



piperazinyl] ethanesulphonic acid (HEPES) used for the purpose of buffering was purchased from Sigma–Aldrich. 5 mol L<sup>-1</sup> HCl and 5 mol L<sup>-1</sup> NaOH were used to adjust the solution pH.

## 2.2. Xanthation of orange peel

Pristine orange peel was washed with double distilled water and dried at 70 °C inside a convection oven for 24 h. The dried orange peel was crushed and sieved to a smaller particle by a bolt with the diameter of 0.15 mm. The obtained product was named as OP for further adsorption study.

About 50 g of OP were soaked in a mixture of 250 mL ethanol and 250 mL 1% NaOH solution at room temperature (20 °C) for 24 h to remove chlorophyll pigments and other low molecular weight compounds. After decantation and filtration, the treated biomass was washed with double distilled water until the solution reached a neutral pH value around 7.0, and then dried at 70 °C inside a convection oven. This dried product was prepared as the raw material for xanthation.

Xanthation process was carried out basically according to Wing et al.'s [17] procedure with some modifications. About 15 g of the dried product was taken in a 300 mL Erlenmeyer flask and 200 mL 4 M NaOH was added into it. The sample was stirred at room temperature for 3 h and again for another 3 h after the addition of 10 mL carbon disulphide (CS<sub>2</sub>). This mixture was then allowed to settle for 1 h and the supernatant was decanted. Excess alkali was removed by washing with double distilled water. The mixture was then washed with acetone and dried and stored at low temperature (6–8 °C). This product was abbreviated as XOP hereafter.

## 2.3. Batch adsorption experiment

The optimum pH for adsorption was determined by mixing 50 mg of the adsorbent OP and XOP and 10 mL 100 mg L<sup>-1</sup> of the Pb<sup>2+</sup> solutions of different initial pH values into separate stoppered bottles, HEPES was used as buffer. The mixture was shaken at a speed of 120 rpm for 3 h at 30 °C. After adsorption, the metal ion concentrations in the supernatant liquor were determined by using an AA-6650 atomic absorption spectro-photometer (Shimadzu).

Adsorption isotherms were conducted by batch experiments at 30 °C and pH 5.0 for 1.5 h. Other experimental parameters were as described above. The kinetic experiments were carried out inside 250 mL stoppered conical flasks, containing 0.5 g adsorbent and 100 mL of 100 mg L<sup>-1</sup> Pb<sup>2+</sup> solution at different temperatures (10 and 20 °C) and pH 5.0 for 2 h. The samples were collected at desired time intervals and filtered immediately.

The amount of metal adsorbed ( $q_e$ ) was determined by using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where  $C_0$  and  $C_e$  represent the initial and equilibrium metal ions concentrations (mg L<sup>-1</sup>), respectively;  $V$  is the volume of the solutions (mL) and  $m$  is the amount (mg) of adsorbent.

## 2.4. Characterization of the adsorbents

FTIR spectra of the adsorbents (OP and XOP) were taken with a Fourier-transform infrared spectrophotometer (JASCO FT/IR-410, Japan). Pressed pellets were prepared by grinding the powder specimens with spectroscopic grade KBr for FTIR spectra test. Zeta potentials of OP and XOP were measured over the pH range of 2.0–7.0 on a Malvern Zetasizer (Model ZEN 2010, Malvern Instrument, Co., UK).

## 3. Results and discussion

### 3.1. Characterization of the adsorbents

FTIR spectra of OP and XOP are shown in Fig. 1. In OP spectrum, the broad and intense absorption peaks at around 3420 cm<sup>-1</sup> correspond to the O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin [18], thus, showing the presence of “free” hydroxyl groups on the adsorbent surface. The peaks at 2924 cm<sup>-1</sup> are attributed to the symmetric and asymmetric C–H stretching vibration of aliphatic acids [19]. The peak observed at 1744 cm<sup>-1</sup> is the stretching vibration of bond due to non-ionic carboxyl groups (–COOH, –COOCH<sub>3</sub>), and may be assigned to carboxylic acids or their esters [19]. The peaks at 1638 and 1434 cm<sup>-1</sup> are due to asymmetric and symmetric stretching vibrations of C=O in ionic carboxylic groups (–COO<sup>-</sup>), respectively [20]. Aliphatic acid group vibration at 1267 cm<sup>-1</sup> may be assigned to deformation vibration of C=O and stretching formation of –OH of carboxylic acids and phenols [21]. Peaks at 1068 cm<sup>-1</sup> may be due to stretching vibration of C–OH of alcoholic groups and carboxylic acids [21]. Some distinct changes are noted in the spectrum of XOP. The broad peak at 3419 cm<sup>-1</sup> in the pristine OP shifts to 3409 cm<sup>-1</sup> in the XOP, which indicates that the hydroxyl groups have combined with CS<sub>2</sub>. The presence of sulfur groups in the XOP has been identified by the appearance of new peaks at 538.3, 1019.6 and 1151.3 corresponding to  $\gamma_{C-S}$ ,  $\gamma_{C=S}$  and  $\gamma_{S-C-S}$  [10].

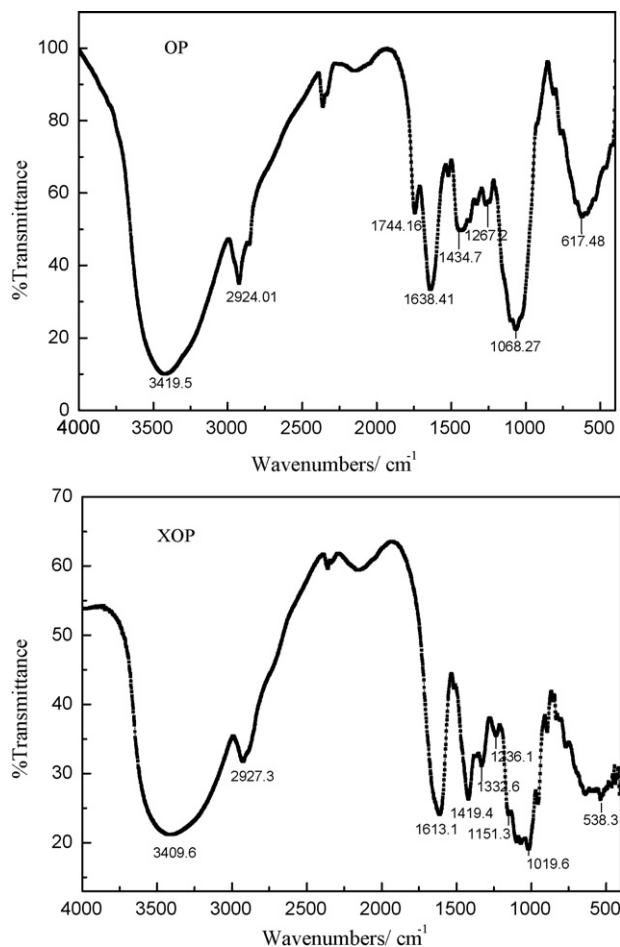


Fig. 1. FTIR spectra of OP and XOP.

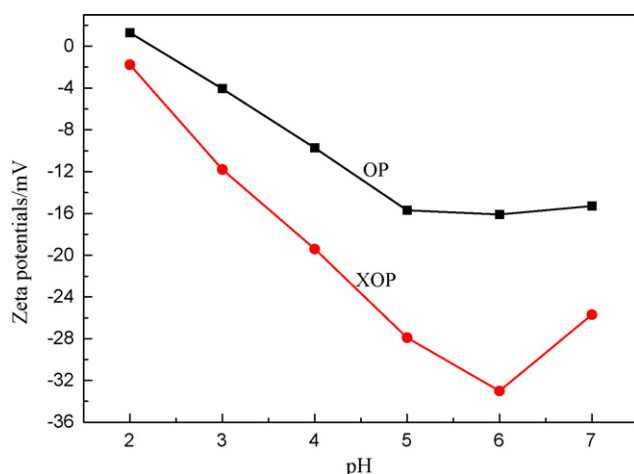


Fig. 2. Zeta potentials of OP and XOP.

The zeta potentials of OP and XOP at the pH range of 2.0–7.0 were measured and the results are shown in Fig. 2. It can be seen that the absolute values of zeta potentials of XOP were larger than those of OP, which indicates that XOP has higher physical stability and surface activity.

### 3.2. Effect of equilibrium pH on adsorption

The metal ion adsorption is affected by the pH of the solution thereby changing the surface charge of the adsorbent and metal speciation. The influence of equilibrium pH on the adsorption of  $Pb^{2+}$  by OP and XOP is shown in Fig. 3. It can be observed from this figure that XOP exhibits higher adsorption efficiencies of  $Pb^{2+}$  than OP within the range of 2.0–7.0, which is consistent with the phenomenon in Fig. 2. Based on the fact that the pH of industrial wastewater is generally around 5, we chose pH 5.0 as the experimental condition for adsorption studies thereafter.

### 3.3. Adsorption isotherms

Both OP and XOP were used as adsorbents to determine the adsorption capacity on lead ions. The equilibrium adsorption isotherm experiments were performed by plotting metal ions adsorbed ( $q_e$ ) against the equilibrium concentration of lead ions ( $C_e$ ) in solution (Fig. 4). Obviously, the adsorption capacity of XOP

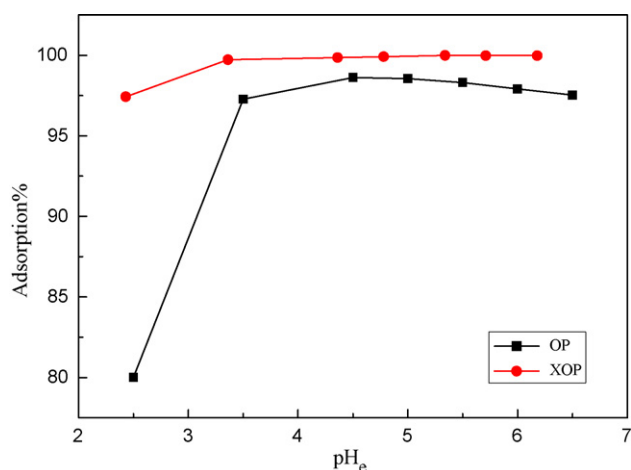


Fig. 3. The effect of  $pH_e$  on  $Pb^{2+}$  adsorption process.

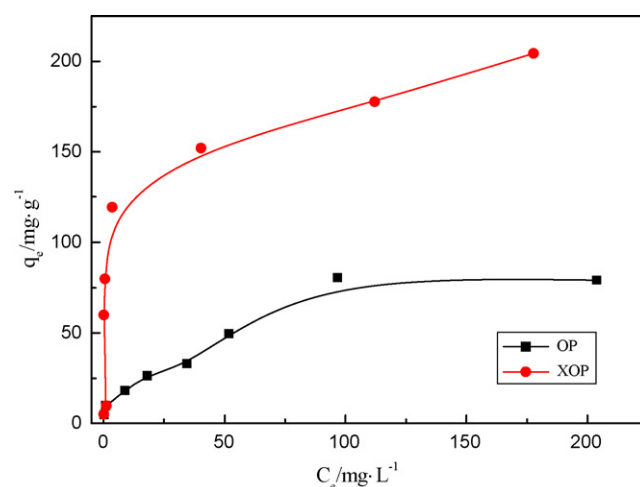


Fig. 4. Adsorption isotherms of  $Pb^{2+}$  on OP and XOP.

is much larger than OP, which indicates the effectiveness of the xanthation process.

Both Langmuir (3) and Freundlich (4) models were used to analyze the isotherm data [22,23]:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where  $q_m$  is the maximum amount of adsorption ( $mg\ g^{-1}$ ),  $b$  the adsorption constant ( $L\ mg^{-1}$ ),  $K_F$  the constant representing the adsorption capacity, and  $n$  is the constant depicting the adsorption intensity.

Table 1 shows the applicability of Langmuir and Freundlich models respectively for  $Pb^{2+}$  adsorption on OP and XOP. For OP, Freundlich model fits better with the isotherm data than Langmuir model, whereas for XOP the opposite is the case. The theoretical monolayer capacity ( $q_m$ ) of  $Pb^{2+}$  on XOP has been obtained as  $204.50\ mg\ g^{-1}$ , which indicates ~150% increase in adsorption capacity towards lead ions compared to that of OP ( $89.77\ mg\ g^{-1}$ ). The enhancement in metal adsorption capacity can be explained on the basis of Pearson rule [24]. According to this rule, soft bases are likely to form stable complexes with metals such as copper, cadmium and lead. Since xanthate group can be classified as soft bases, xanthated biomass will certainly show a much higher adsorption capacity in comparison with that of pristine biomass. A comparison of  $Pb^{2+}$  adsorption capacity of some other biosorbents reported in literatures is listed in Table 2.

### 3.4. Adsorption kinetics

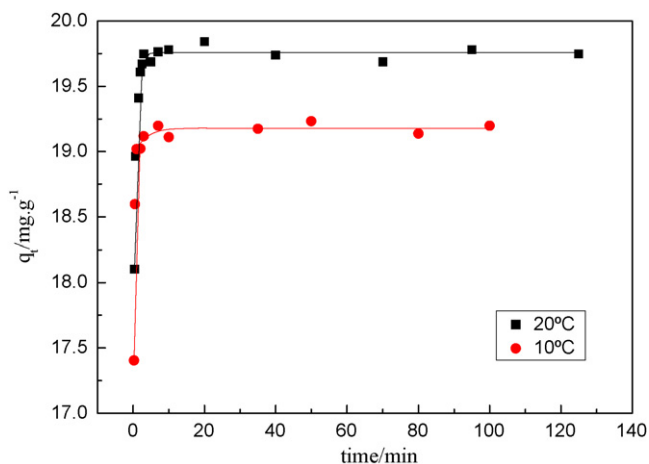
One of the most important features of the adsorbent material is the rate with which the solid phase adsorbs metal ions from the aqueous solutions and attains equilibrium. It can be seen from Fig. 5, at both temperatures, the adsorption of  $Pb^{2+}$  on XOP at an initial metal ion concentration of  $100\ mg\ L^{-1}$  can attain equilibrium within

**Table 1**  
Isotherm data of OP and XOP presented in terms of linearized Langmuir and Freundlich models, respectively.

Adsorbent	Langmuir			Freundlich		
	$q_m$ ( $mg\ g^{-1}$ )	$b$ ( $L\ mg^{-1}$ )	$R^2$	$K_F$ ( $mg\ g^{-1}$ )	$1/n$	$R^2$
OP	89.77	0.0349	0.9263	8.5672	0.4284	0.9703
XOP	204.50	0.1318	0.9810	42.8450	0.3088	0.5195

**Table 2**  
Lead adsorption capacity of some agricultural by-products reported in the literature.

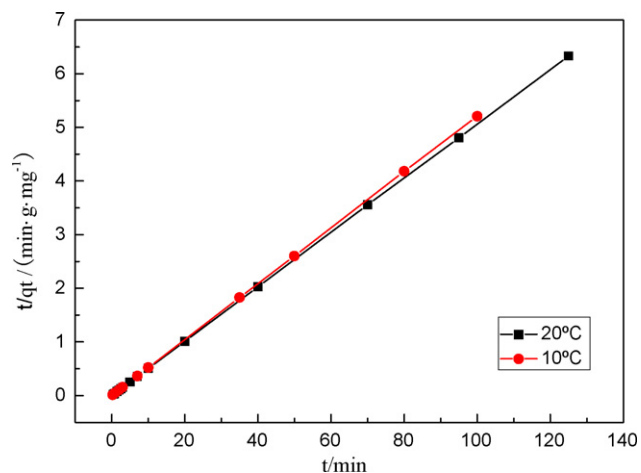
Adsorbent	$q_m$ ( $\text{mg g}^{-1}$ )	References
Orange peel xanthate	204.5	This study
Alfalfa biomass	43	[25]
Sago processing waste	46.6	[26]
Azolla filiculoides	93	[27]
Mango peel waste	99.05	[28]
Olive pomace	114.07	[29]
Maize bran	142.86	[6]
Black oak bark	153.3	[30]
Sugarcane bagasse	196	[31]
Formaldehyde-polymerized peanut skins	205	[32]



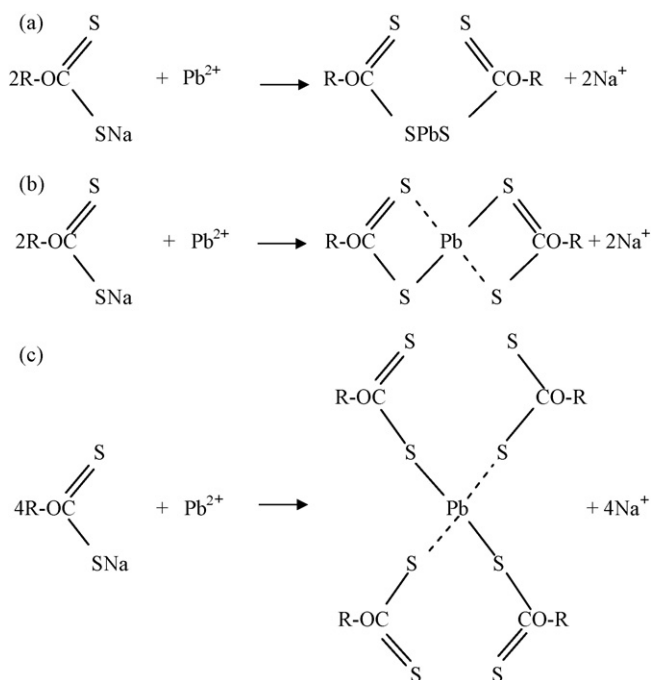
**Fig. 5.** Adsorption of  $\text{Pb}^{2+}$  on XOP at different temperatures.

20 min. The fast adsorption rate reflects good accessibility of the binding sites of the orange peel xanthate to metal ions. This has practical advantages in terms of reducing reactor volumes and time. In addition, as shown in Fig. 6, when the temperature was increased from 10 to 20 °C, the amount of  $\text{Pb}^{2+}$  removed from the solution at equilibrium only increased 0.58  $\text{mg g}^{-1}$ . The insignificant effect of temperature on the adsorbed amount indicates that the adsorption of  $\text{Pb}^{2+}$  by XOP might follow chemisorption as opposed to physical sorption that is temperature dependent [8].

Data were modeled using pseudo-second-order model, which assumes that the rate is proportional to the square of the number



**Fig. 6.** Pseudo-second-order kinetics plot.



**Scheme 1.** Proposed adsorption mechanisms: (a) ion exchange; (b) and (c) complexation.

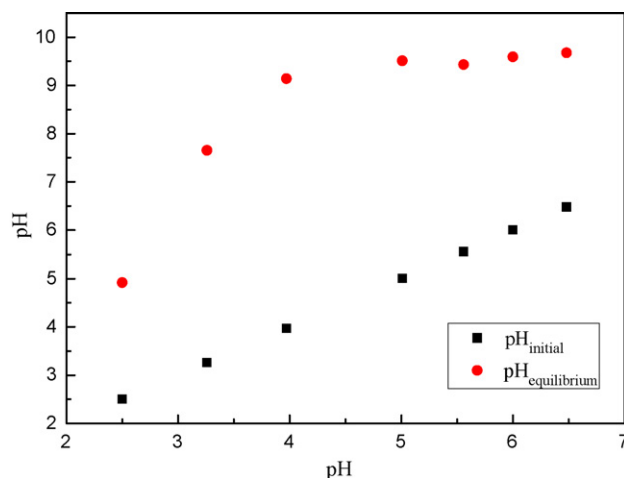
of remaining free surface sites [33]. This model can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the constant of pseudo-second-order rate. The relationship between  $t/q_t$  and  $t$  is linear with a slope of  $1/q_e$  and an intercept of  $1/(k_2 q_e^2)$ . Fig. 6 shows the application of pseudo-second-order model for both temperatures. Obviously, the adsorption process could be well described by the pseudo-second-order equation, indicating the process mechanism to be chemical adsorption [34].

### 3.5. Mechanism of adsorption

The orange peel xanthate can adsorb metal ions through ion exchange, or complexation, or by a combination of both processes.



**Fig. 7.** A plot of  $\text{pH}_{\text{initial}}$  and  $\text{pH}_{\text{equilibrium}}$ .

By ion exchange, two negative charged sulfur atoms of XOP participate in capturing one divalent metal ion. However, complex formation occurs between four sulfur atoms and one divalent metal ion (Scheme 1). It is postulated that  $Pb^{2+}$  adsorption process could undergo both ion exchange and complex formation [9,35]. Because lead belongs to transition metals, which have empty orbitals that can be occupied by electrons to form complex, and considering steric hindrance, mechanism (b) is the most possible adsorption process.

In addition, during the adsorption process on XOP, the equilibrium pH values increased if no buffer solution was added into the experimental solutions (Fig. 7). This phenomenon can be explained by proposing that  $Na^+$  ions were released into the solutions according to both ion exchange and complexation mechanisms, they then combined with  $OH^-$  ions to form alkali, which strengthened the alkalinity of the solutions.

#### 4. Conclusions

The prepared orange peel xanthate has much potential as an efficient and useful adsorbent for the removal of  $Pb^{2+}$  from wastewaters. FTIR study demonstrated the involvement of sulfur groups in the xanthation process. Zeta potentials of XOP were more negative than OP in the range of 2.0–7.0, and in this pH range adsorption efficiencies of  $Pb^{2+}$  are all larger than 95%. Langmuir and Freundlich models were used to analyze the adsorption isotherms of OP and XOP. At 30 °C, pH 5.0, the maximum adsorption capacity of XOP was 204.50  $mg\ g^{-1}$ , thereby attaining about 150% adsorption increment compared with that of the pristine orange peel. Kinetics studies showed that the adsorption rate is very fast and can attain equilibrium within 20 min, and the experimental data are found to fit pseudo-second-order equation. Temperature has little effect on the adsorption process. The adsorption process of XOP on  $Pb^{2+}$  may proceed according to both ion exchange and complexation mechanisms.

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