Photolysis Effect of Muyu Stone/Magnetism Chitosan Microspheres on Chromium in Source Water

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Abstract: In this paper, Fe\textsubscript{3}O\textsubscript{4} magnetism chitosan was made by emulsification crosslinking method. Muyu stone/Magnetism Chitosan Microspheres were prepared by embedding, and then used to photolysis chromium in source water. Based on single factor test, the experimental condition was optimized by quadratic regression orthogonal rotatable composite factorial design. The orthogonal regression model between the removal rate of Cr\textsuperscript{6+} (y) and microspheres dosage (x\textsubscript{1}), solution pH value (x\textsubscript{2}), reaction time (x\textsubscript{3}) was established as

\[ y = 88.335 + 1.380x_1 + 1.468x_2 + 2.217x_3 - 2.556x_2^2 - 1.266x_3^2 + 4.313x_1x_2 - 0.636x_1x_3 \]

Under these conditions, chromium removal rate reaches 93.13%.

1. Introduction

Chitosan (deacetylated chitin) is the only alkaline acylsugar that exists in nature \cite{1}. Based on its comprehensive performance of flocculability, adsorptivity, without secondary pollution, and so on, it has now become a research focus on sewage treatment. However, chitosan also has some shortcomings, such as difficulties in recycling after sewage disposal. Therefore, it is more promising for chitosan in water treatment by combining it with Fe\textsubscript{3}O\textsubscript{4} to prepare magnetic chitosan microspheres \cite{2-4}. This material has properties of both chitosan and the response of magnetic material. It can combine active substances through covalent bonds, and it also has a strong magnetic response to external magnetic fields, which makes magnetic separation easier. In addition, it can also enhance the mechanical strength of materials. Therefore, it can significantly enhance the application value of chitosan \cite{3,5-7}. Muyu stone, known as "the first stone of God", is rich in elemental iron (Fe). In ancient China, it was regarded as a top grade medicine for lengthening longevity. Modern pharmacological studies have shown that Muyu stone has antibacterial, anti-aging, anti-tumor effects, improves immunity, reduces pain, and promotes hemopoietic reconstitution \cite{8}. In this paper,
emulsification cross-linking method was adopted to prepare magnetic chitosan nanoparticles. An embedding method was used for the preparation of Muyu stone / magnetic chitosan microspheres (MMCMs). MMCMs were then used for the purification treatment of source water. The experimental result was expected to be the foundation for research and application of magnetic chitosan nanoparticles used as adsorbent.

2. Materials and Methods

2.1. The Primary Materials
Chitosan (Deacetylation Degree 85%); Muyu stone is purchased from Jinan, Shandong, sieve out 200 mesh for reservation.

2.2. Preparation of Muyu stone / Magnetic Chitosan Microspheres (MMCMs)

2.2.1. Preparation of Magnetic Chitosan
Emulsification cross-linking method [3,7] was adopted to prepare magnetic chitosan microspheres. The magnetic powder of Fe$_3$O$_4$ was added to chitosan acetic acid solution with concentration of 2%, after mixing, it was transferred to a large beaker containing liquid paraffin and little Span-80, adjusted to a pH of approximately 9.0, stirred for 30 min. A certain amount of glutaraldehyde solution was added, and stirring continued for 60 min at 40°C. The reaction finished completely, and then decompressed and filtered. The filtrate was extracted three times with petroleum ether and absolute ethanol, and then dried in vacuum at 50°C to obtain magnetic CS microspheres.

2.2.2. Preparation of Muyu stone / Magnetic Chitosan Microspheres (MMCMs)
The magnetic chitosan microspheres were ground into a powder, and then fully mixed with Muyu stone powder to a 5:2 ratio [9]. The mixed power was used to prepare microspheres with sodium alginate and polyvinyl alcohol with a 7:1:6 ratio [10]. First, sodium alginate and polyvinyl alcohol were heated for 15 min to dissolve, then mixed powder was added and stirred evenly, ensuring the quality of solution at 100g, and cooled for 30 min. The suspension was dropped into 2% calcium chloride solution by a constant flow pump with a constant flow rate to make it solidified [11,12]. The microspheres were filtered out after solidification for 20h, and washed twice for preservation.

2.2.3. Water Sample Purified by MMCMs
50mL water sample containing chromium was pipetted into a 250ml triangular flask, an appropriate amount of MMCMs added, oscillated a certain time in a constant temperature oscillation box under designed experimental conditions, and then stewed and filtered. The chromium content in the filtrate can be determined, and the removal rate of MMCMs to chromium can be calculated. This experiment investigates the effect of MMCMs dosage, pH value and reaction time on test results. Experimental design is shown in Table 1 and Table 2. Each experiment is repeated three times, and a mean value obtained.

2.2.3.1. Single Factor Experiment

| Table 1 Single factor experimental design |
|------------------------------------------|
| Influencing factors | Levels |
|---------------------|--------|
| Dosage of microspheres(g) | 1 | 1.5 | 2 | 2.5 | 3 |
| pH value | 4 | 6 | 8 | 10 | 12 |
| reaction time (min) | 30 | 60 | 90 | 120 | 150 |
2.2.3.2. Orthogonal Rotation of Quadratic Regression

Table 2 Factors and levels of orthogonal tests

| Variables               | Levels          |
|-------------------------|-----------------|
| 1.682                   | 1.00            |
| 0                       | -1.00           |
| -1.682                  | 2.00            |
| 5.41                    | 5.00            |
| 4.00                    | 3.00            |
| 2.59                    | 2.00            |
| 3.29                    | 2.50            |
| 2.50                    | 2.00            |
| 1.50                    | 1.00            |
| pH value                | reaction time (min) |
| dosage of microspheres (g) | 102.43          |
| pH value                | 90.00           |
| reaction time (min)     | 60.00           |
|                        | 30.00           |
|                        | 17.57           |

3. Results and Analysis

3.1. Single Factor Experiment

3.1.1. Effect of MMCMs Dosage

Different dosage of MMCMs were put into six 250mL conical flasks containing 50mL water samples. Each solution’s pH values were adjusted to 6, oscillated for 90min in a constant temperature oscillation box under the conditions of 25°C and 200r/min, and then centrifuged to measure the amount of Cr(VI) in solution. The experimental results for the effect of MMCM dosage on Cr (VI) are shown on Figure 1.

Figure 1 shows that Cr (VI) removal rate in water samples increases with higher MMCM dosage. Cr (VI) removal rate begins to decline at a dosage of 3.00 g. According to the relevant literature reports [13], such a phenomenon is mainly because, as an organic macromolecular compound, chitosan will consume oxygen itself. When the concentration of oxygen consuming substances in solution increases, the adsorption capacity of MMCMs will reduce. With an increasing microsphere dosage, the pH value of the solution will gradually decrease. When the pH value is too low, the chitosan will be significantly dissolved in acid, which is not conducive to the adsorption of Cr (VI) to MMCMs.
3.1.2. Effect of pH Value in Solution

![Fig. 2 Effect of pH on Cr(VI) removal rate](image)

Effect of pH in solution on Cr (VI) removal rate is shown in Figure 2. pH is an important factor of adsorption. Firstly, it affects the existing forms of adsorbed ions in the solution. Secondly, it affects the surface charge formed on the composite adsorbent. Cr (VI) removal rate increases with the increasing of pH in acidic solution, which is converse in alkaline solution. According to the literature reports [14], in acidic solution, protonated NH$_3^+$ groups of chitosan combine with Cr$_2$O$_7^{2-}$ or CrO$_4^{2-}$ anion of Cr (VI) by electrostatic attraction and hydrogen bonding interaction. Acidic conditions are more favorable for the protonation of chitosan NH$_3^+$, which provides conditions for the association of anions such as Cr$_2$O$_7^{2-}$ and ionic bonds. The balance between HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ will move towards Cr$_2$O$_7^{2-}$ with the decreasing of pH. There is also an adsorption site between chitosan protonated NH$_3^+$ and Cr (VI). When interacting with HCrO$_4^-$ it can absorb a Cr (VI), while only half of Cr (VI) can be absorbed by interacting with Cr$_2$O$_7^{2-}$ [15]. In addition, Cr (VI) will be deoxygenated to Cr (III) in acidic conditions, which is easily adsorbed by the adsorbent [16]. Therefore, Cr (VI) can achieve a higher removal effect in the acidic environment. When the pH value is too high, the functional groups of magnetic microspheres mainly existed in the form of -NH$_2$, Cr (VI) is mainly existed in the form of CrO$_4^{2-}$, which will reduce the absorption effect.

3.1.3. Effect of Reaction Time

![Fig. 3 Effect on reaction time to Cr(VI) removal rate](image)

Effect of reaction time on Cr (VI) removal rate is shown in figure 3. It can be seen from figure 3 that the Cr (IV) removal rate increases with increasing time. However, after 90min, Cr (VI) removal rate begin to decline. There are several reasons for this phenomenon. First, both adsorption and desorption
are present in the interaction processes. When the adsorption reaction time is short, the adsorption speed is greater than desorption speed and the curve rises. When the time reaches to 90min, the desorption rate gradually increases and balances the adsorption rate such that the Cr (Ⅵ) removal rate will not change dramatically. Second, there are a large number of free amino groups on the surface of the chitosan microspheres. They can quickly adsorb Cr (Ⅵ) in solution. With the growth of reaction time, the outer layer of particle is getting close to saturation, the adsorption capacity decreasing, so the Cr (VI) removal rate decreases [17]. Third, the microspheres react with the oxygen consuming substances through chitosan polymer to form a floc, affecting the removal effect of Cr (VI) [3]. Therefore, the reaction time of about 90min can achieve a good removal.

3.2. The Orthogonal Rotation Regression to Determine the Optimal Experimental Conditions

3.2.1. Mathematical Model
Adopting DPS data processing system to fit the experimental data of quadratic regression orthogonal rotatable composite design, the regression equation is as following:
\[ Y=88.33510+1.38032x_1+1.46819x_2+2.21738x_3-4.46584x_1^2-2.55665x_2^2-1.26618x_3^2+ \]
\[ 2.36375x_1x_2+4.31375x_1x_3-0.63625x_2x_3 \] (1)

3.2.2. Significance Test of Quadratic Regression Model
In order to test the validity of the regression equation, following the procedures of F1= lack of fit mean square /error mean square, F2= regression mean square/residual mean square, F3= regression mean square/error mean square. Table 3 shows: lack of fit item F0.01(5,8)=6.63>F1= 5.50>F0.05(5,8)=3.69 has reached the significant level at α=0.05, while no at α=0.01. Lack of fit factors may have impacted test results, which may have come from the interaction between factors. F2 is significant at the level of 0.01 （F0.01(9,13)=4.19 < F2 = 26.98, which shows that the coordination between equation and experimental data is feasible and can be used to build the model. Through the test for F3, F3=74.58 > F0.01（9,8）=5.90 has reached a significant level. When considering experimental factors, the regression results of equation are reliable.

| variation sources | Square sum | degrees of freedom | mean square | partial correlation | ratio F | P value |
|-------------------|------------|--------------------|-------------|--------------------|---------|---------|
| regression        | 761.2488   | 9                  | 84.5832     | F2=26.98418        | 0.0001  |
| surplus           | 40.7491    | 13                 | 3.1345      |                     |         |
| lack of fit       | 31.5691    | 5                  | 6.3138      | F1=5.50224         | 0.0062  |
| error             | 9.1800     | 8                  | 1.1475      |                     |         |
| sum               | 801.9979   | 22                 |             |                     |         |

Note: * indicates significance at the level of 0.05, ** indicates significance at the level of 0.01.

3.2.3. Reconstruction of Quadratic Regression Model
According to Table 3, reject no significant items with the significant level at α=0.10, the simplified regression equation is:
\[ Y=88.33510+1.38032x_1+1.46819x_2+2.21738x_3-4.46584x_1^2-2.55665x_2^2-1.26618x_3^2+ \]
\[ 2.36375x_1x_2+4.31375x_1x_3 \] (2)

The correlation coefficient of Cr (VI) removal rate and microsphere dosage, pH value, and reaction time in water samples are R2= regression sum of squares / total sum of squares = 0.9496, which shows
that the effect of the three factors in this mathematical model accounts for 94.96%, while other factors and error account for 5.04%.

3.2.4. Analysis of Main Factors Effect
Fix any of the three factors at zero level with the "method of descent", and then obtain the effects equation of another factor and potential removal rate:

\[ Y = 88.33510 + 1.38032x_1 - 4.46584x_1^2 \]  
\[ Y = 88.33510 + 1.46819x_2 - 2.55665x_2^2 \]  
\[ Y = 88.33510 + 2.21738x_3 - 1.26618x_3^2 \]

According to the regression coefficient (absolute value), the effect order of three factors on the Cr (VI) removal rate in solution is: reaction time \( (x_1) \) ≥ pH value \( (x_2) \) ≥ microsphere dosage \( (x_3) \). The relational graph of each factor and yield with the main effect equation are shown in Figure 4. The relation of microspheres dosage \( (x_3) \) and Cr (VI) removal rate in solution is nearly close to linear in the range \(-1.6818 \sim 1.6818\) as shown in figure 4, where an increase of microsphere dosage in a certain range is in favor of Cr (VI) removal in solution. The effect of reaction time \( (x_1) \) and pH value \( (x_2) \) on the Cr (VI) removal rate in solution is presented as a parabola opening downwards, which shows a reasonable range of factors: when reaction time \( (x_1) \) is at the range of \(-1.682 \sim -0.5\), the Cr (VI) removal rate in solution will increase, while at the level of more than \(-0.5\), the Cr (VI) removal rate in solution will decrease significantly. When pH value \( (x_2) \) is at a range of \(-1.682 \sim 0\), Cr (VI) removal rate in solution will increase, while at the level of more than 0, the Cr (VI) removal rate in solution will decrease significantly.

3.2.5. Optimization of Experimental Conditions

| Table 4 x_i frequency distribution in optimized experimental scheme |
|----------------------|---------------|---------------|---------------|
| factor level         | x_1           | x_2           | x_3           |
| -1.6818              | 0             | 0.0000        | 0             | 0.0000        |
| -1.0000              | 0             | 0.0000        | 5             | 0.1613        | 0.0645        |
| 0.0000               | 14            | 0.4516        | 9             | 0.2903        | 0.2258        |
| 1.0000               | 11            | 0.3548        | 9             | 0.2903        | 0.3548        |
| 1.6818               | 6             | 0.1935        | 8             | 0.2581        | 0.3548        |
| x                    | 0.6800        | 0.5630        | 0.8870        |
According to the established mathematical model in the range of $-1.682 \leq x_i \leq 1.682$ ($i=1, 2, 3$), fetch five levels of each factor ($\pm 1.682$, $\pm 1$ and 0), execute statistical optimization on $5^3 = 125$ programs, then the highest Cr (VI) removal rate available in solution is 93.93% in the test range. At this point the value of each factor is: $x_1 = 1.000$, $x_2 = 1.000$, $x_3 = 1.682$. Assuming an average value of 83.50% of quadratic regression orthogonal composite design experiment as the critical value, 31 programs are obtained with Cr (VI) removal rate greater than the critical value, with the frequency distribution of each variable is shown in table 4.

It can be seen from table 4 that when $x_1 = 0.447 \sim 0.914$, $x_2 = 0.236 \sim 0.890$, $x_3 = 0.606 \sim 1.168$, the corresponding experimental actual values are reaction time of 73.41~87.42min, pH value of 4.236~4.89, and microspheres dosage of 2.303~2.584g. Taking the average program as optimized experimental conditions, $x_1 = 80.415$, $x_2 = 4.563$, $x_3 = 2.444$, the optimal experimental conditions are a reaction time of 80.4min, a pH value of 4.6, and a microsphere dosage of 2.444g. Under these conditions, Cr (VI) removal rate in solution can reach 93.93% according to mathematical model. To confirm these test results, triplicate verification of the experiment according to the obtained conditions show that Cr (VI) removal rate in solution is above 93%, which further confirms the reliability of the analysis.

4. Conclusions

Single factor experiments show that Muyu stone - magnetic chitosan microspheres can be used to remove the Cr (VI) in source water. Microsphere dosage, pH value of solution, and reaction time all have effects on the removal of chromium in wastewater to a certain extent. Under conditions of a microsphere dosage of 3g, pH of 6, and the reaction time of 90min, the removal effect of chromium in wastewater is best.

Based on single factor experiments, applying the theory and method of regression design to determine the optimal experimental conditions through DPS data processing system resulted in: Microsphere dosage of 2.444g, pH value of 4.6 and reaction time of 80.4min. Under these conditions, chromium removal rate reaches 93.13%.

Under the optimal experimental conditions obtained by the model, the chromium removal rates of verification experiments are all above 93%, which is consistent with the best value of model and confirms the reliability of this model.

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