Adsorption behavior of Zn (II) from amidoxime functionalized mesoporous silica SBA-15

Jihua Wang[1, a]

[1]Guangxi Scientific Experiment Center of Mining, College of Environmental Science and Engineering, Guilin University of Technology, Guilin 541004,China

[a]1357673083@qq.com

Keywords: AO-SBA-15, adsorbent, Zn^{2+}

Abstract. The amidoxime mesoporous silica (AO-SBA-15) was prepared and its effects of time, temperature and initial concentration on the adsorption of the aqueous zinc ion were studied. The results indicate that the adsorption performance of zinc ion was good. When the equilibrium concentration was less than 2 $mmol \cdot L^{-1}$, the adsorption capacity increased as the temperature increased. When the equilibrium concentration was over 2 $mmol \cdot L^{-1}$, the adsorption capacity decreased with the increasing of the temperature. As the adsorption continued, the adsorption capacity of zinc ion increased, and tended to reach equilibrium after 120 minutes. The process of adsorption is mainly due to the electrostatic complexation at low Zn^{2+} concentration, whileas it is due to cocalent complexation at high Zn^{2+} concentration.

1. Introduction

With the rapid development of industry, such as metal plating equipment, mining operation, fertilizer production, battery industry, etc., more and more heavy metal wastewater has been emissioned into the environment. Zinc ion is a common type of heavy metal pollutants. Excessive intake of zinc will cause vomiting, diarrhea and other gastrointestinal symptoms, animal experiments will lead to damage of liver or kidney function and immune damage. Common methods of heavy ion removal in water include: electrolysis, chemical precipitation, oxidation-reduction method, adsorption, ion-exchange method, etc. [1]. The adsorption method has advantages of simple operation, safety, simple process and so on, which is often used as a technique to treat the zinc ion in wastewater.

The mesoporous material is the porous material the aperture of which between 2 to 50 nm [2]. The adjustable pore size, pore shape, large specific surface,pore volume and easily surface-functionalization, make it a new adsorbent or carrier. The mesoporous silica molecular sieves have great specific surface area and uniform pore size adjusted within 2~10 nm. Amidoxime is composed of amino and oximido, the oximido (-RC=NOH) is the composite group of alkalescent nitrogen atom and moderate acidic hydroxyl. Therefore, mesoporous silica adsorbent modified by amidoxime has excellent ability of heavy metal adsorption.

This paper using mesoporous silica adsorbent modified by amidoxime (SBA-15) as adsorbent to treat zinc ion, studies the influence on absorption capacity by time,temperature and process condition with initial concentration,providing applicable study data for the clean-up of zinc ion in water.

2. Materials and experimental

2.1 Synthesis of AO-SBA-15 [3]

Amidoxime-functionalized mesoporous silica was synthesized with tetraethylorthosilicate and 2-cyanoethyl triethoxysilane as silicon source, potassium chloride as the crystal structure directing agent and poly (ethylene glycol)-poly (propylene glycol)-poly (ethylene glycol) three block copolymers as template.

2.2 Experimental method

To prepare a series of model wastewater with concentration gradient and add a suitable amount

adsorbent, and to investigate adsorption capacity of the adsorbent at the different initial zinc ion.

In the circumstance of a certain concentration of simulated wastewater and amount of adsorbent dosage, the adsorption capacity of the adsorbent was investigated after a reaction time of a certain gradient. As reported in the literature, when amidoxime groups with a metal ion complex reaction, hydrogen ion will be released. In order to solve the process of complexation reaction, the automatic temperature compensation Sartorius BP-10 pH meter was used to measure the sample acidity before and after the reaction, after calibrating the three-point (4.008,6.865,9.180), referring to *Water Quality-Determination of PH Value-Glass Electrode Method*(GB 6920-86).with reference to *Water Quality-Determination of PH Value-Glass Electrode Method* (GB 6920-86).

2.3 Adsorption tests

The zinc ion in the solution was determined, with reference to *Water quality-Determination of copper, zinc, lead and cadmium-Atomic absorption spectrometry* (GB 7475-87),and the determination method of zinc ion: the wastewater was diluted to a zinc ion concentration varied from 0.1 to 1.5 $mg \cdot L^{-1}$, then was analyzed by A Analyst 700 atomic absorption spectrometer using a lamp current of 10 mA, 213.9 nm, position detector of 0.7 h, acetylene air (flow ratio 2:17), oxidation type flame, and working standard solution concentration of 0.10, 0.20, 0.30 and 0.50, 1.00, 1.50 $mg \cdot L^{-1}$.

The amount of zinc ion retained in the adsorbent phase was calculated by:

$$q = \frac{(c_i - c_e)V}{m}$$

where C_i and C_e are the initial and final (equilibrium) concentration of the zinc ion in solution ($mg \cdot L^{-1}$), V is the solution volume of simulated wastewater added in the adsorption experiment (L), m is the mass of adsorbent (g), and q is the adsorption capacity of the adsorbent obtained by the calculation ($mg \cdot g^{-1}$).

3 The adsorption properties of AO-SBA-15 on the Zn^{2+} ion

3.1 Effects of temperature and initial concentration on the adsorption of Zn^{2+} by AO-SBA-15

Figure 1 shows the adsorption capacity under different initial concentration of zine ion at 20 degrees and 30 degrees. With a lower equilibrium concentration (< 2 $mmol \cdot L^{-1}$) the adsorption capacity would increase with the increase of the temperature, on the contrary, it would reduce with a higher equilibrium concentration (> 2 $mmol \cdot L^{-1}$). Adsorption process of zinc ion presents characteristics of physical adsorption when the concentration increases, and complexation between zinc ion and amidoxime has great effects, During adsorption process, amidoxime may first covalently bound with zinc ion, and then it would not occur stable complex with more zinc ion in a subsequent procedure, but by other effects of zinc ion adsorption.

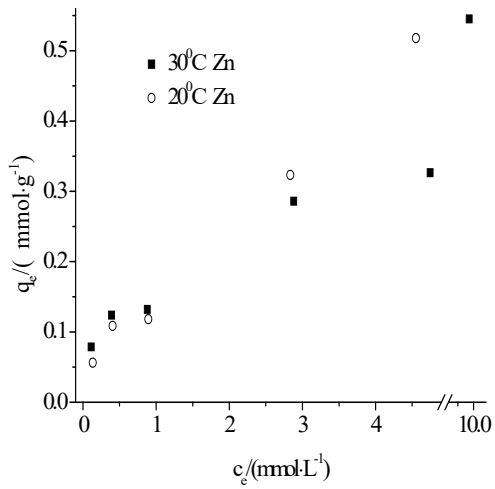

Fig.1. The effect of initial concentration and temperature on AO-SBA-15 adsorbing Zn^{2+}.

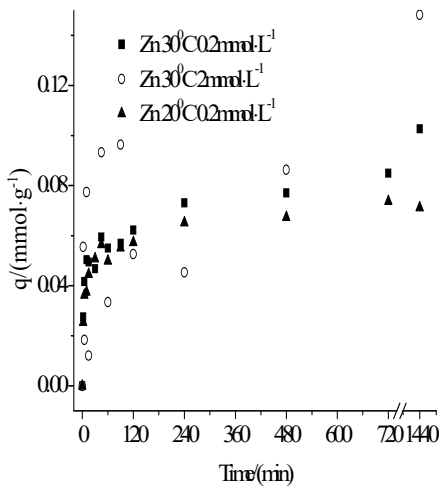

Fig.2. The effect of reaction time on AO-SBA-15 adsorbing Zn^{2+}.

3.2 Effect of reaction time on the adsorption of Zn^{2+} by AO-SBA-15

As shown in Figure 2, the adsorption mainly occurred within 120 minutes, the adsorption capacity slightly increased with the prolonging of time. Subsequent adsorption capacity is not within 2 h significantly increased. However, the adsorption capacity didn't significantly rise in the following 2 h, but the adsorption capacity of 12 h had a certain increase compared with the adsorption of 4 h, so did the adsorption of 24 h compared with the 12 h.

Hydrogen ion adsorption process changes as follows: when the initial concentration was 0.2 $mmol \cdot L^{-1}$,the H^+ decreased and the adsorption reached the peak after 4 h reaction, at 20 degrees, and then H^+ increased slightly; At 30 degrees the adsorption peak appears after 4 h, poses 1/3 of the 20 degrees capacity, and then unchanged. When the initial condition was 2 $mmol \cdot L^{-1}$ and 30 degrees, aqueous H^+ increased at the first 4 h, and released about 0.2 $mmol \cdot L^{-1}$, which doubled the 20 degrees condition; After 4 h, H^+, lower than the origin concentration, began to decrease as time went on, and after 24 h, adsorption capacity of H^+ was slightly higher than the 0.2 $mmol \cdot L^{-1}$, 20 degrees condition. The adsorption process shows that the capacity of Zn^{2+} and H^+ indicates the process is complicated. At low concentration the electrostatic complexing may mainly take control, while at high concentration covalently complex.

4. Results and discussion

This paper discusses the adsorption properties of AO-SBA-15 on the Zn^{2+} by the reaction time, temperature and the initial concentration parameters. The results show that the adsorption of zinc ion had good performance, when the equilibrium concentration was less than 2 $mmol \cdot L^{-1}$, the adsorption capacity increased as the temperature rose; when it was over 2 $mmol \cdot L^{-1}$, the adsorption capacity decreased with increasing temperature. As the adsorption continued, adsorbent adsorption capacity of zinc ion increased. When the adsorption reaction proceeded about 120 minutes, most of the adsorption process completed.

The process of adsorption is mainly due to the electrostatic complexation at low Zn^{2+} concentration, while due to cocalent complexation at high Zn^{2+}. There still exists covalent complex between amidoxime group and zinc ion on the adsorbent after covalent complex. Since the electrostatic force is weaker than the covalent complexation, it presents characteristics of physical adsorption. The adsorption process of zinc ion shows that electrostatic and covalent complex have a certain effect on the adsorption of zinc ion.

Acknowledgements

The author thank the support of National Natural Science Foundation of China (No.51566003) and National Natural Science Foundation of Guangxi (No.2015GXNSFAA139231).

Reference

[1]. Research progress in a new type of adsorbents for removing heavy metals from wastewater. *Industrial Water Treatment*, 2014, 34(7):5-9.

[2]. Sing K S W(UK, Chairman), Everett D H (UK), Haul R A W(F R G), et al Reporting physisorption date for GAS /SOLID systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.*, 1985, 57(4):603-619.

[3]. Chia-min Yang, Yanqin Wang, Bodo Zibrowius, et al. Formation of cyanide-functionalized SBA-15 and its transformation to carboxylate-functionalized SBA-15. Physical Chemistry Chemical Physics, 2004, 6(9): 2461-2467.