Preparation of cellulose-based cationic adsorbents and their removal of Pb (II) from water

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Abstract: Industrial production is a double-edged sword, which not only brings convenience to human beings, but also does some harm to the environment. Water pollution, especially heavy metal pollution, has become a major environmental problem. In this paper, ionization reagent was prepared and attached to cellulose to obtain Cell-IA. The cationic Cell-IA was selected to evaluate the adsorption properties of PbII. The effect of the adsorbent on the actual sewage treatment was studied and whether the adsorbent could be applied in practice was determined.

Keywords: Cellulose; Heavy metal ion; Pb(II); Chemical modification.

1. Introduction

Modern industry has brought much convenience to the world. However, at the same time, inevitably, it has also done much harm to our environment. In the process of industrial procedure, not only the gaining of resources but also the emission of industrial waste would be harmful to the surrounding. Among the various environmental problems, water pollution is rather serious. Especially the pollution caused by heavy metal ion. Too much heavy metal ion will cause a series of trouble. The excess of heavy metal ion in the water will endanger fishes and shrimps and if it becomes more serious, it may lead to the death of these creatures. Then it will destroy the ecosystem in the water. What's more, this can damage the health of people due to the accumulation of these heavy metal ions. Therefore, removing the heavy metal ions and recycling those recyclable ions have been the concerned and studied issues.

Heavy metal waste water is produced widely. Exploitation and smelting of the metal mine mainly produces heavy metal in water. What's more, some industries like electrolysis and chemical industry could also leave some heavy metal in to the water. Such as waste water containing copper and mercury that is discharged from chemical fertilizer plants and waste water containing mercury and lead discharged from chemical plants both can be victims. The water polluted by heavy ions keeps the features such as it is long-term poisonous and difficult to degrade. It may even be absorbed and accumulated by

our bodies from food chain. This accumulation can cause various diseases and dysfunction and seriously destroy our health in the end. The main sorts of metal that cause pollution include Cu, Ni, Hg, Pb, Cd, Cr and so on. The Minamata disease that happened in Japan in 1960s was caused by the excess of mercury in rivers.

The lead is a part of heavy metal. It has high density and strong ductility. It can't be easily degraded in surrounding. It also has highly potential toxicity to our lives and environment. Therefore, the lead is a strong pollutant, too. The lead ions taken in by people would invade their nerve tissue and damage their brains. It may lead to death if it is worsen. Lead and its compounds both contain toxicity. What's more, besides strong oncogenicity, they would do harm to immune system and urinary system after being absorbed by people. Industrial wastewater containing lead, lead deposition in the atmosphere and the dissolution of lead mineral are the main sources of lead in water.

At present, to deal with heavy metal wastewater, we may use chemical method, physical treatment method and biological treatment method. The chemical method would be taken when the concentration of the heavy metal ions is too high in the water. Such as oxidation-reduction method and coagulation method. Adsorption method is often taken by us, too. It is more efficient to remove the heavy metal in the water in this way. Furthermore, costing would be reduced when the cheap cellulose is used to be the adsorption material.

Cellulose, as a important composition of the cell walls, can be found widely. What's more, it is recyclable.

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Because of its biodegradability, it almost does no harm to the environment. It can be processed to be a kind of sorbent through the modification of cellulose so that we can remove the heavy metal in the water. This adsorption material would keep some advantages such as less costing and larger specific area after turning into an adsorption material by chemical modification. This measure that we prepare the cellulose adsorption material would cost less and have higher removal rate. This means has bright applying prospect so it has become the focus of researchers.

2. Materials and methods

2.1 Instruments and reagents

Deionized water is used in this experiment and other chemical reagents and instruments which are made use of are shown in the figure 1 and 2 below.

Tab.1 Main reagents

Names of reagents	purity	Names of manufacturers
Diethyl iminodiacetic acid	98 %	Beijing Lianhe Technology Co., Ltd
Epichlorohydrin	Analytical pure	Aladdin
Dioxane	98 %	Aladdin
NaOH	Analytical pure	Tianjin kemio Chemical Reagent Development Center
K ₂ CO ₃	Analytical pure	Tianjin kemio Chemical Reagent Development Center
HCl	Analytical pure	Tianjin kemio Chemical Reagent Development Center
Pb(NO ₃) ₂	Analytical pure	Aladdin

Tab.2 Instruments and models

Names of instruments	models	Names of manufacturers
Precision acidity meter	PHS-25C	Shanghai Haozhuang Instrument Co., Ltd
Vacuum drying oven	DZF-6050	Beijing Zhongke Environmental Test Instrument Co., Ltd
Analytical balance	AUW220D	Shimadzu
Variable speed multipurpose oscillator	HY-2	Jiangsu Jintan Youlian Instrument Research Institute
Mechanical agitator	RW20	IKA
Precision three purpose thermostatic water tank	HH420-2B	Shanghai Binglin
Nuclear magnetic resonance instrument	Bruker Avance III	Bruker

2.2 The preparation of resources

Fig.1 The composition route of IA

The preparation of IA, the ionizing reagent has been completed. detailed steps are shown below: firstly, weigh 15.0 grams of dimethyl iminodiacetic acid then put it into a double neck bottle whose volume is 150 ml. then add the mixed reagent of water and dioxane(the ratio is 1:1). After stirring the reagent for 30 minutes, add 10.0 grams of epichlorohydrin. They will react for 24 hours in the condition of 30 degree Celsius . then when the reaction is over, filtration is needed. Then we will get the precipitate. Then we need to wash it for 3 times with deionized water and dry out it in the condition of 60 degree Celsius. Finally, we will get the IA that we want 13.25 grams.

Tab.3 The results of characterizing the IA's structure through NMR are shown below.

Compound	¹ H NMR, δ (ppm) 500 MHz, (DMSO- <i>d</i> ₆)	¹³ C NMR, δ (ppm) 125 MHz, (DMSO- <i>d</i> ₆)
IA	3.75 (m, 1H), 3.69 (dd, <i>J</i> = 10.9, 4.2 Hz, 1H), 3.52 (dd, <i>J</i> = 10.9, 5.5 Hz, 1H), 3.46 (s, 4H), 2.75 (dd, <i>J</i> = 13.6, 5.4 Hz), 2.67 (dd, <i>J</i> = 13.6, 6.4 Hz)	174.3, 72.1, 58.4, 53.8, 48.8, 36.4

Fig.2 Composition routine of Cell-IA

The composition routine of Cell-IA is shown in the figure 2. The detailed steps are as follows: firstly, weigh 3.0 grams of cellulose and then add it into the 15% (w / V) NaOH aqueous solution. This reaction will last for 2 hours with mechanical stirrer at 80 ° C. and then, add some IA aqueous to the cellulose. It will take 10 hours to complete this reaction at 80 ° C.

The product needs to be centrifuged after the reaction is over. Then wash the solid with water for twice and next, wash it with absolute ethanol for once. The final step is to freeze and dry out the product and the modified cellulose IA will be done.

2.3 The modified material's ability to absorb Pb(II)

2.3.1 The effect on the absorption of the content of the Cell-IA

Take 20 ml of Pb (II) solution with a concentration of 200 mg L⁻¹. Add it to a 50 ml triangular flask. And then add 0.5 – 3 G L⁻¹ adsorbent cell IA. Adjust the pH to 5.0. start the adsorption at the room temperature. Filter the mixture after 12 hours' adsorption. Then measure the content of Pb(II) in the remaining solution. And then calculate the amount and efficiency of the adsorption. Finally, evaluate the effect of the content of Cell-IA. We need to perform three parallel experiments in each group and repeat three times.

2.3.2 Effect of solution pH on Pb (II) adsorption

Take 20 ml of 200 mg L⁻¹ Pb (II) solution, add it into a 50 ml triangular flask, then add 0.04 g of Cell-IA to the triangular flask. Adjust the solution pH to 1.0-6.0. adsorb it for 12 hours at room temperature. Then filter the product. Then determine the content of Pb(II) in the remaining solution. Then work out the removal rate of Pb(II). Finally, evaluate the effect of solution pH on Pb(II) adsorption. We also need to perform 3 parallel experiments in each group and repeat for 3 times.

2.4 The norm of performance evaluation

This experiment regards the adsorption capacity and removal rate of Pb(II) in the solution as the norm of adsorption performance. Take 20mg composed Cell-IA and place it into 25ml conical flask. Then add 20 mL 200 mg L⁻¹ Pb(II) solution. Shake at a constant temperature of 200 rpm at 20 ° C for 3 hours. Suction filtration is after the reaction. Take some filtrate accurately from the flask. Dilute it and then determine the content of Pb (II) in solution by atomic spectrophotometry. Then, we can calculate the adsorption capacity (QE) and removal rate by formula 2-1 and formula 2-2.

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2-1)$$

$$\text{Removal rate}(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2-2)$$

In the formula, q_e is adsorption capacity (mg g⁻¹) ; C₀ and C_e are the Content of Pb(II) (mg L⁻¹) before and after the adsorption. V is the volume of the solution (L) ; W is the content of sorbent (g) .

3. Result and analysis

3.1 The effect of the content of Cell-IA on Pb(II) adsorption

Fig.3 The effect of the content of Cell-IA on Pb(II) adsorption In the specific condition, the result of the effect of the content of Cell-IA on Pb(II) adsorption is shown in the figure 3.

We can conclude from this figure that when the content of Cell-IA rises from 0.5g L⁻¹ to 2.0 g L⁻¹, the removal rate of the Pb(II) rises from 71 percent to 92 percent consistently. This is because the increase of dosage of the Cell-IA brings more adsorption sites, which are helpful to adsorption. When the dosage is beyond 2 g L⁻¹, its effect on removal rate isn't so obvious like before. Perhaps this is because when the concentration of Pb(II) in the water is low, Pb(II) has lower probability of touching the activated sites. So in the later researches, we keep the dosage of the Cell-IA at 2 g/L.

3.2 The effect of solution pH on adsorption of Pb(II)

Fig.4 The effect of solution pH on adsorption of Pb(II) by Cell-IA

The pH also plays an important role in adsorption process. when the pH is between 1.0 and 6.0, the performance that Cell-IA removes the Pb(II) is shown in the figure 4.

When the solution pH ranges from 1.0 to 5.0, removal rate of Pb(II) increases from 12 % to 93 %.when the solution pH is 6.0, the removal rate of Pb(II) is almost

the same as the rate in pH 5.0. removal rate can change in different pH condition, it may because: when the pH is low, the concentration of H^+ in the reagent is high, which may occupy plenty of activated sites. This will have an influence on adsorption of Pb(II), so with the increase of pH, Cell-IA can remove more Pb(II) when the pH is under 5.0, Pb in the solution is in the form of Pb^{2+} when the pH is near 6.0, Pb in the solution is in the form of $Pb(OH)^+$, this may influence performance of the sorbent, Cell-IA.

4. Outcome and discussion

When the dosage of Cell-IA increases from 0.5 g L⁻¹ to 2.0 g L⁻¹, the removal rate of Pb(II) by Cell-IA increases from 71 % to 92 %, when the dosage of Cell-IA is beyond 2 g L⁻¹, there is no obvious effect on Pb(II). when the solution pH ranges from 1.0 to 5.0, the removal rate of Pb(II) increases from 12 % to 93 %. When the pH is 6.0, removal rate of Pb(II) is almost the same as that in the solution of pH 5.0.

Cellulose is a sort of recyclable resource which can be found widely. It is economical and environmentally friendly. We can prepare sorbent that is applied in adsorbing heavy metal ions by modifying cellulose material and adding some functional groups with good adsorption performance. If we use this prepared sorbent to remove the heavy metal in the water, we will get higher removal rate and less cost, which is in advance in processing heavy metal wastewater. In recent years, more and more people focus on this field. With further studies, I believe that cellulose adsorption material can play a more and more important role in fighting against heavy metal wastewater.

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