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Preparation of SiO₂ modified chitosan and properties in treating dye wastewater

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ABSTRACT

SiO₂ modified chitosan was prepared by modifying chitosan with trimethoxysilane treated SiO₂, and the effects of different factors, like dye solution pH value, adsorption time, dye original concentration and temperature on the adsorption of three types of dyes, methyl orange, acid magenta and crystal violet, using the prepared modified chitosan were studied. The results show that the dye adsorptivity of the modified chitosan increase with the decrease of the solution pH and the increase of initial mass concentration, and it decrease with the rise of temperature. The adsorption equilibrium can be reached within 60 min; Acidic dyes with azo and sulfonic acid group in the structure can be easier adsorbed by the modified chitosan, while the adsorption effect of basic dyes is not ideal.

1. Introduction

In recent years, the pollution issue of dyeing wastewater to environment has become more and more serious, and the treatment of dye wastewater has become a common concern. Dyeing wastewater mainly comes from dyes and dye-intermediates production industry and utilization industry. Many methods have been developed to treat dyeing wastewater. Among these methods, biological adsorption method with adsorbent has more superiority compared with other common technologies. It is because that the adsorbent is cheap and easy to get, the amount of adsorption is large, good selectivity, wide range of operating conditions and the adsorbent can be recycled etc.[1-3].

Chitosan molecular structure contains a large number of free amino and hydroxyl groups, which make it not only have high efficiency flocculation, but also have non-toxic side effects and is easy to degrade. It is an ideal biocative adsorbent. Chitosan and its derivatives are rich in resources, easy to source, non-toxic, harmless, and have a variety of characteristics. So it is a green water treatment adsorbent, which has important application value in sewage treatment. The study on adsorption performance of chitosan on organic dyes has important practical significance in the treatment of soluble dye wastewater. However, it is soluble in acidic solution and has some degree of swelling, which limits its application in some fields [4, 5]. The hybrid materials combined with chitosan and inorganic materials have the advantages of inorganic materials and organic materials, and have excellent performance and have become an effective way to improve the performance of chitosan.

Therefore, In this work, SiO₂ modified chitosan was prepared by modifying chitosan with trimethoxysilane treated SiO₂, and the effects of different factors, like dye solution pH value, adsorption time, dye original concentration and temperature on the adsorption of three types of dyes, methyl orange, acid magenta and crystal violet, using the prepared modified chitosan were studied.

2. Experimental

2.1 Main experimental reagents

2.2

Chitosan: deacetylation degree is 95%, Hengtai county jinhu products co., LTD.; Trimethoxysilane treated SiO₂: Henan nano-technology co., LTD.; Sodium acetate, Glacial acetic acid, Succinic anhydride, n-Butanol: Analytical pure, Tianjin Guangfu fine chemical research institute; Methyl

orange, Acid magenta, Crystal violet: Analysis pure, Shanghai reagent the third plant.

2.3 experimental instruments

UV725 uv visible spectrophotometer: Shanghai yuke instrument co., LTD.; PHS-3C precision acidity meter: Shanghai precision science instrument co., LTD.; 80-2 centrifugal precipitator: Jiangsu province jintan city zhongda instrument factory; HH-2 Digital constant temperature water bath pot: Jiangsu province jintan city instrument manufacturing co., LTD.

2.4 Preparation of modified chitosan

5g trimethoxysilane treated SiO₂ and 3g butyric acid anhydride reacted for 2h under 50 °C. the product was dried in the oven with vacuum pump getting solid powder; On the other hand, 1 g chitosan was scattered in n-butyl alcohol, and then added the solid powder; the solution was heated to 80 °C and maintained for 7 h. Then it was filtered and dried in the oven getting the white solids, which was modified chitosan [6].

2.5 Adsorption experiment of modified chitosan on organic dyes

2.4.1 Mass concentration of dye solution and absorbance

0.03 g methyl orange, 0.03 g acid magenta and 0.01 g crystal violet were accurately weighed, and dissolved in deionized water fixing the capacity to 1000 ml. Methyl orange solution with a mass concentration of 30 mg/L, acid fuchsin solution with a mass concentration of 30 mg/L and crystal violet solution with a mass concentration of 10 mg/L were obtained. Then diluted to the required concentration in turn. At the corresponding maximum absorption wavelength (methyl orange: 500nm; Acid magenta: 550nm; Crystal violet: 590 nm), The absorbances (A) of dye solutions with a series of different mass concentration (ρ) were determined and A-ρ working curves were drawn.

2.4.2 Determination of adsorptive capacity

The modified chitosan (0.10 g) was weighed and put into 40.0ml dye solution with a certain mass concentration in a 250mL conical bottle. Then 20.0 mL acetic acid - sodium acetic acid buffer solution was added. It was covered with the plastic film and oscillated for a certain time at a certain

temperature. After the adsorption process, it was centrifuged for 5 min under 3000 r/min. Then the supernatant fluid was taken and its absorbance was determined under the corresponding maximum absorption wavelength, and according to the corresponding working curve to calculate the adsorptive capacity of chitosan and the concentration of residual dye in the solution. The calculation formula of adsorptive capacity is:

$$q = \frac{V(\rho_0 - \rho_e)}{m}$$

In formula, q is the adsorptive capacity of chitosan with unit mass (mg/g), V is the volume of solution (L), ρ_0 is the original mass concentration of dye solution before adsorption (mg/L), ρ_e is the mass concentration of dye solution when getting to equilibrium (mg/L), m is the mass of the chitosan (g).

2.4.3 Effects of different factors on adsorption properties of modified chitosan

The effects of organic dye solution pH, adsorption time, adsorption temperature and dye initial concentration on adsorption performance were investigated.

Modified chitosan and dye solution were put into conical flask respectively. Then it was covered with preservative film, oscillated for a period of time, centrifuged, and its supernatant fluid was taken and determined at the corresponding maximum absorption wavelength using ultraviolet visible spectrophotometer getting the absorbance of the dye solution. Then according to the corresponding A- ρ working curves to calculate the concentration of the residual dye solution and the adsorptive capacity of chitosan.

3. Results and discussion

3.1 Mass concentration and absorbance curves of dye solutions

The curves of the mass concentration versus absorbance of the three dye solutions which are shown in Figure 1.

Figure 1. The curves of the mass concentration versus absorbance of the three dye solutions

A- ρ regression equation of three dye solutions were obtained by A- ρ working curves that are shown in Table 1. As is shown in Table 1, in the mass concentration range of dye solution determined, the mass concentration of the three kinds of dye solutions and their absorbance exists a good linear relationship, which means the curves can be used to determine the accurate quantity of dye concentration in the solution.

Table 1. A- ρ regression equation of three dye solutions

Dyes	A- ρ regression equation	R ²
Methyl orange	$A=0.0564\rho+0.0013$	0.9990
Acid magenta	$A=0.0639\rho+0.0016$	0.9987
Crystal violet	$A=0.1595\rho-0.0011$	0.9992

3.2 Effects of different factors on adsorption properties of modified chitosan

3.2.1 the effect of pH value on adsorption

The three kinds of dye solutions with the mass concentration of 10 mg/L were treated by oscillating adsorption for 1 h at room temperature 25°C investigating the effect of dye solution pH on chitosan adsorption, the results are shown in Figure 2.

Figure 2. Effects of pH values on adsorption

It can be seen from Figure 2 that the adsorption effect of modified chitosan on dyes is greatly affected by the pH value of the dye solution, and the adsorption capacity increases gradually with the decrease of pH value of dye solution. In addition, azo dye methyl orange is relatively less affected by pH, while the other two kinds of triphenylmethane dyes are relatively more affected by pH value.

The pH value of the solution has great influence on the adsorption effect, which affects not only the surface charge of the adsorbent, but also the chemical behavior of the degree of ionization of the dye in the solution. The change trend shown in Figure 2 May be related to the molecular structure of modified chitosan. Because that the modified chitosan is a kind of weak base, it is insoluble in water and organic solvents, but soluble in dilute acid solution, and free -NH₂ on the modified chitosan molecular chain translates into positively charged NH₃⁺, thus improving its hydrophilicity, strengthened the adsorption capacity of amine with water soluble ion of organic molecules[7]. Therefore, the decrease of the pH value of the dye solution is beneficial to the protonation of -NH₂ on the modified chitosan, which makes it easier to combine with the negatively charged group in the dye molecules to promote the adsorption of the modified chitosan to the dye. However, when the pH value falls to 3.2, cationic polyelectrolyte reaches a certain amount, modified chitosan can't keep a good particle shape, and become sticky, centrifugation is difficult, some modified chitosan dissolved, greatly reducing the transfer number of dye molecules from liquid to solid phase and making adsorption effect weakened. So it is advisable to deal with the pH value at 3.6.

3.2.2 The effect of adsorption time on adsorption

The three kinds of dye solutions with the mass concentration of 10 mg/L were oscillating adsorption for a certain time at room temperature 25 °C and pH 3.6, investigation the effects of different adsorption time on adsorption. The results are shown in Figure 3.

Figure 3. The effects of adsorption time on adsorption

As shown in Figure 3, the adsorption rate of modified chitosan on dyes is relatively fast, most of adsorption occurs in the first 10 min, and then the adsorption speed is relatively slow. When the adsorption time reached 0.5 h, the adsorption basically reached saturation. The adsorption effect of modified chitosan on dyes is not significantly changed after 1.0 h, which indicates that the adsorption process reaches equilibrium within 60 min. The modified chitosan has the largest adsorption capacity for dual azo dye methyl orange, followed by acid dye acid magenta with sulfonic acid group, and the minimum amount of adsorption for crystalline violet without azo group and sulfonic acid group

Adsorption time is an important factor in the adsorption process. Controlling the adsorption time suitably can make the adsorption react fully, save time, and improve the adsorption efficiency in the unit time. The effects of adsorption time on adsorption are shown in Figure 3. In the

initial stage, the number of free $-NH_2$ on chitosan is more, there are a large number of adsorption sites, the impetus (concentration difference) is larger; adsorption rate of dye is faster. With the extension of reaction time, the adsorption equilibrium can reach between the modified chitosan and dye, active site gradually reduce, repulsive force between dye molecules adsorbed on solid surface and the dye molecules in the solution gradually increases, the driving force is weakened and resulting in the decrease of the adsorption rate.

3.2.3 The effect of temperature on adsorption

The three kinds of dye solutions with the mass concentration of 10 mg/L were oscillating adsorption for 1h at a certain temperature and pH 3.6, investigation the effects of different adsorption temperature on adsorption. The results are shown in Figure 4.

Figure 4. The effects of temperature on adsorption

It can be seen from Figure 4 that the adsorption of modified chitosan for crystal violet is influenced by temperature more greatly, and the adsorption of methyl orange and acidic magenta is less affected by temperature. The ability of the modified chitosan to adsorb the three dyes decreased with the increase of temperature. Therefore, the appropriate adsorption processing temperature should be room temperature 25 °C.

3.2.4 The effect of the initial mass concentration of dyes on the adsorption effect of modified chitosan

The three kinds of dye solutions were oscillating adsorption for 1h at room temperature 25°C and pH 3.6, investigation the effects of different initial mass concentrations of dyes on adsorption. The results are shown in Figure 5.

Figure 5. influence of initial mass concentration on adsorption

As is shown in Figure 5, the effects of three kinds of initial dye concentration on the absorption ability of modified chitosan are relatively larger. The higher the initial mass concentration is, the higher the adsorption amount is, and the adsorption amount and initial mass concentration had good linear relationship within a certain range.

4. Conclusions

SiO₂ modified chitosan was prepared by modifying chitosan with

trimethoxysilane treated SiO₂, and the effects of different factors, like dye solution pH value, adsorption time, dye original concentration and temperature on the adsorption of three types of dyes, methyl orange, acid magenta and crystal violet, using the prepared modified chitosan were studied. The conclusion are as follows:

(1) the modified chitosan has an easy adsorption of acidic dyes with azo and sulfonic acid in the structure, and the adsorption effect of basic dyes without azo and sulfonate is not ideal. The adsorption amount of methyl orange and acid magenta were more than 90 % within the first 10 min of adsorption, the adsorption process reached equilibrium within 60 min.

(2) The lower pH value of the solution is advantageous to the adsorption of modified chitosan on dye. But when pH value is less than 3.6, the modified chitosan will be partly dissolved, which can affect the subsequent processing, so the optimum adsorption pH value is 3.6.

(3) the adsorption capacity of modified chitosan on methyl orange and acid magenta was less affected by temperature, but the effect on crystal violet was slightly larger. The ability of the modified chitosan to adsorb the three dyes decreased with the increase of temperature. So the optimal temperature should be room temperature 25 °C.

(4) The initial concentration of dye solution on the absorption ability of modified chitosan is larger, the higher the initial mass concentration is, the larger the adsorption amount is, and the adsorption amount and initial mass concentration has a linear relationship within a certain range.

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