VARIOUS TECHNOLOGICAL PROCESSES

Preparation of Modified Alginate Nanoflocculant and Adsorbing Properties for Pb^{2+} in Wastewater[1]

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Abstract—A novel nano flocculant was prepared through the modification of sodium alginate. In the preparation partially oxidised sodium alginate reacted with triethylenetetramine (TETA) and then reacted with carbon disulfide. The structure of the flocculants was confirmed by elemental analysis, Fourier transform infrared and UV spectrophotometry. The flocculant showed nanoparticle sizes with diameters of 300–350 nm in aqueous solution, and became precipitates after flocculation with Pb^{2+} ions. The flocculant was employed to adsorb Pb^{2+} in wastewater, and the influence of flocculant concentration, flocculation temperature, pH, and time on the adsorption properties were investigated. The results showed that adsorption capacity of the flocculant for Pb^{2+} could reach up to 3.43 mmol g^{-1}, and the removal rate for Pb^{2+} was over 97%. The adsorption processes corresponded to pseudo second order kinetics and Langmuir isotherm model. The adsorption mechanism involved electrostatic attraction, chemical chelation, netting and sweeping actions.

INTRODUCTION

In recent years, with the development of manufacturing and mining, water pollution by heavy metal lead ions (Pb^{2+}) is getting worse. Due to the toxicity and non-excretory, Pb^{2+} is easy to accumulate in human bodies and causes serious diseases [1, 2]. The treatment of lead-contaminated wastewater has been greatly concerned. Conventional lead-contaminated wastewater treatment methods include chemical precipitation, ion exchange, membrane separation, adsorption and flocculation method [3–8]. The materials for treating wastewater containing Pb^{2+} usually are activated carbon, microbial adsorbents, synthetic polymer materials, and new nanomaterials [9–13]. But complicated operations, high cost, and secondary pollution were inevitably accompanied with the methods and materials.

Sodium alginate (SA), as a natural polymer, is biodegradable, non-toxic, and widely occurred in the word [14–18]. SA possesses a large number of carboxylic groups which are capable of adsorbing heavy metal ions

in water, and it is a promising material used as flocculant for heavy metal ions. Wang et al. applied sodium alginate aqueous solution to remove heavy metals (Pb^{2+}, Cu^{2+}, and Cd^{2+}) from polluted water [19], but the adsorption capacity and removal rate are not satisfactory, especially in high concentrated metallic ion solutions.

More scholars employed modified SA to treat wastewater of heavy metal ions. Ren et al. [20] prepared alginate–carboxymethyl cellulose (CMC) gel beads, and studied adsorption mechanism for Pb(II) with low concentration of waste water, but they observed slow adsorption speed. Lu et al. [21] prepared SA microspheres using glutaraldehyde as a crosslinker, and investigated adsorption behaviors for methylene blue dye and a variety of heavy metals. However, this preparation method was relatively complicated, and the equilibrium adsorption time was as high as 36 h.

In order to improve removal rate and accelerate adsorption speed for Pb^{2+} in wastewater, we developed a novel chelating flocculant through a modification of sodium alginate. SA was partly oxidized and then reacted with triethylenetetramine (TETA) and carbon disulfide,

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[1] The text was submitted by the authors in English.

producing amino and thio carboxylate groups. The novel chelating flocculants were used for removing Pb^{2+}, the preparation, adsorption ability and mechanism were investigated. To our knowledge, this new approach has not been reported.

MATERIALS AND METHODS

Materials. Sodium alginate (SA, analytical grade, viscosity ≥ 0.02 pa.s in an aqueous solution of 1.0 wt %, 20°C), triethylenetetramine (TETA, analytical grade), carbon disulfide (CS$_2$, analytical grade), and Pb(NO$_3$)$_2$ (analytical grade) and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd., sodium periodate (NaIO$_4$, analytical grade) and NaBH$_4$ (96%) were purchased from Aldrich. All the raw materials were used as received without further purification.

Preparation of modified alginate chelating flocculants. In a flask with magnetic stirring apparatus，4.95 g SA (0.025 mol structure units) powder was dispersed in 50 mL of anhydrous ethanol, 50 mL of an aqueous solution containing 0.015 mol sodium periodate (NaIO$_4$) was added. The mixture was stirred for 6 h in dark at room temperature, to give the partial oxidized sodium alginate (OSA). The solution was dialyzed against distilled water and lyophilized [22]. The OSA was dissolved in 120 mL of water, then 3.66 g TETA was added dropwise slowly. The reaction was carried out at 50°C in water bath with magnetic stirring for 12 h. Afterwards, the reacted mixture was cooled to room temperature, then 0.96 g NaBH$_4$ was added dropwise, and the reaction was continued for additional 12 h at 25°C. Carbon disulfide (CS$_2$, 0.025 mol) and 20 mL NaOH aqueous solution (0.05 wt %) were added to the mixture, the reaction was continued for 6 h at 40°C. Different flocculant samples were synthesized by changing feed ratio of SA to CS$_2$.

Characterizations for flocculants. The structures of the flocculants were characterized by Fourier transform infrared spectra (FTIR, Nicolet 6700, USA), the samples were scanned in the range of 400–4000 cm^{-1}; Percentages of C, N, S in the samples were determined by elemental analyzer (Elementar, Vario ELIII); UV absorption of the flocculant aqueous solution was measured on a UV-visible spectrophotometer (Shimadzu UV-2300) within the wavelength range of 200–400 nm; Colloid particle sizes and Zeta potentials of the flocculants were measured with a nanometer particle size analyzer. (US Brookhaven company ZetaPALS).

Flocculation property test. Accurately weighted flocculant (1.00 g) was dissolved in deionized water (100 mL) to form a fluocculant solution with concentration of 1 wt %, and Pb(NO$_3$)$_2$ (1.6561 g) was dissolved in deionized water (1000 mL) to form a Pb^{2+} solution with concentration of 0.005 mmol mL^{-1}.

In a conical flask 2 mL of the flocculate solution was added to 50 mL of Pb(NO$_3$)$_2$ solution. The flocculation was carried out with oscillation for 30 min, and was remained stationary for additional 30 min. The flocculation was performed with different flocculant concentration, flocculating time, pH value and temperatures respectively. After separation of the flocculant precipitate the concentrations of Pb^{2+} in the solutions were determined by atomic absorption spectrophotometry (Brookhaven company Spectr AA-220/220Z，USA), and the removal rate R and adsorption capacity Q for Pb^{2+} were calculated using the formula [23].

$$R, \% = \frac{C_0 - C}{C_0} \times 100, \qquad (1)$$

$$Q = \frac{(C_0 - C)V}{W} \times 100, \qquad (2)$$

where R is Pb^{2+} removal rate, %; Q is the adsorption capacity, mmol g^{-1}, V is solution volume, mL, C_0 and C are concentrations of Pb^{2+}, mmol mL^{-1}, before and after flocculation, respectively; W is the weight of dry flocculant, g.

RESULTS AND DISCUSSION

Preparation of flocculants. At the presence of sodium periodate, sugar rings of alginate were partly oxidized to produce aldehyde groups, the oxidation degree was 20% by a determination. Then, the aldehyde groups reacted with triethylenetetramine followed by reduction of C=N at the presence of sodium borohydride. Finally, a modified alginate flocculant was obtained after reaction with carbon disulfide. The scheme was showed in Fig. 1.

Elemental analysis results were indicated in Table 1. It was observed that the modified alginate flocculants contain certain proportions of N, S elements, indicating the success introduction of triethylenetetramine and carbon disulfide into alginate. The element S percentages increased from sample SA-TETA-S1 to SA-TETA-S5 due to the increase of CS$_2$ content in the feed.

FTIR of the flocculants. As shown in Fig. 2, there were observable wide peaks around 3328 cm^{-1} for
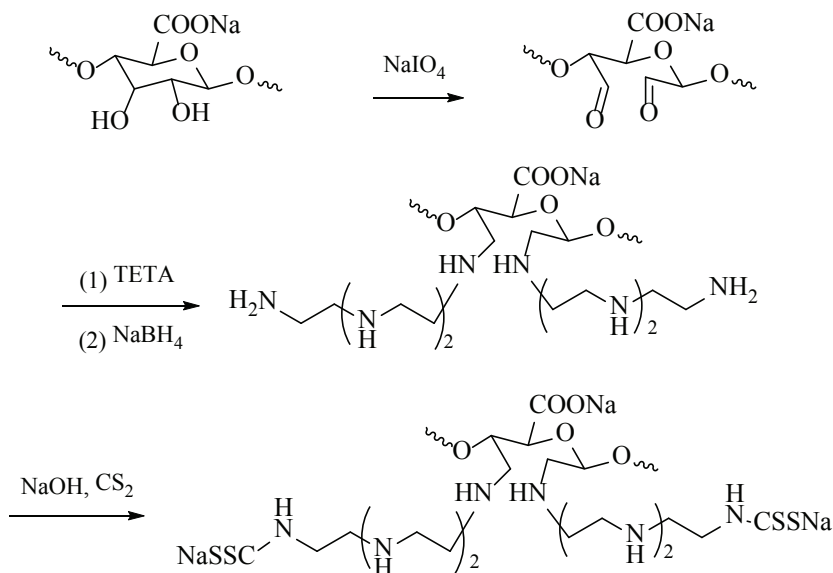
Fig. 1. Scheme of preparation of modified alginate flocculants.

the three samples. They were attributed to the overlap of –NH$_2$ and –OH stretching vibration; The peak at 1596 cm^{-1} was N–H deformation vibration peak; The 1029 cm^{-1} was ascribed to the C–N stretching vibration of primary amines; The N–C stretching in thioamide (N–C = S) was found at 952 cm^{-1}, and the C–S stretching vibration in dithio carboxy (–C(=S)–S–) was observed at 879 cm^{-1}, respectively. The FTIR confirmed that amino and carboxyl dithio groups were involved in the modified alginate flocculants [24].

UV spectrum. Double C=S bonds were present in dithio carboxy groups which had ultraviolet absorption [25–27]. As could be seen in Fig. 3, the modified alginate flocculants displayed ultraviolet absorption at 261 and 287 nm. It was explained that the peak at 261 nm was resulted from π–π* electronic transitions in N–C=S, and 287 nm was ascribed to π–π* electronic transitions in S–C=S. As a comparison, alginate did not

show adsorption peaks in the range of ultraviolet. This observation verified that –C(=S)–S– groups existed in the flocculants.

Morphology and Zeta potential. After modification, amino and dithiocarboxyl groups were introduced into the modified alginate which contained positive and negative charges under certain pH conditions. Therefore, they could form colloidal particles with diameters of 300–350 nm through self-assembly in an aqueous solution. The fact was evidenced by scanning electron microscopy and Zeta potential determination. The flocculants exhibited petal shaped colloidal particles in aqueous solutions (e.g., Fig. 4a: SA-TETA-S1 and Fig. 4c: SA-TETA-S3); However, the flocculants became larger irregular particles which precipitated from the solutions as soon as they flocculated with Pb^{2+} (e.g., Fig. 4b: SA-TETA-S1-Pb^{2+} and Fig. 4d: SA-TETA-S3-Pb^{2+}). It was also noted that negative Zeta potential increased with the pH increase

Table 1. Elemental analysis results of the modified alginate flocculants

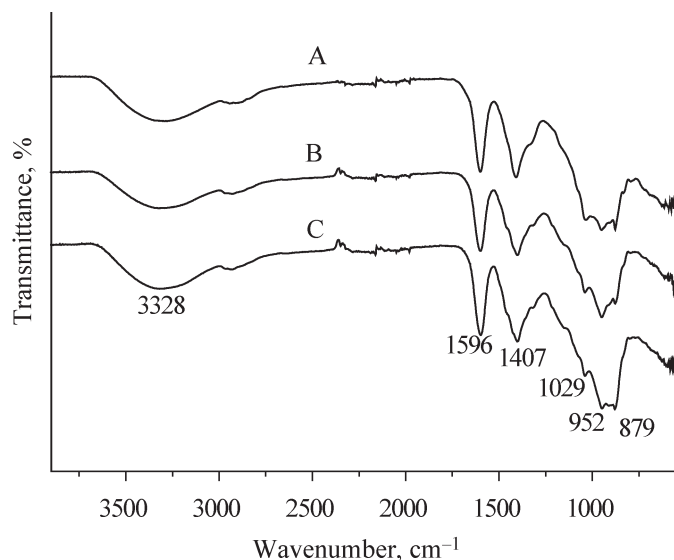| Sample ID	Molar ratio SA : CS$_2$	Yield, g	Element		
			C（%）	N（%）	S（%）
SA-TETA-S1	1 : 1	3.97	24.39	3.89	1.89
SA-TETA-S3	1 : 3	6.85	23.97	3.77	9.03
SA-TETA-S5	1 : 5	7.93	21.68	3.67	9.74

Fig. 2. FTIR spectra of (A) SA-TETA-S1, (B) SA-TETA-S3, and (C) SA-TETA-S5.
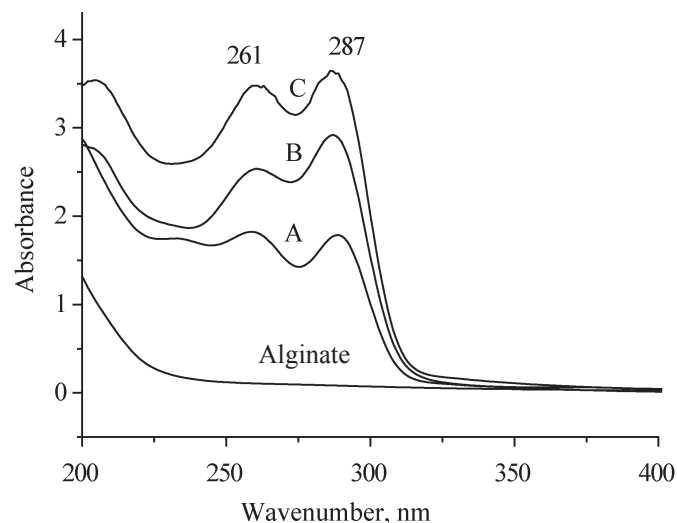

Fig. 3. Ultraviolet absorption of the samples: (A) SA-TETA-S1, (B) SA-TETA-S3, (C) SA-TETA-S5 and alginate.

from 2 to 8 (Table 2). It was because that as the pH increased, ammonium ion deprotonated gradually, leading to the decrease of positive charges. Meanwhile, ionization of the dithiocarboxyl groups was enhanced under basic conditions, resulting in the increase in negative Zeta potentials.

Floccculation properties. By using the static adsorption method, we have measured adsorption capacities and removal rates of the modified alginate flocculants for Pb^{2+}, and the results were shown in Table 2. The flocculant SA-TETA-S5 displayed adsorption capacity for Pb^{2+} as high as 4.81 mmol g^{-1}, and removal rate as high as 96.67%, respectively, much higher than unmodified alginate adsorbents. For example, Wang et al. [20] reported that the unmodified alginate possessed maximum adsorption capacity of 2.19 mmol g^{-1} for Pb^{2+} under optimized
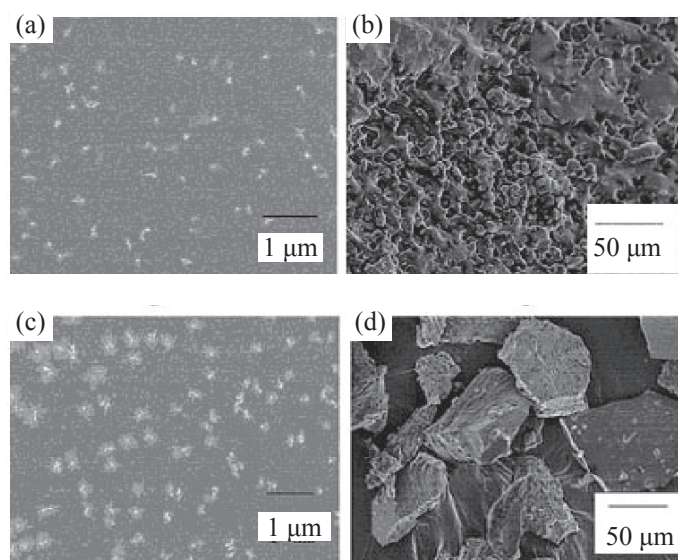

Fig. 4. SEM photographs of colloidal particles: (a) SA-TETA-S1 and (c) SA-TETA-S3); (b) precipitate SA-TETA-S1-Pb^{2+} and (d) SA-TETA-S3-Pb^{2+}

Table 2. Adsorption capacity and removal rate of flocculants[a] for Pb^{2+}

pH	Zeta Potential, mV			Removal rate, %			Adsorption capacity, mmol g^{−1}		
	A[a]	B[a]	C[a]	A	B	C	A	B	C
2	−0.12	−0.43	1.64	8.71	24.06	27.78	0.42	1.19	1.38
3	−12.72	−15.86	−14.26	11.55	25.18	30.00	0.56	1.25	1.49
4	−20.51	−20.73	−17.86	14.38	29.64	35.56	0.70	1.47	1.77
5	−20.63	−20.78	−25.58	18.92	39.14	45.56	0.92	1.94	2.27
6	−20.43	−27.85	−31.69	56.34	65.38	70.00	2.75	3.24	3.48
7	−23.10	−25.81	−29.00	81.86	89.39	93.33	3.99	4.42	4.64
8	−24.00	−26.59	−29.44	93.76	96.65	96.67	4.57	4.78	4.81

[a] Samples (A) SA-TETA-S1, (B) SA-TETA-S3, (C) SA-TETA-S5, 1 wt % solution; 0.005 mmol mL^{−1} of Pb(NO$_3$)$_2$.

conditions. This implied that the flocculation properties could be greatly improved through the modification of alginate. In this work, we also investigated the effect of the pH value on the floccculation properties. As seen in Table 2 both of the adsorption capacity and removal rate increased with pH increase from 2 to 8. Obviously, it was because that the negative charges carried by the molecular chain were gradually dominant with the increase of pH value, which was beneficial for adsorbing positively charged Pb^{2+} [28].

Effect of flocculant concentration on the removal rate. To approach optimal removal efficiency for Pb^{2+}, we investigated the effect of flocculant concentration on the removal rate. As shown in Fig. 5, with the increase in the flocculant concentration, the removal rate was gradually increased. When the concentration was 1.4 wt % the removal rates reached up to equilibrium values, 93.6, 97.0, and 98.7% for SA-TETA-S1, SA-TETA-S3, and SA-TETA-S5, respectively. Apparently, the flocculant with higher concentration could carry more functional groups, therefore, the removal efficiency would be higher.

Temperature influence on flocculation properties. The temperature influence on the flocculation was studied at different temperatures. The removal rate varied from 96.59 to 97.75%, and the adsorption capacity varied in the range of 3.44–3.49 mmol g^{−1} when temperature changed from 25 to 55°C. This observation indicated that the flocculation was less sensitive to temperature change. The main reason was that the stable flocculating substance could be produced through chelation and electrostatic adsorption between the flocculants and the metallic ions.

Adsorption isotherm. To investigate the adsorption mechanism we studied the adsorbing isotherm of SA-TETA-S3 for Pb^{2+} at temperature 25°C. Langmuir proposed a monomolecular layer adsorption model when studying the adsorption of solids for gases. The model was expressed as follows [29]:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m}, \tag{3}$$

where C_e is the concentration of a metal ions in the equilibrium adsorption state, Q_e and Q_m are equilibrium and maximum adsorption capacities, respectively, K_L is the Langmuir constant. Through regression analysis linear relationships between C_e/Q_e and C_e is observed. The coefficients is 0.9940 and K_L is 6.56 respectively.
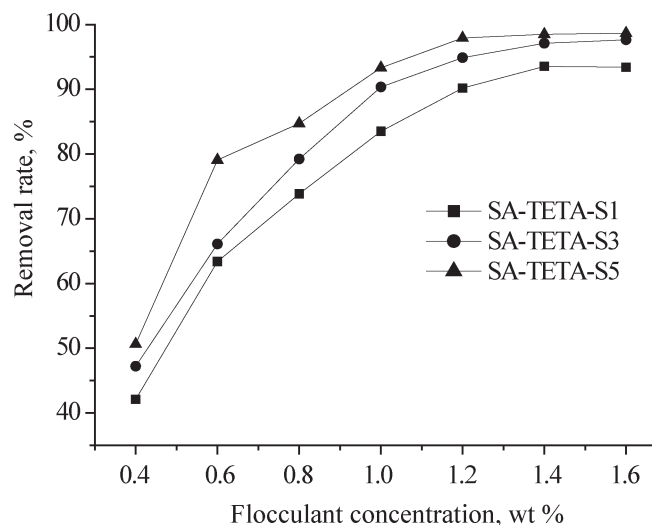

Fig. 5. Removal rate dependence on flocculant concentrations. Pb(NO$_3$)$_2$ solution: 50 mL, 0.005 M; flocculant volume: 5 mL, pH = 7.
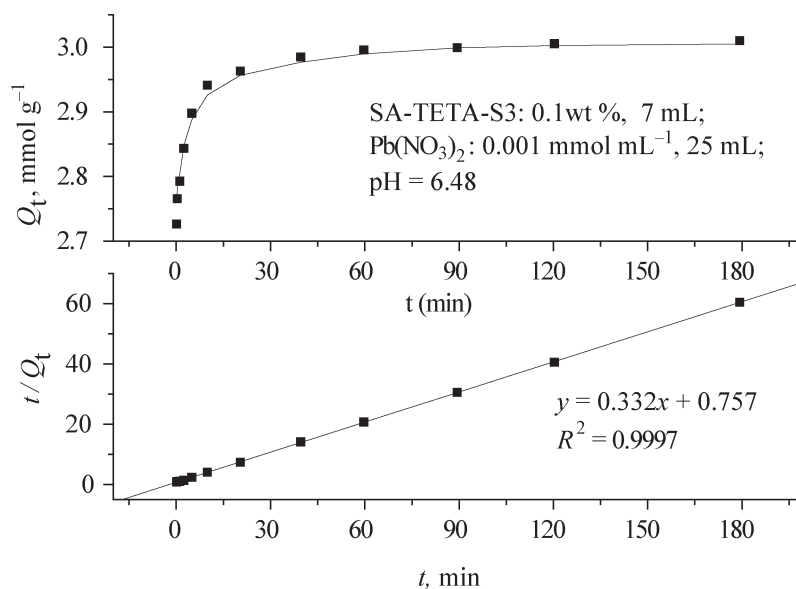
Fig. 6. Quasi-second-order kinetics study of SA-TETA-S3 adsorbing Pb^{2+}.

The basic attribute of Langmuir isotherm can be described by a dimensionless parameters R_L, which is defined as [30]:

$$R_L = \frac{1}{1 + K_L C_0},\qquad(4)$$

In the formula (4), when $R_L = 0$, $0 < R_L < 1$, $R_L = 1$ and $R_L > 1$, the adsorption is irreversible adsorbed, easily adsorbed, a linear adsorbed and non-adsorbed, respectively [31]. In this study the $R_L = 0.0296$, implied that the adsorption is easily adsorbed. The main reason is that there is double interactions between the flocculant and metal ions, which is not only electrostatic adsorption but also chelating action due to the existance of dithiocarboxyl and amino groups. This indicates that the adsorption corresponds to the Langmuir monomolecular layer adsorbing mechanism, which is mainly chemical adsorption.

Adsorption kinetics. Taking SA-TETA-S3 as an example, we have studied the relationship between the adsorption capacity and time. The flocculant was put in 0.001 mmol mL^{-1} of Pb(NO$_3$)$_2$ solution, and the adsorption capacity at various time was recorded. It is clear that the initial adsorption was fast, then the adsorption gradually slowed down. The equilibrium adsorption is arrived after 20 min. We employed two models to study the adsorption kinetics respectively. Quasi-first-order and Quasi-second-order kinetics were expressed as follows [31–33]:

$$\ln (Q_e - Q_t) = \ln Q_e - k_t t,\qquad(5)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e},\qquad(6)$$

where Q_e and Q_t are adsorption capacities, mmol g^{-1}, at the equilibrium and at time t, respectively; k_1 is a quasi first order kinetic constants, k_2 is a quasi second order kinetic constants. The parameters were obtained through regression analysis. According to the obtained correlation coefficient, the Quasi-second-order kinetic model ($R^2 = 0.9997$) is more suitable for describing the adsorption kinetics than Quasi-first-order model ($R^2 = 0.8810$). The Quasi-second-order kinetics study of SA-TETA-S3 adsorbing Pb^{2+} were displayed in Fig. 6.

It was proposed that the mechanism for the flocculation process contained three steps: (1) The flocculant colloidal particles adsorbed Pb^{2+} through electrostatic attraction and chelating action, forming mesh structure polymer; (2) The mesh structure polymer caught more Pb^{2+} ions by netting and sweeping actions, yielding larger flocculant particles; (3) The large particles were converted into solid precipitates after further cohesion and settlement.

CONCLUSIONS

Novel chelating flocculants were prepared through the modification of sodium alginate under mild synthetic conditions. The new flocculants demonstrated significantly high adsorption capacities and removal rates for Pb^{2+}. The

adsorption isotherm agreed with Langmuir model. The kinetics was correspond to Quasi-second-order kinetics absorption process. The flocculants had the advantages of simple synthetic method, cheap raw materials, and excellent flocculating behaviors for Pb^{2+}. The flocculants have potential applications in wastewater treatment as a new flocculant.

ACKNOWLEDGMENTS

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