Preparation of Diamine-modified Ordered Mesoporous SBA-15 and Its Adsorption Property to Pb^{2+}

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Abstract. With the method Hydrothermal-photosynthesis, respectively prepare mesoporous silica adsorbent with different content of diamine-modified, 5%2N-SBA-15 、 10%2N-SBA-15 、 15%2N-SBA-15 、 20%2N-SBA-15. All mesoporous materials were characterized by X-ray diffraction(XRD), Fourier transform infrared spectroscopy(FT-IR)、N_2 adsorption-desorption and scanning electron microscopy(SEM). Discuss on how the system factors such as pH value, adsorption time and adsorption temperature affect on the adsorptive property of Pb^{2+} in the water. The result is that, the optimal adsorption time, adsorption temperature, and pH value, is 60min, 40℃, and5, wich means material shows the best performance of Pb^{2+} adsorption under such condition. The optimal range of content diamine photosynthesised on SBA-15 is 10%~15%.

Introduction

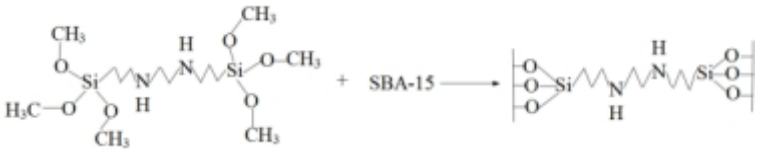
Heavy metal pollution is environment pollution caused by metal or other chemical compound the density of which higher than 5[1]. The pollution manly caused by development of mine, release of waste, or the use of heavy metal, with the property of enrichment and hard to degrade[2]. Among the heavy metal, Pb, Hg, As, Cd, have the most toxic effect on human's body. These metal can't resolve in water, become more toxic after being drink in, combine with other poison in water form organics with stronger toxicity[3,4]. Now there're Variety of methods to reduce the heavy metal pollution in water, the most common is adsorption method[5,6], it's a way to use mesoporous absorpting and separate harmful substance in water[7]. There's been a booming of mesoporous materials in recent decades especially Mesoporous silica materials, has became a hit research area since it's easy to prepare and have larger specific surface area and mesopore volume[8-11]. Mesoporous SBA-15 has highly ordered Two-dimensional six square channel[12], pore size can range from 5nm to 30nm[13]. However, pure silicon mesoporous SBA-15's structure only consists of silicon and oxygen, the lack of active center cause a poor ion-exchange capacity. So the main idea of this paper use photosynthesis add different amounts of Diamine to pure silicon SBA-15 to increase the material's absorbability to Pb^{2+} in water.

Experimental

The preparation of Diamine of different content

Pure silicon SBA-15 was synthesized refers to paper by a sol-gel method[14]. In a typical synthesis，1g pure silicon SBA-15 was added into round-bottom flasks, drying over night at 120℃ vacuum drying oven. Then 30mL dried methylbenzene was added, and then different amounts of N-3-(Trimethoxysily)propylethylenediamine was added. The reaction mixture was then stirred at room temperature for 24h. The resulting solid was altered and rinsed with methylbenzene and ethanol

repeatedly and dried over night to obtain a dry white solid. The solid was then further dried at 80 °C under vacuum for 24 h to give mesoporous silica materials contain different amount of diamino termed 5%2N-SBA-15、10%2N-SBA-15、15%2N-SBA-15、20%2N-SBA-15.



Scheme1. Synthesis of diamine-modified materials(2N-SBA-15)

Characterization of the samples

Test the mesoporous materials' structure by D/max-2200/PC type X-ray diffractometer. Small Angle XRD scan's range is 0.4 ~ 5 °. Step-length :0.02°. The sample's fourier transform infrared (FT-IR) spectral analysis use Rontier LR64912C type spectrometer, using KBr sample preparation. Measure specific surface and pore volume by 3H-2000PS2 type adsorption instrument.

Adsorption experiments and The determination methods of Pb^{2+}.

Separately add 50mL SBA-15 with different contain of diamine into 40mL100mg/L $Pb(NO_3)_2$ solution, using magnetic blender mixing time, take the supernatant fluid, with Z-5000 atomic absorption spectrometer to determine residual concentrations of Pb^{2+}.

Results and Discussion

Characterization of the prepared samples

Figure.1 shows spectrograms of Pure silicon SBA-15 and SBA-15 contains different amount of diamine, it can be seen that, pure silicon SBA-15 has a strong (100) crystal plane characteristic peak at 0.8° . Material grafted different quantity of diamine has strong characteristic peak at 0.8° ~ 0.9°,confirms that modified material still has the typical ordered six-party pore structure[15-18],(110) and (200) characteristic peak intensity gradually decline with the increase of diamine the material contain.When the content of grafted diamine up to 20% (110) and (200) characteristic peak almost disappeared, that means grafting reactive too much will affect the order of mesoporous materials.

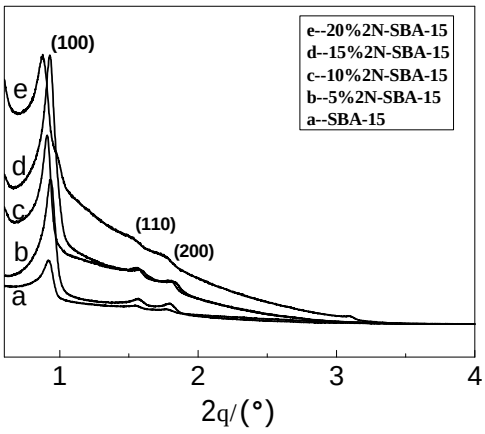


Fig.1 Powder X-ray diffraction patterns

Figure.2 is the infrared spectrogram of pure silicon SBA-15,5%2N-SBA-15、10%2N-SBA-15、15%2N-SBA-15 and 20%2N-SBA-15.All the materials shows a wide absorption peak at about 3442.02cm^{-1}, belongs to the stretching vibration peak of Si-OH. At about 775.69cm^{-1} belongs to Si-O-Si symmetric stretching vibration peak, and 1120.87cm^{-1},asymmetric stretching vibration peak[19].And, 1632.78cm^{-1} for the vibration of the water -OH; Compared with pure silicon SBA-15,

diamine SBA-15 appeared absorption peak in the vicinity of 1596.94cm^{-1}, -NH_2 characteristic peak confirms successfully grafted onto the SBA-15 successfully.

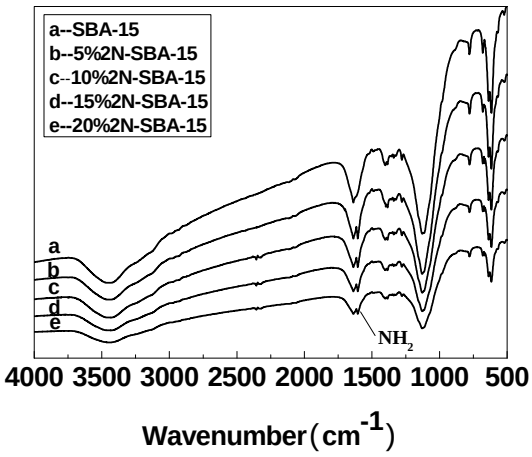


Fig.2 IR spectra of samples

Figure.3 is the N_2 adsorption-desorption isotherms and pore size distribution of pure silicon and different content of diamine SBA-15 mesoporous materials. According to the IUPAC division method, all curve shows a type IV type isotherm and H1 hysteresis loop, and there is an obvious wool stoma condensation phenomenon, it's the mesoporous structure[20]. Table 1 shows SBA-15's parameters such as specific surface area before and after grafted diamine. According to the table, after grafting diamine, SBA-15 specific surface area, pore diameter and pore volume are reduced. This is because the introduction of active group occupied part of the channel, due to the increase in grafting of reactive, materials for the adsorption of Pb^{2+} in water keep increase.

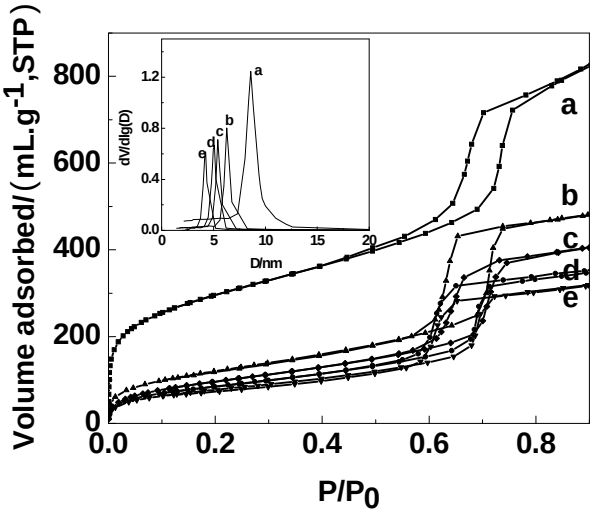


Fig.3 Nitrogen adsorption-desorption isotherms of samples
(a)SBA-15 (b) 5%2N-SBA-15 (c)10%2N-SBA-15 (d)15%2N-SBA-15(e)20%2N-SBA-15

Table 1 Structural and physic-chemical properties of mesoporous material

Sample	Surface area（m^2/g）	Pore volume（cm^3/g）	Pore size（nm）
SBA-15	874	1.27	9.42
5%2N-SBA-15	449	0.79	7.10
10%2N-SBA-15	398	0.69	6.93
15%2N-SBA-15	317	0.62	6.68
20%2N-SBA-15	286	0.58	6.39

Figure.4 is SEM image of 5%2N-SBA-15、10%2N-SBA-15、15%2N-SBA-15、20%2N-SBA-15. It can be seen that 2N-SBA-15 is highly ordered mesoporous material with smooth channel. Tiny particles appear on channels as the increase in the amount of the grafted diamine , confirms that diamine has been successfully grafted onto the SBA-15. When the grafted diamine reached 20%, the channel of mesoporous materials were a lot of congestion, order was damaged. So consider of the structure, diamine grafted is better between 10%~15%.

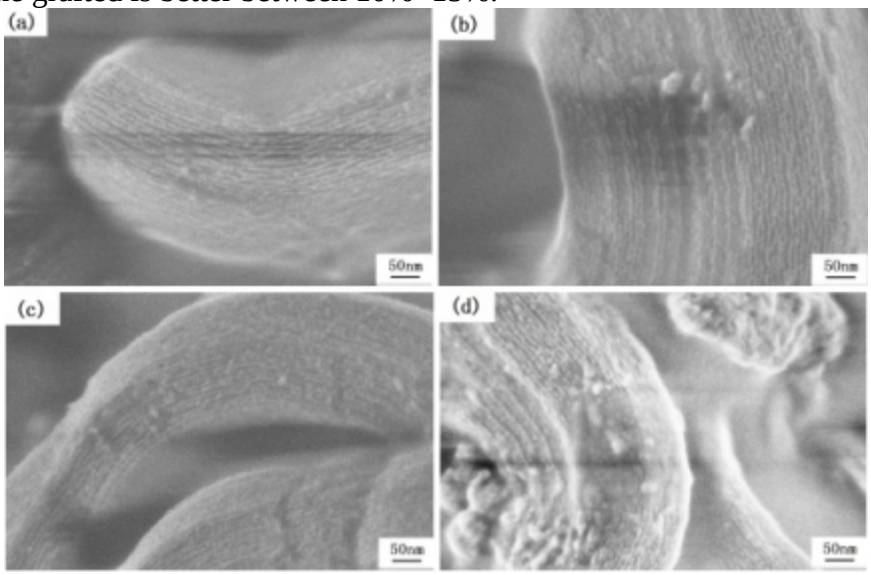


Fig. 4 SEM image of SBA-15 with different diamine
(a) 5%2N-SBA-15;(b)10%2N-SBA-15;(c)15%2N-SBA-15;(d)20%2N-SBA-15

Study on adsorption properties

The effect of pH on Pb^{2+} adsorption

The greatest influence on adsorption properties of mesoporous materials is the pH of the system. With other conditions of the adsorption constant, regulate the pH of Pb^{2+} by adding 0.01 mol/L HCl or NaOH. The experimental results is shown in figure5.Results show that, the material's adsorption properties of Pb^{2+} in water increase when more diamine grafting on, as more active centre created by that. But after grafting diamine content more than 10%, the adsorption rate of change is small, from the point of saving material and characterization results, 10% ~ 15% of the grafted diamine is most appropriate. For 2N-SBA-15 of different content, adsorption trend of Pb^{2+} in water is basically the same, when pH<4, materials for the adsorption of Pb^{2+} in water rate is kind of low, the adsorption become a equilibrium of reaction when pH reaches 5 , so the material the best adsorption system pH value of 5.

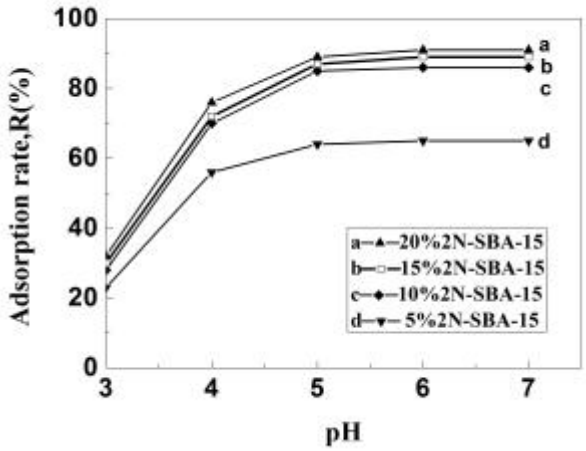


Fig.5 Effect of solution pH on adsorption efficiency

Influence of adsorption time on the absorption of Pb^{2+}

2N-SBA-15 adsorpt Pb^{2+} in a rapid progress, the adsorption efficiency can reach a large value within 20min. It can be seen from Fig.6, adsorption rate of all materials grafted with different content of diamine increase obviously as the passage of time. But after grafting amount is more than 10% materials for the adsorption of Pb^{2+} rate change is small, so the grafting quantity between 10% to 15% is the best. We can also see that the adsorption rate of 0~40min5% 2N-SBA-15、10%2N-SBA-15、15%2N-SBA-15 and 20%2N-SBA-15 increase regularly, as the reaction time keep on, the reaction reach a balance almostly , so the best adsorption time, 60min.

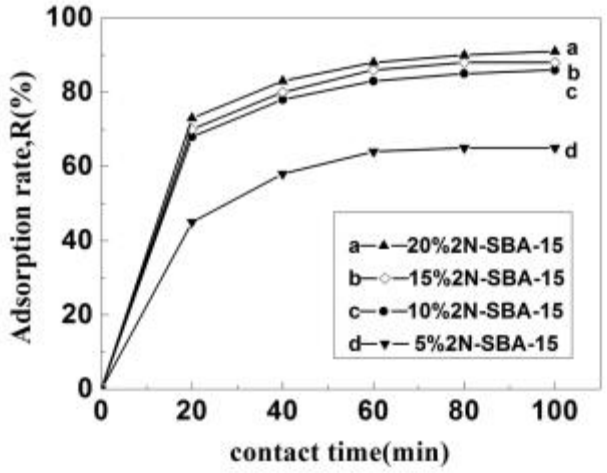


Fig.6 Effect of contact time on adsorption efficiency

The adsorption temperature's effect on the adsorption of Pb^{2+}

Temperature doesn't make a great difference on the adsorption rate.Fig.7 shows, the adsorption trend of Pb^{2+} in water of these materials grafted with different content of diamine are basically the same, adsorption rate increase when the temperature rise, the rate reaches a stable when the temperature is 40℃, adsorption is saturated. So select the temperature 40℃ as the best adsorption temperature of the system.And,also we made the collusion from this figure that, the material's adsorption rate of Pb^{2+} in water keep increase when the diamine coment grafted on range from 5% to 20%, when the content above 10%, the rate had no obvious change. Consider all the information, the most appropriate diamine content is at 10%~15%.

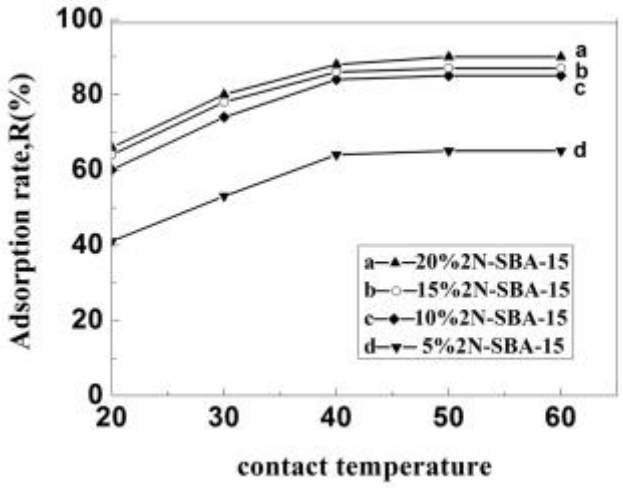


Fig.7 Effect of contact temperature on adsorption efficiency

Conclusions

This experiment prepare different content of diamine modified mesoporous silica adsorbent 5%2N-SBA-15、10%2N-SBA-15、15%2N-SBA-15、20%2N-SBA-15 with the method of hydrothermal-photosynthesis, SBA-15 shows a better adsorption efficiency of Pb^{2+} in water after grafted with diamine,and,the more diamine content in the material, the better absorption efficiency of Pb^{2+} it shows. But the adsorption rate doesn't change obviously when the content is above 10%,so the most appropriate content is 10%~20%. Other conclusion is, the best system pH value of adsorption is 5, time 60min, temperature 40℃, based on a large amount of experimental.

Acknowledgements

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