Cr(VI) removal from synthetic wastewater by amine functionalized SiO₂: pH, Isotherm and kinetic studies

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Abstract. The purpose of this study was to investigate the possibility of the utilization of amine functionalized SiO₂ as an adsorbent for removing Cr(VI). The structure property of adsorbent was characterized by N₂ adsorption-desorption isotherm, XPS, SEM and CO₂-TPD. The maximum adsorption capacity of amine functionalized SiO₂ was 27.78 mg/g at initial pH=2, which calculated by Langmuir isotherm model. But SiO₂ does not have the ability to adsorb Cr(VI) before functionalized. Additionally, the adsorption can be described by the pseudo-second-order kinetic model, which illustrated that the “surface reaction” was the controlling step in adsorption process. From the result of CO₂-TPD and adsorption energy, the electrostatic attraction between Cr(VI) species and protonated amine or hydroxyl group were regards as mainly adsorption mechanism.

1. Introduction

In recent years, a larger number of hexavalent chromium (Cr(VI)) have been discharged into the aquatic environment and ecosystem because of the excessive human activity, such as mineral exploitation, smelting and manufacturing industrial activities [1]. Then Cr(VI) entered the cell of human from water and gathered in the body, which caused mutagenesis and carcinogenesis [2]. So, Cr(VI) has been classified as one class EPA water priority pollutants [3]. And in China, it has also been listed as the focus of prevention and control of heavy metal pollutants [4]. Therefore, the effective separate Cr(VI) from water has become an important global issue.

Up to date, more and more techniques have been employed to remove Cr(VI), including ion-exchange, adsorption, membrane, precipitate, and so on. Compared with other techniques, the method of adsorption has been considered as a very attractive option because of the outstanding simplicity, low
cost and good selectivity [5]. And most materials are employed as Cr(VI) adsorbents, such as activated carbon [6], layered double hydroxides (Mg-Al and Ni-Al) [7], bio-adsorbent [8], etc. Among these, more attention has been focused on silica based material due to the better mechanical and chemical stability [9]. A perfect example can be found that excellent Cr(VI) adsorption performance was exhibited in imidazole-functionalized SBA-15. However, more attention and investment were focused on imidazole and synthesis SBA-15. To avoid the shortcomings, further studies about using silica based material to uptake Cr(VI) were desired.

As previous report, amine group could be protonated easily in acid solution [10]. And in general, Cr(VI) exists in solution as the form of HCrO₄⁻, CrO₄²⁻ and Cr₂O₇²⁻. Therefore, in this contribution, hexadecyl trimethyl ammonium bromide was used as modifier to graft amine group over traditional silica surface. And the obtained material was employed to removal Cr(VI) from aqueous solution. Additionally, the adsorption isotherm models of Langmuir and Freundlich were used to analyze the equilibrium experiment data. The adsorption kinetic was assessed by the pseudo-first-order, pseudo-second-order and kinetic model. Finally, the adsorption mechanism was discussed by the CO₂-TPD and adsorption energy.

2. Experiment

2.1. Prepared amine functionalized SiO₂

The traditional silica was got from the market as the carrier, and hexadecyl trimethyl ammonium bromide was used as the active component. 2 g hexadecyl trimethyl ammonium bromide were dissolved in 36 mL deionized water in the corresponding beakers, then mechanically stirred (120 rpm) until it was completely dissolved. Then 20 g silica material was added in the beaker mentioned above. After mixed completely, the obtained mixture was standing at room temperature for 3h. Subsequently, the mixture was placed at 110 ℃ constant temperature drying box for 12h. And then washed by 2.5L deionized water and filtered. Finally, the solid was putted in the constant temperature box at 80 ℃ for 12 h to dry the sample.

2.2. Characterization

N₂ adsorption-desorption isotherms of sample was determined by ASAP 2020 apparatus under -196 °C. X-ray photoelectron spectra (XPS) of sample before and after adsorption Cr(VI) were tested by PHI 5000 Versa Probe instrument. Diphenyl carbamide spectrophotometric method (GB7467-87) was used to test the concentration of Cr (VI) solutions after adsorption. Scanning electronic microscopy (SEM) images were obtained on a Philips XL-30 environmental scanning electron microscope. The intensity of weak and strong alkalinity of adsorbent before and after adsorption Cr(VI) were determined on a CO₂-TPD instrument equipped with a TCD detector.

2.3. Cr(VI) adsorption

Batch adsorption experiments were carried out by shaking a series of bottles containing amine functionalized SiO₂ and various amounts of heavy metal Cr(VI) solutions at different pH. The preparation of Cr (VI) solutions are as follows. Taking K₂Cr₂O₇ out and prepare solutions of different concentrations. First of all, an adsorbent of 100 mg was applied to a 100 mL conical flask containing 50 mL Cr (VI) solution. Then, flasks were placed in a constant temperature oscillator (190 rpm) for a
certain time interval. Next, the adsorption liquid was centrifuged, the supernatant was separated and the Cr (VI) content could be measured. The sampling time was about 0.5, 1, 2, 5, 9, 15, 24, 36 h.

3. Results and discussions

3.1. Characterization of amine functionalized SiO$_2$

In order to understand the characteristics of surface morphology of silica raw material and the changes after modification, scanning electron microscopy were determined, and the result were displayed in Figure 1. As can be seen from Figure 1(A), the silica material presents an irregular amorphous state, the particle size is about 10 ~ 100 μm. Modified (B) particle size and morphology did not change significantly [11]. The N$_2$ adsorption-desorption isotherms of the sample traditional silica and amine functionalized silica were illustrated in Figure 1(C). According to the IUPAC classification, these two isotherms were all belong to the type IV and H$_1$ type wide hysteresis loop, which demonstrated that the mesoporous structure were occurred in silica before and after functionalized by amine [12]. And the corresponding result of BET surface area, BJH pore size and pore volume were listed in Table 1. The BET surface area increased as the graft of amine group, but the pore size was decreased. To determine the graft of amine group further, the XPS was used to test sample. High-resolution XPS spectrum of N 1s was shown in Figure 1(D). It can be found that the spectrum can be fitted with three peaks centered at ca. 401 ev, 405.9 ev and 406.84 ev, which is fitted with binding energy of N atoms in (-C$_6$H$_5$NH-)$_n$ [13], (NO$_2$)C$_6$H$_4$(CH$_3$)$_2$NHNCHCH$_3$Br [14] and C$_3$H$_6$N$_2$O$_6$ [15], respectively. These results indicated the successfully functionalization of amine on SiO$_2$. 

![Image](image_url)
Figure 1. SEM image of (A) traditional silica and (B) amine functionalized silica. (C) N$_2$ adsorption–desorption isotherms of (a) traditional silica and (b) amine functionalized silica. (D) High-resolution XPS spectrum of N 1s for sample amino functional SiO$_2$.

Table 1. BET surface area and BJH pore properties of SiO$_2$ before and after functionalized by amine.

|                  | BET surface (m$^2$/g) | BJH pore volume (cm$^3$/g) | BJH diameter (nm) |
|------------------|-----------------------|-----------------------------|-------------------|
| SiO$_2$          | 539.01                | 1.14                        | 9.40              |
| Functionalized SiO$_2$ | 565.96          | 1.19                        | 7.60              |

3.2. Effect of initial pH

As well known that solution pH is one of the crucial factors that influence the adsorbate separate performance. The influence of initial pH on Cr(VI) uptake over amine functionalized SiO$_2$ were investigated in the range of 2-8, and the obtained experiment results were shown in Figure 2. As can be seen from Figure 2, the performance of adsorbing Cr(VI) over amino functionalized SiO$_2$ was greatly influenced by pH. And Cr(VI) uptake was decreased with the increasing of initial pH, which might be attributed to the fact that the electrostatic attraction between Cr(VI) species and protonated amine group was decreased under high pH value due to the weaken of amine group protonation. When initial pH increased from 2 to 8, Cr(VI) uptake decreased from 18.39 mg/g to 3.32 mg/g. Therefore, the optimal uptake was achieved at pH 2.
Figure 2. Influence of initial pH on uptake Cr(VI) from aqueous solution.

3.3. Adsorption isotherm

The models of Langmuir, Freundlich and Dubinin-Radushkevich (D-R) are applied to evaluate the relationship between adsorbate and adsorbent. The correlation parameters of these mentioned models are displayed in Table 2. Obviously, the value of regression coefficient of Langmuir model ($R^2=0.998$) is larger than that of Freundlich ($R^2=0.830$) and D-R ($R^2=0.949$). And it indicated that the experiment data of Cr(VI) adsorbed over amino functionalized SiO$_2$ has an excellent fit to the Langmuir adsorption isotherm model, and adsorbed Cr(VI) species is in the monolayer type. The maximum monolayer adsorption capacity is 27.78 mg/g. Additionally, it can be found from D-R that the adsorption energy value $E$ (2.6 KJ/mol), which can be obtained by the equation $E=(2K_{D-R})^{1/2}$, is lower than 8 KJ/mol. As previous report, the process of Cr(VI) adsorption over amine functionalized SiO$_2$ is dominant by physical adsorption for $E<8$ KJ/mol [16].

Table 2. Isotherm parameters and regression data for Cr(VI) adsorption on amino functional SiO$_2$

|      | Langmuir | Freundlich | D-R   |
|------|-----------|------------|-------|
|      | $Q_{max}$ (mg/g) | $K_L$ | $R^2$ | $K_F$ | $n$ | $R^2$ | $Q_{max}$ (mg/g) | $K_{D-R}$ | $R^2$ | $E$ |
|      | 27.78     | 0.621      | 0.998 | 13.167 | 6.63 | 0.830 | 45.12          | 0.073      | 0.949 | 2.6 |

$Q_{max}$ is the maximum adsorption capacity of adsorbent; $K_L$ is Langmuir adsorption constant; $K_F$ and $1/n$ are empirical constants of Freundlich; $K_{D-R}$ is D-R constant.

3.4. Kinetics

The kinetic equations of pseudo-first-order and pseudo-second-order were used in this report to assessment the adsorption process. The calculated results of the corresponding parameter are tabulated in Table 3. Obviously, the linear relationship of pseudo-first-order model to experiment data was poor ($R^2=0.859$). And the Qecalc value (14.584 mg/g) of pseudo-first-order kinetic is much smaller than that of the experimental adsorption capacity Qeexp (26.987 mg/g). This difference reached minimum in the pseudo-second-order model (Qecalc value is 27.397 mg/g), and the corresponding regression
coefficient ($R^2=0.991$) is nearly 1.0. The result indicated that pseudo-second-order provided better
fitting result to experiment data, and the process of Cr(VI) adsorption over amine functionalized SiO$_2$
obeys pseudo-second-order model. This implied that the mainly rate controlling step was “surface
reaction”.

Table 3. Kinetic parameters and regression data for Cr(VI) sorption on amino functional SiO$_2$

| $k_1$ | $Q_{e}^{calc}$ (mg/g) | $Q_{e}^{exp}$ (mg/g) | $R^2$ |
|------|----------------------|----------------------|-------|
| 0.002 | 14.584 | 26.987 | 0.859 |

| $k_1$ | $Q_{e}^{calc}$ (mg/g) | $Q_{e}^{exp}$ (mg/g) | $R^2$ |
|------|----------------------|----------------------|-------|
| 0.0004 | 27.397 | 26.987 | 0.991 |

3.5. Adsorption mechanism

Figure 3 showed the CO$_2$-TPD of Cr(VI) before and after adsorption over amine functionalized SiO$_2$. It can be found that two peaks were appeared in the adsorbent, which indicated that two different basic
group were occurred in amine functionalized SiO$_2$. Combined with analysis of the chemical property,
hydroxyl and amine group have been deemed as the mentioned basic group. And the peak assigned to
weak basic group was decreased after uptaking Cr(VI), which illustrated that the hydroxyl group was
involved in the adsorption. In addition, the peak attributed to the strong basic group is shift to low
temperature slightly, which indicated that amine group plays a role in Cr(VI) adsorption. Combined
with the result of adsorption energy, the mechanism of Cr(VI) adsorption over amine functionalized
SiO$_2$ under pH=2 can be proposed as the following: (i) the hydroxyl group was firstly protonated in
the acid condition, and then Cr(VI) species $HCrO_4^{-}$ was uptake over adsorbent surface by electrostatic
attraction; (ii) the amine group removal Cr(VI) by the equation $[CH_3(CH_2)_{15}]^+ (CH_3)_3N + HCrO_4^{-} \rightarrow [CH_3(CH_2)_{15}]^+ (CH_3)_3N—HCrO_4$. 

Figure 3. CO$_2$-TPD of Cr(VI) before (a) and after adsorption (b) over amine functionalized SiO$_2$.

4. Conclusions
Amine functionalized SiO₂ with mesoporous structure was successfully synthesized via employed hexadecyl trimethyl ammonium bromide and available traditional SiO₂ as the active component and carrier, respectively. And the performance of separate Cr(VI) from aqueous solution was investigated by batch experiments. It was found that the adsorption performance dependent on the solution pH, and Cr(VI) removal was decreased with the increase of initial pH in the investigated pH range (2 - 8). The obtained experiment data was fitted by Langmuir and Freundlich model, and the better fitting result was gained in Langmuir equation. The maximum adsorption capacity was 27.78 mg/g at pH=2, which calculated by Langmuir. Additionally, Cr(VI) removal was decreased with the presence of foreign ions. And the adsorption energy 2.6 KJ/mol is lower than 8 KJ/mol, which illustrated that physical adsorption was dominated to the adsorption process. And the electrostatic attraction between Cr(VI) species and protonated hydroxyl group and amine group was found to the mainly adsorption mechanism.

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