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Iodide adsorption from aqueous solutions by bis(trimethoxysilylpropyl)amine polycondensate/silver chloride composites

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ABSTRACT

Composite adsorbents for iodide were prepared with AgCl as an adsorption active component and bis(trimethoxysilylpropyl)amine (TSPA) as a gel precursor. The prepared composite adsorbents were used to adsorb iodide from aqueous solutions by considering the effects of initial iodide concentration, temperature, initial solution pH, and coexisting NaCl. The loading of AgCl in the prepared composite adsorbents was 5.5 mmol/g, much higher than that in the reported silver or silver chloride-impregnated activated carbon (around 0.097 mmol/g). The high AgCl loading ensures that the prepared composite adsorbents have a high adsorption capacity. At the initial adsorption stage of 0–12 h, the adsorption rate increases with increasing initial iodide concentration from 2 to 8 mmol/L. When the initial iodide concentration further increases from 8 to 14 mmol/L, the adsorption rate does not have an obvious increase. Pseudo-second-order model fits the experimental kinetic data quite well. The initial adsorption rate increases greatly from 1.97 to 7.32 $\text{mmol g}^{-1}\ \text{h}^{-1}$ as adsorption temperature rises from 25 to 55°C. The equilibrium adsorption amount is insensitive to solution pH and coexisting NaCl, but it increases slightly with the increasing adsorption temperature. The adsorption isotherms are of H2 type, indicating that the adsorption is chemical adsorption. The comparison of the energy dispersive spectroscopy (EDS) spectra and X-ray diffraction (XRD) patterns of the composite adsorbents before and after adsorption shows that after adsorption, all AgCl in the original adsorbents changes into AgI, confirming the chemical nature of the adsorption. The composite adsorbents prepared in this work have a high adsorption capacity, a good selectivity, and good chemical and mechanical stabilities. They are very suitable for the adsorption of iodide form aqueous solutions.

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Keywords: Iodide; Adsorption; Bis(trimethoxysilylpropyl)amine polycondensate; Silver chloride

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1. Introduction

In natural environments, iodine compounds are of interest mainly for three reasons: (1) when oxidation treatments are used in the processes of drinking water production, the presence of I^- may lead to the formation of harmful iodine-containing substances [1]. (2) Radioactive iodine isotopes, ^{131}I and ^{129}I are harmful, their migration, transformation, and accumulation are of great concern [2]. (3) Natural iodine resources in salt lakes, underground brines, etc. are very important for the production of useful iodine or iodate compounds. (4) During the refinement of some inorganic salts, it is necessary to remove the iodide or iodate impurities. In natural environments with low to neutral pH values and positive redox potentials, I^- is the dominant iodine species [3]. Adsorption would be a suitable method for the removal or recovery of iodide. In natural waters, iodide is usually co-exited with common anions including Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, etc., which can present strong competition with iodide during physical adsorption, and therefore, the uptake of iodide through chemical adsorption is more attractive.

There have been some reports on chemical adsorption of iodide by colloidal silver [4], metallic copper and cupric compounds [5], cuprite [6], Ag composites [7], and AgCl composites [8,9]. Although Cu_2O, Ag, and AgCl can present specific chemical interactions with I^-, if they are used in the form of fine particles, the adsorption operation is not convenient. A practical way is to prepare composite adsorbents using Cu_2O, Ag, or AgCl as an adsorption active agent. In the preparation of the composite adsorbents, the selection of the adsorbent matrix materials is very important. When activated carbon was used as an adsorption matrix material, the loading of the adsorption active components was not high, and there was the leaching problem [7,8]. Therefore, it is quite necessary to look for better matrix materials to prepare I^- adsorbents with a high loading of adsorption active agents and without leaching.

Sol–gel silica-based materials are amorphous and porous materials. They are usually obtained in a dry (xerogel) and porous form from wet gels that form upon hydrolysis and condensation of liquid alkoxysilane precursors. Each step of the gel preparation is carried out in mild conditions. Sol–gel silica-based materials have been used for the preparation of adsorbents, catalysts, sensors, optical, and electrochemical devices [10,11]. The preparation of adsorbents using sol–gel silica-based materials has attracted more and more attention [11]. When sol–gel silica-based materials are used to prepared composite adsorbents, there are mainly two ways: (1) the modification or hybridization of silica based materials by the attachment of organic functionalities [12,13]. (2) The entrapment of an adsorption active component in the silica based materials. Although sol–gel-derived silica-based materials have many advantages, there still exist some problems: (1) most of the precursors do not dissolve in water. In order to get a uniform sol, an organic solvent, such as ethanol or methanol must be added, the latter been known by its toxicity [12]. (2) When an organosilane is added to improve the textural properties of the gels and to adjust the reactions, in order to have an obvious effect, the organosilane should have a long carbon chain. Unfortunately, in this case the gel time is usually long and the gel may not be good in quality. Among the investigated silanes, bis(trimethoxysilylpropyl)amine (TSPA) is more environmentally compliant, since it is fully soluble in water due to the presence of the hydrophilic amine group, and the gel time is quite reasonable [10–12].

In this work, composite adsorbents for iodide were prepared with AgCl as the adsorption active component and TSPA as the gel precursor. The prepared composite adsorbents were used to adsorb iodide by considering the effects of initial iodide concentration, temperature, initial solution pH, and coexisting NaCl. The adsorption isotherms were obtained and the adsorption mechanisms were investigated.

2. Experimental section

2.1. Preparation of the TSPA/AgCl composite adsorbents

About 2.4 mol/L aqueous suspension of AgCl was prepared by adding 0.06 mol of AgCl into 25 mL distilled water with stirring. Thereafter, 7.5 mL of TSPA (Gelest) was mixed rapidly with the aqueous suspension of AgCl under stirring. After gelation, the gel composites were aged for 24 h, followed by drying overnight in an oven at 30°C. The dried composites were grinded and sieved. The composite particles with a diameter between 250 and 750 μm were selected and stored for the adsorption experiments.

2.2. Analytical methods

Iodide concentrations in aqueous solutions were determined by an ultraviolet visible spectrometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd.) at 226 nm. Solution pH values were measured with a Sartorius PB-10 pH meter. XRD patterns of the adsorbents were collected on an X′ Pert PRO (PANalytical) diffractometer with Cu Kα radiation ($\lambda = 0.15419$ nm) over a 2θ range from 5 to 80°. SEM images of the adsorbents were taken on a JSM-5610LV SEM instrument. Before taking the SEM images, the adsorbents were coated with a thin gold film. The energy dispersive spectroscopy (EDS) spectra of the adsorbents were obtained using an Oxford INCA instrument.

2.3. Batch adsorption experiments

About 0.1 g of the TSPA/AgCl adsorbent was added into 100 mL of KI solution in a water bath at a constant shaking speed of 160 rpm at the desired I^- concentration, temperature, initial solution pH, and coexisting NaCl concentration. The solution pH was adjusted with dilute HCl or NaOH solutions.

The adsorption amount of iodide onto the TSPA/AgCl adsorbents was calculated by a mass balance relationship:

$$q_t = \frac{V(C_0 - C_t)}{m} \tag{1}$$

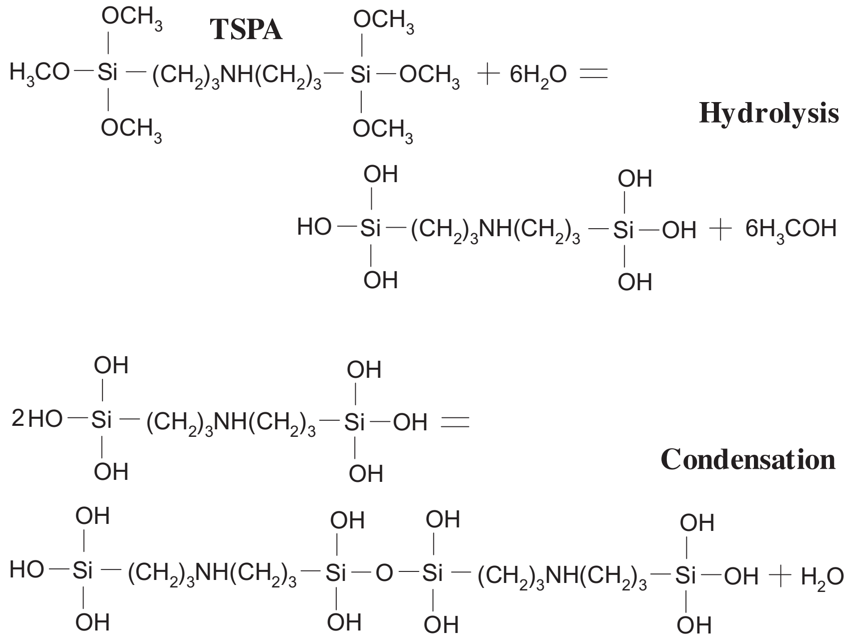
where q_t is the adsorption amount of iodide onto the adsorbents (mmol/g) at time t, V is the volume of the solution (L), m is the mass of the adsorbents (g). C_0 and C_t are iodide concentrations in solutions at beginning and time t (mmol/L). When equilibrium iodide concentration C_e is used instead of C_t in Eq. (1), equilibrium adsorption amount, q_e, is obtained (mmol/g).

3. Results and discussion

3.1. Preparation of the composite adsorbents

TSPA has six carbon atoms and one amine group in the bridging chain. After dissolving in water, its trimethoxysilyl groups, –Si(OCH_3)$_3$, hydrolyze stepwise to give the corresponding silanols. The hydrolysis products ultimately condense to siloxanes (Fig. 1). The hydrolysis of the trimethoxysilyl groups is relatively fast, while the condensation reaction of the silanol groups is slower [14]. Both the hydrolysis and condensation reactions are stepwise reactions. So there are many kinds of hydrolysis and condensation products. The composition of the sol is allowed to be adjusted in a wide range for easy entrapment of AgCl.

In general, for chemical adsorption using composite adsorbents, the adsorption capacity is mainly dependent on the amount of adsorption active components entrapped in the composite adsorbents. Therefore, the maximization of the adsorption active component loading in the composite adsorbents can



$$H_3CO-Si(OCH_3)_2-(CH_2)_3NH(CH_2)_3-Si(OCH_3)_2-OCH_3 + 6H_2O = HO-Si(OH)_2-(CH_2)_3NH(CH_2)_3-Si(OH)_2-OH + 6H_3COH$$

$$2HO-Si(OH)_2-(CH_2)_3NH(CH_2)_3-Si(OH)_2-OH = HO-Si(OH)_2-(CH_2)_3NH(CH_2)_3-Si(OH)_2-O-Si(OH)_2-(CH_2)_3NH(CH_2)_3-Si(OH)_2-OH + H_2O$$

Fig. 1. Hydrolysis and condensation reactions.

ensure a high adsorption capacity. However, during the preparation of the composite adsorbents, if overmuch adsorption active components were used, it was difficult to get composite gels with a good mechanical strength. Therefore, a suitable content of the adsorption active component, AgCl, was selected to ensure both a relatively high adsorption capacity and a good mechanical strength. In this study, the loading of AgCl in the composite adsorbents was 5.5 mmol/g, which was much higher than that in the reported silver or silver chloride–impregnated activated carbon (around 0.097 mmol/g) [3,8].

3.2. Adsorption kinetic curves

3.2.1. Effect of initial iodide concentration on adsorption kinetics

The effect of initial iodide concentration on adsorption kinetics was studied by increasing the initial iodide concentration from 2 to 14 mmol/L at 25°C. As seen from Fig. 2, at the initial adsorption stage of 0–12 h, the adsorption rate increases with increasing initial iodide concentration from 2 to 8 mmol/L. When the initial iodide concentration further increases from 8 to 14 mmol/L, the adsorption rate does not have an obvious increase.

The results in Fig. 2 indicate that the adsorption equilibrium time is about 72 h. When the initial iodide concentration increases from 2 to 6 mmol/L, the adsorption amount at 72 h increases quickly. While with the further increase in initial iodide concentration from 6 to 14 mmol/L, the adsorption amount increases slowly, indicating that the adsorption is nearly saturated. In the following experiments about the effects of temperature, solution initial pH, and coexisting NaCl on the adsorption, the initial iodide concentration was fixed at 8 mmol/L.

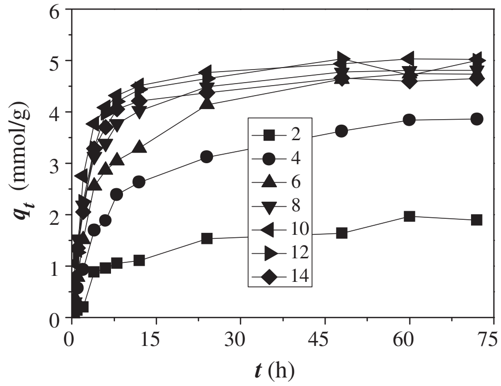


Fig. 2. Effect of initial iodide concentration (mmol/L) on the adsorption kinetics at 25°C. No HCl, NaOH, or NaCl was added.

3.2.2. Effect of temperature on adsorption kinetics

The effect of temperature on adsorption kinetics is shown in Fig. 3. Both the adsorption rate and adsorption amount increases slightly with the increasing adsorption temperature. This may means that iodide diffuses faster at a higher temperature, and the adsorption may be an endothermic process. For iodide adsorption onto organo-clay minerals, high temperatures reduce iodide adsorption only to a certain extent, but more pronounced for DPyDD-clay minerals [15], probably due to the conformational changes of the alkyl chains. Dehydration reactions occurring at distinct temperatures for the organo-vermiculites may be another reason [16].

3.2.3. Effect of initial solution pH on adsorption kinetics

Fig. 4 presents the effect of initial solution pH on the adsorption kinetics. The results show that neither the adsorption rate nor the adsorption amount changes obviously with the changes in the initial solution pH in the range from 1 to 11. During adsorption, Cl^- anions are replaced by I^- anions as a result of the solubility difference between silver chloride and silver iodide (K_{sp} 10^{-10} and 10^{-17} for AgCl(s) and AgI(s), respectively) [8,9]:

$$AgCl(s) + I^-(aq) = AgI(s) + Cl^-(aq) \tag{2}$$

Due to the nature of the above transformation reaction, solution pH does not affect the reaction obviously. In the initial solution pH range from 1 to 11, the TSPA/AgCl composite adsorbents present very good chemical and mechanical stabilities.

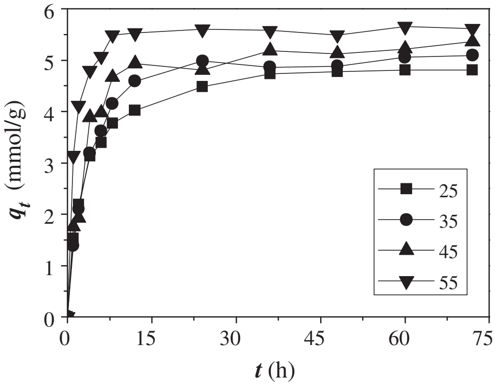


Fig. 3. Effect of temperature (°C) on adsorption kinetics. The initial iodide concentration was 8 mmol/L. No HCl, NaOH, or NaCl was added.

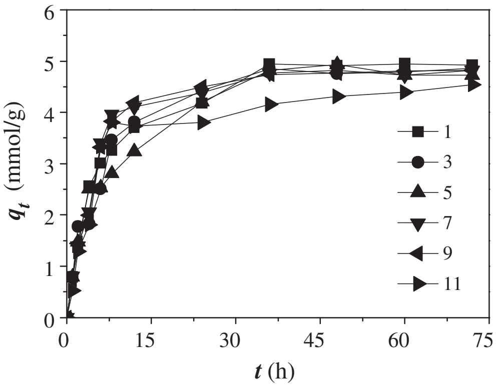


Fig. 4. Effect of initial solution pH on adsorption kinetics at 25°C. The initial iodide concentration was 8 mmol/L. No NaCl was added.

3.2.4. Effect of coexisting NaCl on adsorption kinetics

The effect of coexisting NaCl on adsorption kinetics is shown in Fig. 5. In general, the adsorption is insensitive to coexisting NaCl, indicating that the TSPA/AgCl composite adsorbents are very suitable for the uptake of iodide from solutions with NaCl coexisted. For the adsorption of iodide by Cu_2O [6] and Ag-doped carbon aerogels [7,17], the presence of NaCl was found to suppress the adsorption. For the adsorption of iodide by calcium alginate-silver chloride composite adsorbent [9], the adsorption was also found to be insensitive to the coexisting NaCl.

In this study, in solutions with a NaCl concentration ranging from 0 to 5 mol/L, the TSPA/AgCl composite adsorbents also present very good chemical and mechanical stabilities.

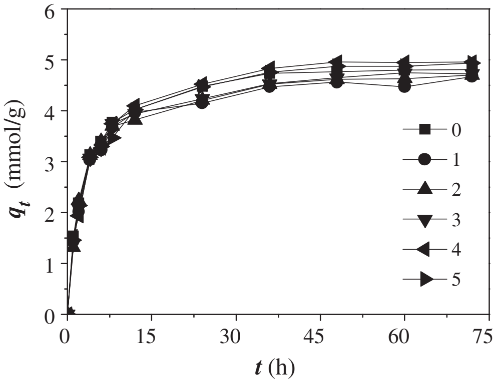


Fig. 5. Effect of coexisting NaCl concentration (mol/L) on adsorption kinetics at 25°C. The initial iodide concentration was 8 mmol/L. No HCl or NaOH was added to adjust the solution pH.

3.3. Adsorption kinetic analyses

To deeply understand the adsorption kinetic processes, adsorption kinetics models, including pseudo-first order [18] and pseudo-second order [19], have been used to treat the experimental kinetic data, respectively.

$$\text{Pseudo-first-order model: } q_t = q_e - \frac{q_e}{e^{k_1 t}} \tag{3}$$

$$\text{Pseudo-second-order model: } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

In the above equations, q_t and q_e are the adsorption amount at time t and at equilibrium, and k_1 and k_2 are the adsorption rate constant for pseudo-first- and pseudo-second-order models, respectively. The adsorption kinetic data at 25°C in Fig. 3 were used for the fitting. The fitting results are shown in Fig. 6. As can been seen, pseudo-second-order model fits the experimental data quite well.

Based on pseudo second-order-model, using the data in Fig. 3, the initial adsorption rates at 25, 35, 45, and 55°C were calculated according to the following expression:

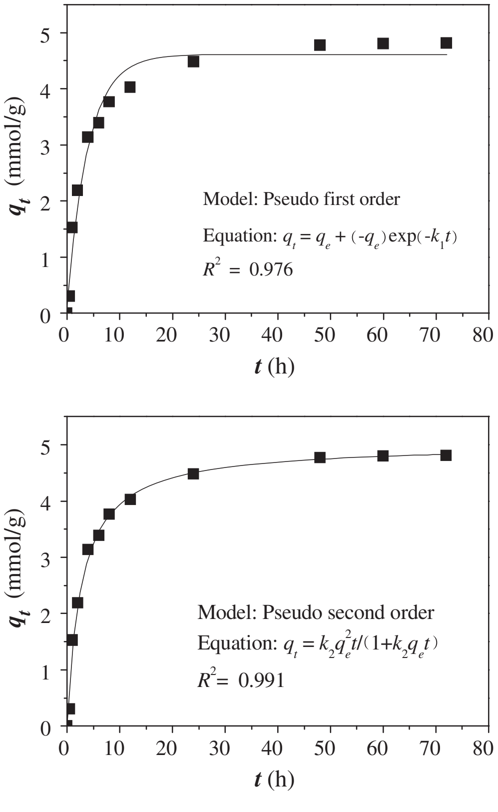


Fig. 6. Kinetic fitting results.

Table 1
Fitting results of the pseudo-second-order model and the kinetic parameters

T (°C)	Experimental	Pseudo-second-order model			Kinetic parameters	
	$q_{e,exp}$ (mmol/g)	$q_{e,cal}$ (mmol/g)	k_2 (g $mmol^{-1}$ h^{-1})	R^2	u_0 (mmol g^{-1} h^{-1})	E_a (kJ/mol)
25	4.81	4.98	0.080	0.991	1.97	25.5
35	5.10	5.34	0.069	0.994	1.97	
45	5.36	5.52	0.080	0.973	2.44	
55	5.62	5.75	0.221	0.996	7.32	

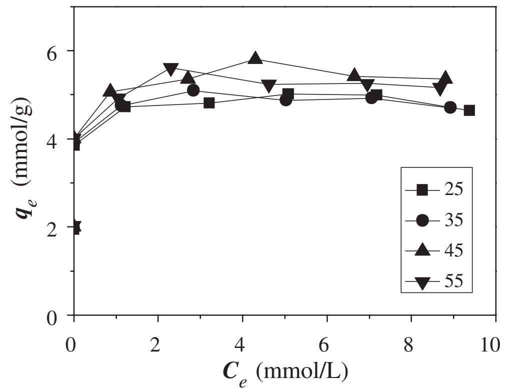


Fig. 7. Adsorption isotherms. The adsorption time was 72 h. No HCl, NaOH, or NaCl was added.

$$u_0 = k_2 q_e^2 \tag{5}$$

The fitting results of the pseudo-second-order model and the corresponding kinetic parameters are listed in Table 1. In Table 1, $q_{e,exp}$ and $q_{e,cal}$ are the experimentally determined adsorption amount and the calculated adsorption amount, respectively. The initial adsorption rate increases greatly from 1.97 to 7.32 mmol g^{-1} h^{-1} as adsorption temperature rises from 25 to 55°C. Apparent adsorption activation energy (E_a) of the adsorption was obtained using Arrhenius equation:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{6}$$

The plot of ln k_2 vs $1/T$ was used to evaluate E_a, which was found to be 25.5 kJ/mol (Table 1).

3.3. Adsorption isotherms and mechanisms

Adsorption isotherms of the iodide ions onto the TSPA/AgCl adsorbent at 25, 35, 45, and 55°C are shown in Fig. 7. In general, the adsorption amount at

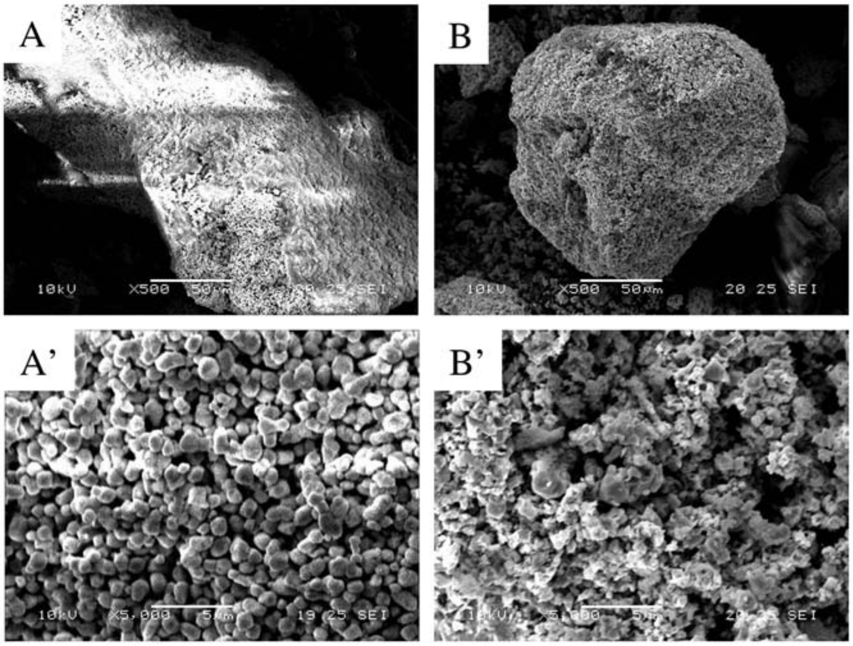


Fig. 8. SEM of the adsorbent before (A) and after (B) adsorption.

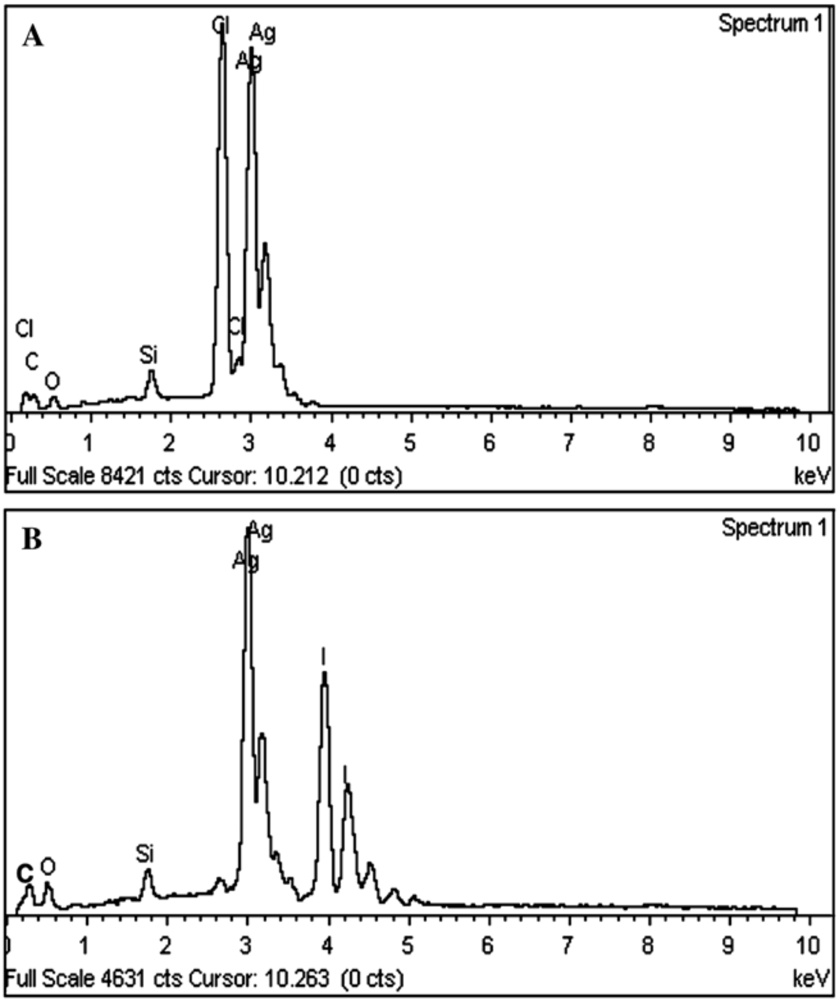


Fig. 9. EDS spectra of the adsorbent before (A) and after (B) adsorption.

equilibrium increases slightly with increasing temperature and iodide concentration. The adsorption isotherms are of H2 type, indicating that the adsorption is chemical adsorption [20]. There exist strong interactions between I^- anions and the adsorbents.

The SEM images of the dried composite adsorbents before and after adsorption are shown in Fig. 8. The SEM images show that there are cavities in the composite adsorbents, indicating the porous nature of the composite adsorbents. The SEM images also show that after adsorption there are changes in the morphology of the composite adsorbents. Fig. 9 shows the EDS spectra of the dried composite adsorbents before and after adsorption. After adsorption, the chlorine peaks disappear, while the iodine peaks present. The XRD patterns of the composite adsorbents before and after adsorption were compared in Fig. 10, which shows that after adsorption, all AgCl in the original adsorbents changes into AgI. The results of EDS and XRD confirm that during adsorption, the chemical precipitation transformation reaction shown in Eq. (2) occurs, and the adsorption is chemical adsorption.

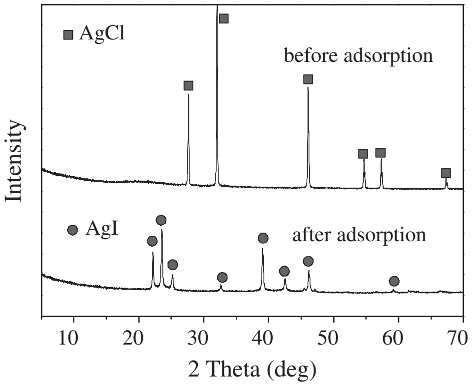


Fig. 10. XRD patterns of the TSPA/AgCl adsorbent before and after adsorption.

4. Conclusions

TSPA/AgCl composite adsorbents for iodide have been prepared. The adsorption behavior and mechanism have been investigated.

(1) The prepared composite adsorbents have a high adsorption capacity, a good selectivity, and good chemical and mechanical stabilities. They are very suitable for the adsorption of iodide form aqueous solutions.
(2) Pseudo-second-order model fits the experimental kinetic data quite well. The initial adsorption rate increases greatly from 1.97 to 7.32 $\mathrm{mmol\,g^{-1}\,h^{-1}}$ as adsorption temperature rises from 25 to 55°C. The apparent adsorption activation energy was calculated to be 25.5 kJ/mol.
(3) The adsorption amount is insensitive to solution pH and coexisting NaCl, but it increases slightly with the increasing adsorption temperature.
(4) The adsorption isotherms are of H2 type, indicating that the adsorption is chemical adsorption. The comparison of the EDS spectra and XRD patterns of the composite adsorbents before and after adsorption shows that after adsorption, all AgCl in the original adsorbents changes into AgI, confirming the chemical nature of the adsorption.

Acknowledgments

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