorption temperature to 6.0, 50 g/L and 30°C, respectively.

Table 2
Estimated kinetic model parameters for Pb(II) ion adsorption on IOTP

Intra-particle diffusion model $Q_t = c + k_m t^{1/2}$			
Initial Pb(II) ion concentration (mg/L)	c	k_m (mg/(g·min$^{0.5}$))	R^2
10	1.4056	0.0753	0.9508
40	5.1289	0.3459	0.9338
50	5.7987	0.4848	0.9337
60	5.9606	0.6641	0.9671
100	7.9581	0.8663	0.8824
Elovich model $Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$			
Initial Pb(II) ion concentration (mg/L)	α (mg/(g·min)	β (g/mg)	R^2
10	57.7169	4.9123	0.9933
40	61.6319	1.0630	0.9859
50	30.1188	0.7586	0.9858
60	15.0201	0.5642	0.9835
100	18.2336	0.4189	0.9565
Pseudo-first-order model $\ln(Q_e - Q_t) = \ln Q_e - k_1 t$			
Initial Pb(II) ion concentration (mg/L)	k_1 (min^{-1})	Q_e (mg/g)	R^2
10	0.03131	2.0682	0.9915
40	0.02932	8.1980	0.9734
50	0.02720	10.1833	0.9656
60	0.02656	12.1146	0.9743
100	0.02414	15.9217	0.9061
Pseudo-second-order model $\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$			
Initial Pb(II) ion concentration (mg/L)	k_2 (g/(mg·min))	Q_e (mg/g)	R^2
10	0.1410	2.0881	0.9998
40	0.0304	8.2583	0.9999
50	0.0206	10.2135	0.9998
60	0.0121	12.2654	0.9970
100	0.0117	15.7803	0.9997

were fitted to Langmuir and Freundlich equations. The fitted Langmuir and Freundlich plots are shown in Fig. 10 (a) and (b), respectively. The isotherm constants, correlation coefficient (R^2) are listed in Table 3. The R^2 values indicate that Langmuir plots are better fitted with the experimental data as compared to the Freundlich plots. So the isothermal of Pb (II) ion adsorption on the IOTP obeys the Langmuir equations. The trend also suggests that IOTP has a relatively higher monolayer adsorption capacity, which supports the possibility of the adsorption mechanism mentioned above.

Compared to other low-cost adsorbents, IOTP is one of the most promising materials to remove Pb(II) ion. As seen from Table 4, the maximum adsorption capacity (Q_{max})

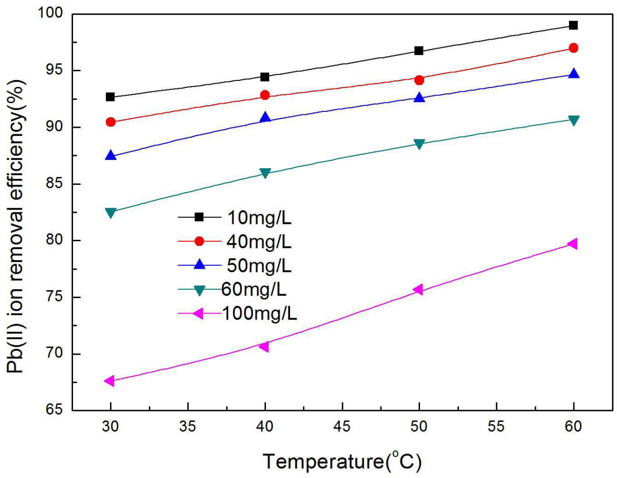

Fig. 9. Effect of adsorption temperature on Pb(II) ion removal by IOTP, where the initial pH, IOTP dosage, and adsorption time were fixed to 6.0, 50 g/L and 30 min, respectively, and the initial Pb(II) ion concentration varied from 10 to 100 mg/L.

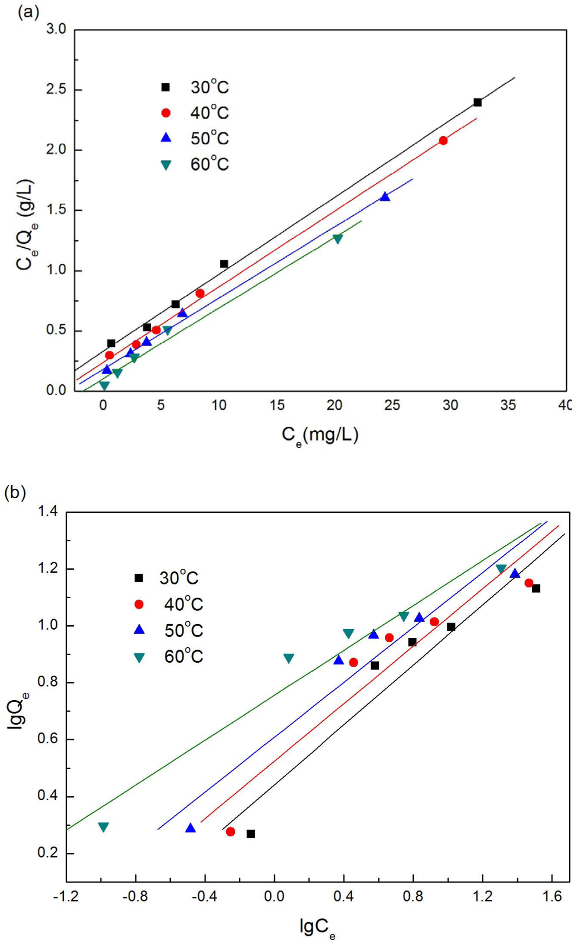

Fig. 10. Linearized form plots of isotherm for Pb(II) ion adsorption on IOTP: (a) Langmuir isotherm; (b) Freundlich isotherm, where the initial pH, IOTP dosage, and adsorption time were fixed to 6.0, 50 g/L and 30 min, respectively, and the initial Pb(II) ion concentration varied from 10 to 100 mg/L.

Table 3
Estimated isotherm parameters for Pb(II) ion adsorption on IOTP

Temperature/°C	Langmuir isotherm $\frac{C_e}{Q_e}=\frac{1}{bQ_{\max}}+\frac{C_e}{Q_{\max}}$			Freundlich isotherm $\lg Q_e=\lg k+\frac{\lg C_e}{n}$		
	b (L/mg)	$Q_{\max}$ (mg/g)	R^2	k ($mg^{1-1/n}L^{1/n}/g$)	$1/n$	R^2
30	0.1933	15.62	0.9977	2.7645	0.5267	0.9086
40	0.2606	15.92	0.9980	3.3476	0.5049	0.8869
50	0.3245	16.90	0.9966	4.0622	0.4825	0.9316
60	0.5624	17.03	0.9882	5.7030	0.3945	0.9522

Table 4
Comparison of maximum of Pb(II) ion adsorption conditions and capacities of different adsorbents

No.	Material	Initial Pb(II) ion concentration (mg/L)	pH	Temperature (°C)	Adsorption capacity (mg/g)	References
1	Manganese oxide-coated sand	20–320	4.0	45	9.22	[47]
2	Fly ash	5–150	6.6	20	15.08	[45]
3	Bentonite	0–100	11.0	30	6.00	[46]
4	Iron oxide	5–25	5.5	55	36.00	[48]
5	Activated carbon	5–150	6.0	30	35.00	[49]
6	Oxidized MWCNTs	500–10000	6.0	20	2.06	[43]
7	Turkish clay (Celtek)	50–500	7.0	20	18.08	[50]
8	Kaolin	50–100	6.0	25	4.5	[44]
9	Blast furnace slag	50–100	6.0	25	5.52	[44]
10	IOTP	10–100	6.0	60	17.03	This study

Table 5
Computation result of R_0

R_0 C_0 (mg/L) b (L/g)	10	40	50	60	100
0.1933	0.3409	0.1145	0.0938	0.0794	0.0492
0.2606	0.2773	0.0875	0.0713	0.0601	0.0370
0.3245	0.2355	0.0715	0.0580	0.0488	0.0299
0.5624	0.1510	0.0426	0.0343	0.0288	0.0175

of IOTP is 17.03 mg/g at ambient temperature for 30 min when pH = 6.0, and initial Pb(II) ion concentration are 10–100 mg/L. The adsorption capacity of IOTP is about 8.26 times of the adsorption capacity of Oxidized MWCNTs [43], 3.78, 1.13 and 2.83 times of the adsorption capacity of Kaolin [44], fly ash [45] and bentonite [46], respectively.

In present work, the essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant (R_0) , the R_0 values on the initial Pb(II) ion concentrations of 10 mg/L, 40 mg/L, 50 mg/L, 60 mg/L and 100 mg/L are listed in Table 5. The R_0 values were found to be in the range of 0–1 for all the concentrations of Pb(II) ion studied. Pb (II) ions adsorption by IOTP is therefore considered to be a favorable adsorption.

3.6. Thermodynamic parameters of adsorption

Adsorption isotherm results indicate that Pb(II) ion adsorption on the IOTP is endothermic reaction. Thermodynamic parameters including standard free energy ($\Delta G°$), standard enthalpy ($\Delta H°$) and standard entropy ($\Delta S°$) were determined, in order to explain the effect of temperature on the Pb(II) ion adsorption.

Thermodynamic parameters for the adsorption of Pb(II) ion on IOTP are listed in Table 6, the values of $\Delta G°$ were –9.29, –10.38, –11.30 and –13.17 kJ/mol at 303, 313, 323 and 333 K, respectively. The negative values of $\Delta G°$ indicate the spontaneous nature of adsorption and thermodynamically favorable. The decrease in $\Delta G°$ values with temperature increasing implies that higher temperature favor the adsorption of Pb(II) ion onto IOTP. Values of $\Delta H°$ and $\Delta S°$ are calculated from the slope and intercept of $\Delta G°$ against T (Fig. 11). The endothermic nature of Pb(II) ion adsorption at 30–60°C is exemplified by positive values of $\Delta H°$. Moverover, the positive value of $\Delta S°$ suggests that the randomness at the solid-solution interface increase during the Pb(II) ion adsorption, which is attributed to the water molecules released from the hydrated ions or water molecules present on the surface of IOTP during the adsorption process [51].

Endothermic adsorption of Pb(II) ion has also been observed on wheat bran [52], sawdust [53] and peat [54,55], and the value of $\Delta H°$ in present work (28.91 KJ/mol) is

Table 6
Thermodynamic parameters for the adsorption of Pb(II) ion on IOTP

Temperature (K)	$\Delta G°$ (KJ/mol)	$\Delta H°$ (KJ/mol)	$\Delta S°$ (J/mol K))
303	–9.29	28.91	125.60
313	–10.38		
323	–11.30		
333	–13.17		

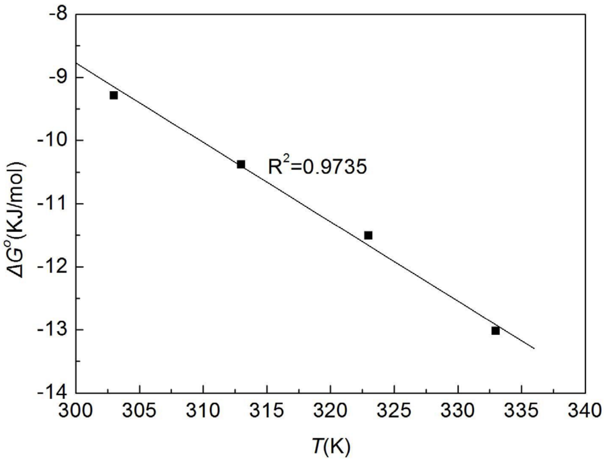

Fig. 11. Plot of $\Delta G°$ vs. T for Pb(II) ion adsorption by IOTP, where the initial pH, IOTP dosage, and adsorption time were fixed to 6.0, 50 g/L and 30 min, respectively, and the initial Pb(II) ion concentration varied from 10 to 100 mg/L.

almost equal to that of Pb(II) ion adsorption on sawdust (31.47 KJ/mol). In addition, the value of $\Delta H°$ indicates the nature of Pb(II) ion adsorption on IOTP is chemical adsorption (physical adsorption (2.1~20.9 kJ/mol) or chemical adsorption (20.9~418.4 kJ/mol))[56].

4. Conclusions

IOTP, a low-cost industrial waste was used as an adsorbent to remove Pb(II) ion from aqueous solution. The influence of pH value on Pb(II) ion adsorption capacity was investigated. In addition, Pb(II) ion adsorption kinetics, adsorption isotherm and thermodynamic parameters of adsorption were evaluated. Based on the results of this study, the following conclusions can be reached.

(1) pH value has a significant effect on the adsorption of Pb(II) ion on IOTP. The optimum pH value for Pb(II) ion adsorption is 6.0. FTIR analyses indicates that Pb(II) ion adsorption onto IOTP follows complexation mechanism when pH sits in the range of 1.5–7.0. While pH > 7.0, the chemical precipitation played an important role in Pb(II) ion removal.

(2) The adsorption capacity of IOTP increases with the initial Pb(II) ion concentration increasing. IOTP removes Pb(II) ion from aqueous solution rapidly. The adsorption kinetics are well described by the pseudo-second-order kinetic model. The mechanism of the Pb(II) ion removal process is mainly controlled by chemisorption, which is the rate-determining step.

(3) Elevating adsorption temperature favors the adsorption of Pb(II) ion on IOTP. The isotherm of Pb(II) ion adsorption on the IOTP at different temperatures agrees well with Langmuir equations. The maximum adsorption capacity of IOTP is 17. 03 mg/g at 60°C.

(4) Thermodynamic studies indicated that the Pb(II) ion adsorption on IOTP is spontaneous and endothermic.

(5) IOTP have the potential to be utilized for cost-effective removal of Pb (II) ion from aqueous solution, based on its low cost and good adsorption capability.

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