Adsorption performance for Bromine ion using bromide ion-lanthanum nitrate modified chitosan imprinted polymer

Haifeng Wu, Junhong Qiu(Corresponding author. E-mail address: qiujh66@126.com)
State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou, 310014, People's Republic of China

Based on the molecular imprinting technique, taking lanthanum nitrate modified chitosan as the functional monomer, the bromide ion as the imprinting template, glutaraldehyde as the cross-linker, the imprinted polymer of bromide ion-lanthanum nitrate modified chitosan was prepared in this paper by using the surface imprinting method. Using H_2O_2 oxidation-extraction photometric method for the determination of bromide ion concentration, the selective adsorption performances of the resulting imprinted polymer for bromide ion from aqueous potassium bromide solution and artificial seawater were investigated. The experiments showed that the adsorption equilibrium time was 30 min and the maximum adsorption capacity was 4.81 mg/g for potassium bromide solution, while the adsorption rate of artificial seawater was 71.57 % and the adsorption capacity was 2.505 mg/g, the imprinted polymer had good reusability and its SEM was researched. Further research indicated that Cl^- and F^- in seawater had significant impact on the adsorption performance of the imprinted polymer, but SO_4^{2-} and HCO_3^- had less effect.

Keywords: molecular imprinting technique; Bromide ion-lanthanum nitrate modified chitosan imprinted polymer; Adsorption performance; Bromide ion; Anions.

1. Introduction

Bromine is one of the important chemical raw materials in national economy and technological development. Bromide and its derivatives have a wide range of applications in fields such as flame retardants, drilling fluids, brominated pesticides, pharmaceuticals, refrigeration, sterilization, dyeing, and water treatment, etc[1][2] . Bromine mainly exists in environment including ocean, littoral underground brine, rock salt mines of ancient marine sediments, terrestrial underground brine, salt lake brine, oil and gas fields associated brine. About 99% of bromine on the earth exists in seawater, so it is called the marine element. The concentration of bromine (element) in seawater is about 67mg/L. There are three kinds of raw materials for industrial bromine, underground brine, salt lake brine (including the Dead Sea brine) and seawater, but the first two raw materials are more commonly used. The world's production capacity of elemental bromine has reached 600,000 tons/year, this strong demand for bromine has directly led to the continuous decline of the reserves and grade of underground brine and salt lake water resources. The large-scale use of enormous quantities of seawater as a major raw materials for manufacturing bromine will eventually become a choice[3][4][5].

There are some methods for the extraction of bromine from seawater, such as the earliest tribromoaniline precipitation method, air blow-out method, gaseous membrane method, emulsion liquid membrane method, agitated bulb membrane absorption method, adsorbent method, ion exchange resin method, etc[6][7]. As the mainstream method for bromine production at present, air blow-out method developed by U.S. Dow Chemical Company has the advantages of strong adaptability for bromine-containing raw materials and ease of automatic control, so it can be used for the extraction of bromine from seawater with low bromine content. However, it's shortcomings of requiring high equipment investment, high energy consumption, and high production cost lower the economic efficiency. Thus only a few of bromine producers in the world use this method for the extraction of bromine from seawater[8][9]. Each of other methods has certain advantages, relatively speaking, gaseous membrane method and ion exchange resin method show more commercial application prospects among them. But their inherent defects result in no one successful instance of industrial production employing two methods so far[10][11][12][13]. It could be forecasted that the fully mature air blow-out method will be gradually replaced by the new extracting bromine method with the advantages of energy-saving and low consumption. The low bromine content and other ions coexistence with bromine in seawater set higher requirement for extraction of bromine from seawater. If give an evaluation from the index of economic benefits, all of the methods mentioned above should not adapt perfectly to the requirements of extracting bromine from seawater. Therefore, research and exploitation of new method for extracting bromine is the necessary way to the revival and sustainable development of commercial extraction of bromine from seawater[14][15].

Judgment from the adsorption mechanism, the effect of chemical bromine adsorption from seawater using adsorbent is better than that of physical bromine desorption from seawater. Therefore, seeking an excellent adsorbent with a performance of orientated adsorption for bromine should be the correct path. Molecular imprinted polymers not only have highly selective adsorption performance for specific substances[16][17], but also have stable chemical properties[18], excellent resistance to harsh environments[19], good durability and long service life[20], and also are easy to prepare[21]. As adsorption materials with highly selective affinity, imprinted polymers can be used as directional adsorbents. Ion imprinting technique is the branch of molecular imprinting technique[22], and the polymerization reactions usually conduct in the aqueous phase using cations or anions as templates. Although cationic and neutral templates have been researched for many years[23], less attention has been paid to the inorganic anion templates by reason of restrictions on polymer preparation and anion recognition by lower charge to radius ratio, sensitive to pH values, hydrophobic interactions, etc[24][25][26]. Research for the use of anionic Br^- as a template has not been reported so far[27].

In this paper, a new method for the extraction of bromine from seawater was suggested by mean of ion imprinted polymers. Using the surface imprinting method, bromide ion-lanthanum nitrate modified chitosan imprinted polymer was prepared for the first time. The oriented adsorption performances of the resulting imprinted polymer for bromide ion from aqueous potassium bromide solution and artificial seawater were researched. Since bromide ion can be directly adsorbed by the imprinted polymer, two steps for air blow-out method or ion exchange resin method, which are the first oxidization of Br^- into Br_2 and the next reduction of Br_2 into Br^- after air blow-out or resin adsorption could be cancelled. In addition, the preparation process is relatively simple, and the raw material, *i.e.* a biomass product named chitosan is cheap and easily obtainable. Therefore, compared with the air blow-out or ion exchange resin method, the new extracting bromine method has the advantages of higher extraction ratio, less consumption, lower cost and more environmental friendliness. This research performed the exploratory work for the development of the new extracting bromine method[28][29].

2 Experimental section

2.1 Materials

Chemical reagents, *e.g.* Chitosan and lanthanum nitrate were purchased from Xiya Reagent Co., Ltd (Chengdu, China). Degree of deacetylation for chitosan was 95%. Potassium bromide was supplied by Shanghai No.4 Reagent & H.V. Chemical Co., Ltd (Shanghai, China). Glutaraldehyde was bought from Shanghai Chemical Reagent Purchase And Supply Wulian Chemical Factory (Shanghai, China). Seawater crystal was received from Blue Star Salt Products Co., Ltd (Hangzhou, China). All other chemicals used were analytical grade and obtained commercially. Deionized water was used throughout this work.

2.2 Equipment

The samples were weighed by Electronic balance (JA5003N) and pH values of the samples was measured by pH meter (PHS-2F, Shanghai Precision & Scientific Instrument Co., Ltd, China). The samples were stirred by desktop constant temperature oscillator (THZ-C, Taicang Huamei Biochemistry Instrument Factory, China). The filter cakes were dried by electric thermostat blast oven (DHG-9035A, Shanghai Yiheng Technical Co., Ltd, China) and the absorbance of the samples were detected by UV-Vis spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd, China).

2.3 Bromide Ion Analysis: H_2O_2 Oxidation-Extraction Photometric Method

Using hydrogen peroxide as an oxidant and concentrated sulfuric acid to enhance its oxidization performance, Br^- was oxidized into Br_2. Photometric determination was conducted after carbon tetrachloride extraction. This method can be used for the determination of bromine concentration in seawater, brine, and other water bodies[30].

Aqueous potassium bromide solution with bromide ion concentration of 20、40、60、80、100 mg /L were prepared as standard solutions. 10 mL standard solution was pipetted in 125 mL separatory funnel, then added 7 mL concentrated sulfuric acid. After the mixture was cooled to room temperature, 0.5 mL 36 wt % hydrogen peroxide was added to react 3 min; then added 5 mL carbon tetrachloride to extract 5 min. The mixture was left to stand until complete lamination, the lower liquid was received with a 1 cm colorimetric ware and its absorbance was measured at 414 nm wavelength. The calibration curve was drawn with bromide ion standard concentration as abscissa (x) and absorbance as vertical coordinate (y).

2.4 Preparation of bromide ion-lanthanum nitrate modified chitosan imprinted polymer

2.4.1 Preparation of lanthanum nitrate modified chitosan

Each of 100 mL beakers was added into 0.4 g chitosan, 2.0 g $La(NO_3)_3\cdot 6H_2O$, and 50 mL deionized water. Put them on the desktop thermostat oscillator to oscillate with rotation speed of 120 r/min for 8 h at room temperature. The contents were filtered and the filtrate was repeatedly washed with deionized water. It was reserved after 50 ℃ vacuum drying[31].

2.4.2 Preparation of bromide ion-lanthanum nitrate modified chitosan

0.5 g lanthanum nitrate modified chitosan was added in 25 mL bromide ion solution with concentration of 100 mg/L for potassium bromide solution and pH 5.0, then stirred for 20 min on desktop constant temperature oscillator at room temperature. The contents were filtered and the filtrate was repeatedly washed with deionized water. Bromide ion-lanthanum nitrate modified chitosan was obtained after 50 ℃ vacuum drying[32].

2.4.3 Preparation of crosslinking bromide ion-lanthanum nitrate modified chitosan polymer

Each of 100 mL beakers was added into 10 mL deionized water, 1 mL 25 wt % glutaraldehyde solution, and 0.5 g bromide ion-lanthanum nitrate modified chitosan, successively, and made bromide ion-lanthanum nitrate modified chitosan suspension. Put them on the desktop thermostat oscillator to oscillate for 10 h at room temperature. The completely crosslinking contents in beakers were filtrated and the filter cakes were repeatedly washed with deionized water, ethanol and ether, successively. The crosslinking bromide ion-lanthanum nitrate modified chitosan polymer was obtained after 50 ℃ vacuum drying.

2.4.4 Preparation of bromide ion-lanthanum nitrate modified chitosan imprinted polymer

1.0g crosslinking bromide ion-lanthanum nitrate modified chitosan polymer was added into 50 mL 1 mol/L sodium hydroxide solution and soaked for 8 h. Bromide ion was eluted from polymer and bromide ion concentration of the eluent was measured. The soaked polymer was repeatedly washed with deionized water until it contained no bromide ion. Bromide ion-lanthanum nitrate modified chitosan imprinted polymer was finally obtained after 50 ℃ vacuum drying.

2.5 Adsorption capacity of the imprinted polymer for bromide ion in potassium bromide solution

Adsorption time and adsorption capacity of bromide ion-lanthanum nitrate modified chitosan imprinted polymer prepared in the same batch were investigated. Considering the fast adsorption rate of the bromide ion imprinted polymer as the kind of surface molecularly imprinted polymer, adsorption time of 10, 20, 30, 40, 60, 120 min was chosen.

0.5 g bromide ion imprinted polymer and a given volume (15 mL, 20 mL, 25 mL, 30 mL, 35 mL, 40 mL) of 100 mg/L standard solution were added into 100 mL beaker. The beaker put on the desktop thermostat oscillator was oscillated for 30 min at room temperature to ensure complete adsorption of bromide ion. The material in beaker was then filtrated and the filter liquor was collected. According to the same operation conditions and operation steps as mentioned above, the filtrate absorbance was measured. Adsorption capacity Q (mg/g) was calculated as follows [33]:

$$Q = \frac{V(C_0 - C)}{M} \quad (1)$$

where C_0 and C are the concentrations of bromide ion in the standard solution and in the filtrate, respectively, mg/L; V is the volume of the aqueous phase, mL; M is the mass of the imprinted polymer, g.

2.6 Desorption and reusability

Repeat use of the imprinted polymer is an important performance index in the study of molecular imprinting technique, static adsorption experiment was repeated on the same batch of the imprinted polymer to investigate the changes in adsorption capacity for obtaining reusability.

0.5g bromide ion imprinted polymer was added in 25mL solution containing 100mg/L of bromide ion for the adsorption progress. Then bromine ion in the imprinted polymer was desorbed by 1mol/L NaOH for stirring for 8h on desktop constant temperature oscillator at room temperature. Adsorption–desorption cycle was repeated four times by using the same imprinted polymers for reusability. The imprinted polymer was washed with 1mol/L NaOH solution after each use and then reloaded.

2.7 Adsorption performance using the imprinted polymer from artificial seawater

2.7.1 Adsorption performance for bromide ion in seawater

300 g seawater crystal and 0.644 g NaBr were added into 10 kg deionized water for preparing artificial seawater with bromide ion concentration of 70 mg/L. 0.5 g bromide ion imprinted polymer was added into 25 mL artificial seawater for adsorption. The following operations were similar to those as mentioned above. The adsorption performance was evaluated by the adsorption capacity Q. The experiment was repeated five times under the same conditions and lanthanum nitrate modified chitosan was directly used for comparation.

2.7.2 Effect of major anions in seawater on adsorption

Seawater is a very complex multi-component aqueous solution. Major cations are Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}. Major anions are Cl^-, SO_4^{2-}, Br^-, $HCO_3^-(CO_3^{2-})$, F^-, etc. These ions, especially the major anions have a competitive adsorption when the imprinted polymer adsorbs bromine ion. The concentrations of major anions in seawater are Br^- 0.067 g/L, Cl^- 19.35 g/L, SO_4^{2-} 2.712 g/L, $HCO_3^-(CO_3^{2-})$ 0.142 g/L, F^- 0.0013 g/L, respectively[34]. In order to investigate the effects of major anions in seawater on bromine adsorption, salt solutions of KBr + Cl^-, KBr + SO_4^{2-}, KBr + HCO_3^-, and KBr + F^- were prepared, respectively. Referring to the above-mentioned concentration values of major anions in seawater, the concentrations of bromide ion in four kinds of salt solutions were all 67 mg/L, and other anions were set different concentration gradients as shown in Table 1. Each solution was pipetted 25 mL for adsorption with 0.5 g bromide ion imprinted polymer. The following operations were similar to those as mentioned above. The anionic effect on bromide ion adsorption was assessed by the adsorption capacity Q.

Table1 The concentration range of seawater anions

Anions	Concentration range(g/L)	Average(g/L)
Cl^-	10.0, 12.5, 15, 17.5, 20.0	19.35
SO_4^{2-}	1.0, 1.5, 2.0, 2.5, 3.0	2.712
$HCO_3^-(CO_3^{2-})$	0.11, 0.12, 0.13, 0.14, 0.15	0.142
F^-	0.6, 0.8, 1.0, 1.2, 1.4 ($\times 10^{-3}$)	1.3 ($\times 10^{-3}$)

3 Results and discussion

3.1 Standard curve of H_2O_2 oxidation-extraction photometric method

The absorbances were measured with bromide ion concentrations of 0, 20, 40, 60, 80, 100 mg/L by H_2O_2 oxidation-extraction photometric method. The standard curve was shown in Figure 1, corresponding to the linear relationship equation as

$$y = 0.0019x + 0.0187, \quad R = 0.9991 \tag{2}$$

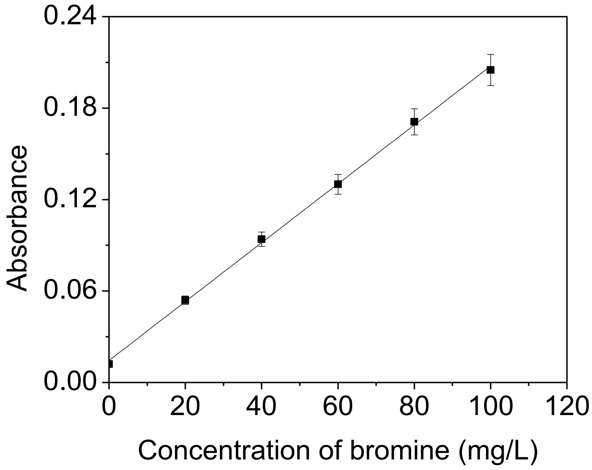

Figure 1 Standard curve of H_2O_2 oxidation-extraction photometric method

3.2 Adsorption capacity

Figure 2 showed that the adsorption capacity of bromide ion imprinted polymer in potassium bromide solution changed with adsorption time from 10 min to 120 min. High adsorption capacity was observed at the beginning and the plateau value (adsorption equilibrium) was reached within 30 min, then it had certain degree of decline due to desorption. This showed the adsorption process was rapid. The reason was obviously that the adsorption sites were in the surface of the imprinted polymer, since the imprinted polymer was prepared by surface molecularly imprinting method.

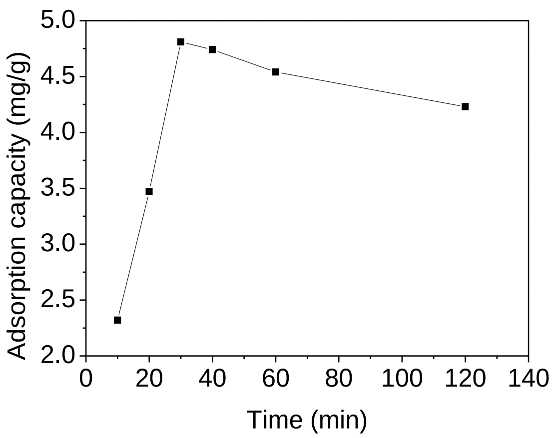

Figure 2 Adsorption capacity varied with time

Adsorption capacity was determined when fixed quantity (0.5 g) of the imprinted polymer was added into potassium bromide solutions with different volume. As shown in Figure 3, with the increase of solution volume, the adsorption capacity increased rapidly in a linear trend at the beginning. It reached the maximum value of 4.81 mg/g at 25 mL potassium bromide solution, The maximum adsorption capacity was 4.81 mg/g for the prepared imprinted polymer in potassium bromide solution.

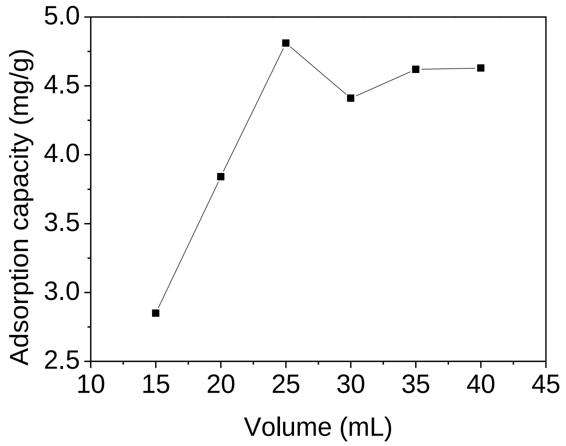

Figure 3 Adsorption capacity varied with solution volume

3.3 Reusability

The reusability of the imprinted polymer was shown in figure 4 through repeating five static adsorption experiments for the imprinted polymer at the same conditions. Recycled number 1 represented the imprinted polymer was used for the first time, then it was desorbed by 1.0 mol/L NaOH, next it was used for the second time, corresponding to Recycled number 2, and so on. The adsorption capacity for the fifth experiment still reached 80.9% of the first use. This result showed that the adsorption capacity of the imprinted polymer had small changes in repeated trials, and the imprinted polymer had good reusability.

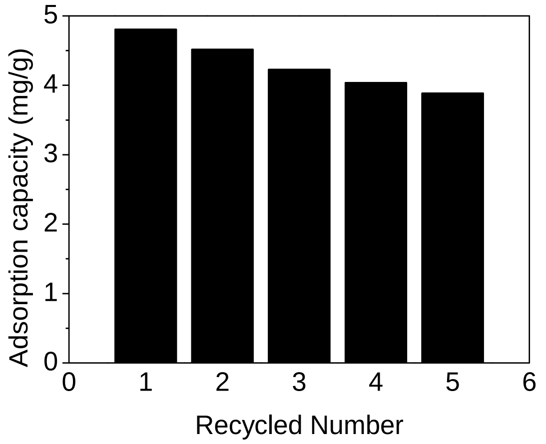

Figure 4 Reusability of the imprinted polymer

3.4 Characterization of the imprinted polymer

The microstructure of the imprinted polymer was analyzed by Scanning Electron Microscope (SEM). Two SEM images with different amplification factor were shown in figure 5. The imprinted polymer after grinding had the following characteristics: irregular shape, rough surface with fracture, sheet and loose texture, and uniform distribution of particle size. The imprinted polymer could be dispersed to particle morphology when diluted in a solution or crushed simply, and the polymer particles had a certain pore structure, so benefited the adsorption of bromide ion.

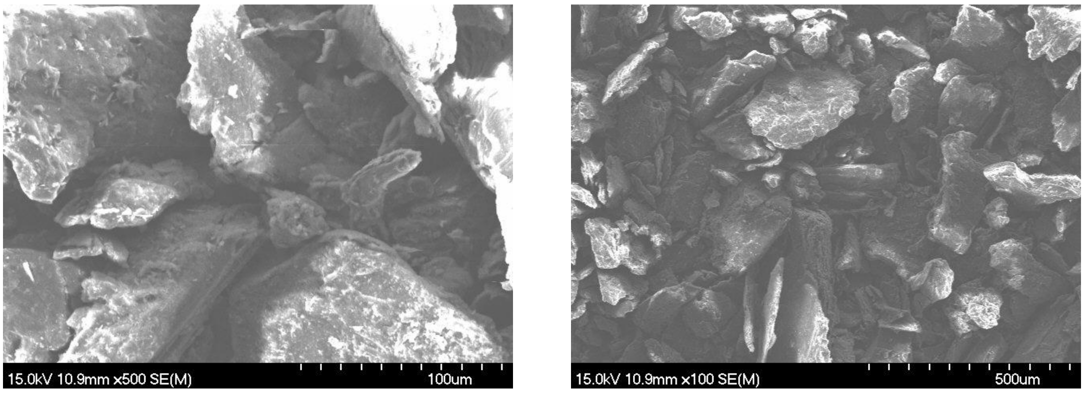

Figure 5 SEM of the imprinted polymer

3.5 Adsorption performance of bromide ion imprinted polymer in artificial seawater

As could be seen from table 2, when the imprinted polymer was used in artificial seawater for bromine adsorption, the average adsorption rate and average adsorption capacity could reach 71.57 % and 2.505 mg/g, respectively. The adsorption rate and adsorption capacity were 26.31 % and 0.921 mg/g when lanthanum nitrate modified chitosan was directly used in artificial seawater. The compared experiment results indicated that lanthanum nitrate modified chitosan imprinted polymer had an excellent recognition property for bromide ion and greatly improved adsorption effect.

Table 2 Adsorption performance in artificial seawater

Number	Adsorption rate	Adsorption capacity
1	71.71	2.510
2	71.43	2.503
3	71.57	2.505
4	71.71	2.510
5	71.43	2.503
Average	71.57	2.505

3.6 Effect of major anions in seawater on bromide ion adsorption

3.6.1 Effect of chloride ion

It could be seen from Figure 6 that concentration of chloride ion had a significant effect on bromide ion adsorption performed by the imprinted polymer. Adsorption rate of bromide ion rapidly declined with the increase of chloride ion concentration. When chloride ion concentration increased from 10 g/L to 20 g/L, the adsorption capacity decreased rapidly from 2.82 mg/g to 2.51 mg/g. The reason, which chloride ion had a great influence on the imprinted polymer for bromide ion recognition, was that Cl and Br are in the same group of the Periodic Table of Elements, and the concentration of chloride ion in seawater is much higher than bromide ion. In view of the fact that it is impossible to remove chloride ion from seawater, the more feasible approach should be to optimize the preparation of the imprinted polymer *via* the improvement of selectivity for bromide ion.

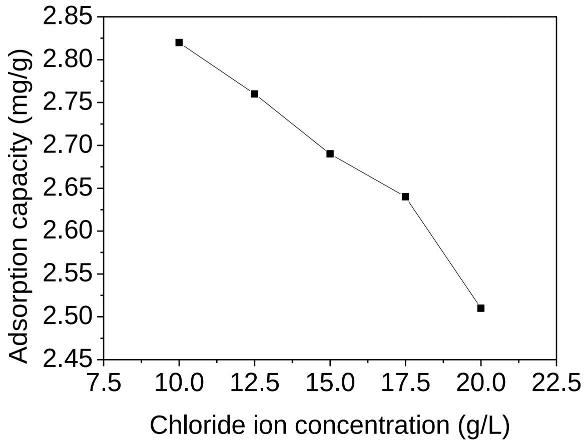

Figure 6 Effect of chloride ion on bromide ion adsorption

3.6.2 Effect of fluoride ion

For the same group element of bromine, fluoride ion had also a significant effect on bromide ion adsorption performed by the imprinted polymer. As was shown in Figure 7, when fluoride ion concentration increased from 0.6 g/L to 1.4 g/L, adsorption capacity reduced from 2.82 mg/g to 2.69 mg/g. Since the concentration of fluoride ion is much lower than chloride ion, fluoride ion had less effect on bromide ion adsorption than chloride ion.

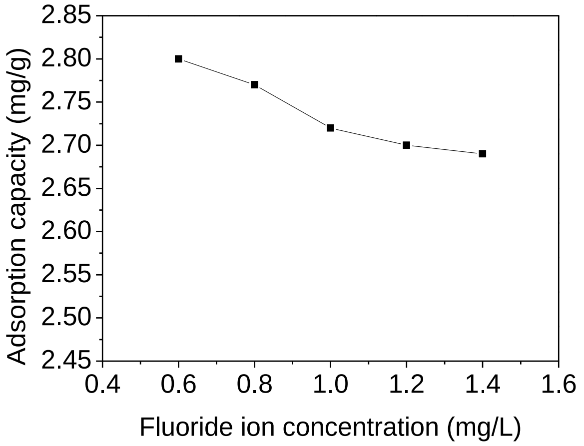

Figure 7 Effect of fluoride ion on bromide ion adsorption

3.6.3 Effect of SO_4^{2-} and HCO_3^- in seawater on bromide ion for adsorption

It could be seen from Figure 8 and Figure 9 that the adsorption capacities decreased slowly with the increase in concentrations of SO_4^{2-} and HCO_3^-, and the two anions had less effect on bromide ion adsorption in the common concentration range of them in seawater. This reflected that the prepared imprinted polymer had excellent selective adsorption ability.

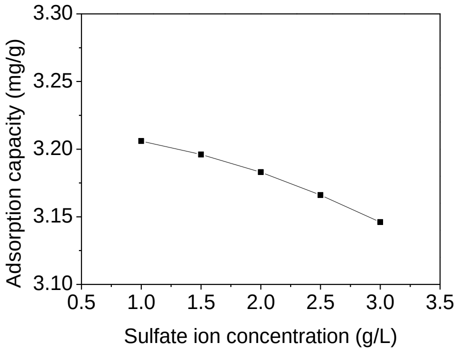

Figure 8 Effect of SO_4^{2-}

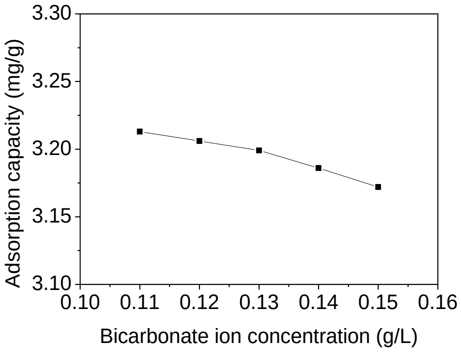

Figure 9 Effect of HCO_3^-

4 Conclusions

In this paper, bromide ion-lanthanum nitrate modified chitosan imprinted polymer was firstly prepared for bromide ion adsorption. The adsorption rate for potassium bromide solution was 96.2 % and the maximum adsorption capacity was 4.81 mg/g. The weaker adsorption effect was observed for the imprinted polymer in artificial seawater, corresponding to the adsorption rate of 71.57 % and the adsorption capacity of 2.505 mg/g. The imprinted polymer had good reusability and its SEM was given. This was attributed to the negative impact of major anions in seawater on bromide ion adsorption performed by the imprinted polymer. Chloride ion and fluoride ion had strong competitive adsorption, but SO_4^{2-} and HCO_3^- had less effect on bromide ion adsorption.

The adsorption performance of the imprinted polymer in artificial seawater was better than that of lanthanum nitrate modified chitosan. The prepared imprinted polymer had an excellent recognition property for bromide ion and improved adsorption effect to a certain extent. Therefore, selection of the imprinted polymer as adsorbent for bromide ion adsorption had the superiority. The new method for the extraction of bromine from seawater was suggested by mean of ion imprinted polymers.

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SEM of bromide ion-lanthanum nitrate modified chitosan imprinted polymer which had an excellent recognition property for bromide ion adsorption