Preparation Method of Iron Oxyhydroxide Nanosheets for Treating Organic Dyes

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Abstract. Considering the promoted purification requirement for industry sewage, the discharge of azo dye wastewater will have a serious impact on the environment, iron oxyhydroxide nanosheets were designed and prepared, and the purification effects and application conditions were investigated in this work. We have used its structural advantages to perform adsorption tests on Congo red (CR). It found that it has very excellent properties. It has strong adsorption capacity for Congo red under the condition of low dosage and no adjustment of PH. By employing iron oxyhydroxide nanosheets with optimized molar ratio of reducing agent to Fe, it was found that the adsorption efficiency increase in the removal percentage for CR from industry sewage could be achieved at the large specific surface area and pore volume of B-Fe Nanosheets.

Keywords: Dye Wastewater, Congo Red, Adsorption, Oxyhydroxide Nanosheets.

1. Introduction

Dyes and other organic pollutants from paint, textile and paper industries are discharged into the environment and controlling water-pollution has become the main concern of society today \cite{1, 2}. In particular, organic dyes in waste water present a serious threat to aquatic life, microorganism, and human beings because they are toxic and potentially carcinogenic. Thus, it is crucial to remove or to minimize organic dyes before being discharged into water resources.

The pollution of Congo red anionic dye in organic colored wastewater has been widely concerned. Congo red is a representative chemical in benzidine direct azo dyes. It has various applications in textile, paper, rubber and plastic industries. However, Congo red is very easy to lose; it will cause environmental pollution during production and use. At the same time, it has strong toxicity and carcinogenicity \cite{3, 4}. Therefore, from the perspective of health and environment, it must be removed from the wastewater and then discharged into the water. Up to now, various technologies, such as adsorption, membrane filtration, chemical precipitation, biological treatment and photocatalytic degradation have been proposed to treatment the dye wastewater \cite{5, 6}. Compared to the developed technologies, the adsorption technology shows it is likely better due to its easy operation and cost effectiveness in waste water
treatment [7, 8]. The novel ultrathin 2D nanosheets with enrichment of active sites and large surface areas demonstrate a great potential as adsorbents to remove organic pollutants and inorganic contaminants [9, 10]. There has been reported on the adsorption of organic pollutants over hydroxide nanosheet materials, though the 2D nanostructures have demonstrated superior structure-activity with abundant exposed iron active sites and high surface area, enhancing the adsorption for dye molecules and hydrogen peroxide [11, 12].

Accordingly, in this paper we report a new facile and green-chemical method of FeOOH ultrathin nanosheets for treating organic dyes. The materials synthesized by this method have large specific surface area and pore size; the nanosheets achieved excellent adsorption performance for Congo red (CR), a dye usually used in the textile industry. More importantly, as-synthesized nanosheets were used as the heterogeneous Fenton catalysts for photo degradation of organic dyes under Xe light, revealing their superior degradation abilities and cycle stabilities. Additional, some key preparation and operating factors were also discussed to optimize the performance of FeOOH nanosheets in CR removal from aqueous solution. Our research shows that as-prepared nanosheets have great potential to be applied in wastewater treatment.

2. Experimental

2.1. Preparation of 2D FeOOH Ultrathin Nanosheets

2D Ultrathin FeOOH nanosheets were synthesized by an approach similar to the chemical reduction method for the preparation of metal-boron amorphous alloy with NaBH4. In a typical synthesis, iron nitrate (10.1 g) and 250 mL water were placed in a 500-mL three-necked flask. 50 mL of aqueous solution containing 3.783 g sodium borohydride (NaBH4) with NaBH4/Fe molar ratio of 4 and 0.2 M sodium hydroxide (NaOH) was added dropwise to the above salt solution under vigorous stirring over 90 min to form the black participates. After stirring for 2.0 h to completely reduce the metal cations, the resulting precipitate was washed with water and ethanol and carried out in a beaker containing 150 mL ethanol. The solution was left under stirring for six hours at room temperature and the color of suspension gradually became brown-yellow during exposure to ambient air. The products were obtained by centrifugation with several times of washing with ethanol and water, the samples were dried at room temperature, denoted as FeOOH Ns-1. For comparison, the FeOOH Ns-2 and FeOOH Ns-3 were prepared by the similar method as mentioned above, merely with different NaBH4/Fe molar ratio of 3 and 5, which were 2.84 g NaBH4 and 4.73 g NaBH4, respectively.

2.2. CR Adsorption Experiments

The experiments were carried out as a function of contact time and CR concentration in a beaker (250 mL) and the stock dye solutions with required concentrations (50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L, 300 mg/L) were prepared by dissolving the corresponding dye in ultrapure water. The removal of CR is carried out by mixing 0.01 g of the nanosheets into 100 mL of CR solution without pre-adjusting the pH of the initial solution for desired time periods (10 min, 20 min, 30 min, 40 min, 50 min, 60 min, 120 min or 6 h) under magnetic stirring at room temperature. According to Beer-Lamber law, the change of CR concentration was observed at the maximum absorbance of CR dye (496 nm) by UV-vis spectrophotometer. For the adsorption capacity at time t, CR removal rate (%) can be calculated by formula (1), and equilibrium adsorption capacity qt (mg/g) can be calculated by formula (2). In the formula, the initial CR concentration of C0 and the CR concentrations at initial and time t of Ct (mg/L); V(L) represent the volume of the solution; m (g) represents the mass of adsorbent used. Equilibrium adsorption capacity is the adsorption capacity when the adsorption reaches equilibrium adsorption. It is close to a constant, expressed by (qe, mg/g).

\[
CR_{\text{removal}}(\%) = \frac{(C_0 - C_t)}{C_0} \times 100\%
\]

(1)
\[ q_r = \frac{(C_0 - C_r)V}{m} \]  \hspace{1cm} (2)

2.3. Characterization
Use JEM-2100 (JEOL Co., Japan) for transmission electron microscopy (TEM) analysis, X-ray powder diffraction (XRD) experiments were carried out on a Persee XD-3 X-ray diffractometer at a scan rate of 2°min\(^{-1}\) in the angle range of 5-90 using Cu K\(\alpha\) radiation. N\(_2\) physical adsorption at 77K in autosorb iQ2 analyzer (Quantachrome), UV-vis spectrophotometer (Agilent Technologies Cary 60).

3. Results and Discussion

3.1. The Morphology of the Sample

![Figure 1](image_url)  
**Figure 1.** Effect of different NaBH4/Fe additions on sample morphology  
a. 3B-Fe Ns; b. 4B-Fe Ns; c. 5B-Fe Ns

The typical FeOOH ultrathin nanosheets were synthesized by spontaneous transformation from precursors following chemical reduction method using NaBH4 as a reducing agent. NaBH4 as the only precipitating or reducing agent, the BH4/Fe molar ratio is an important influential factor for morphology of the prepared nanosheets. Figure 1 (b) present the typical TEM images of the FeOOH Ns-1 sample with the NaBH4/Fe molar ratio is 4, revealed that the sample displays a curved and graphene 2D sheet-like morphology. FeOOH Ns-1 sample and FeOOH Ns-3 sample with the BH4 /Fe mole ratio of 3 and 5 were investigated by TEM measurements, respectively. In contrast to the 2D sheet-like Ns-1 sample, Ns-2 sample is present in the form of irregular nanoparticles with the surrounding of a few nanosheets. In the case of Ns-3 sample, the morphology reveals a fluffy appearance that is comprised of agglomerated nanosheets, and these crumpled and tiny nanosheets are overlapping with each other.

3.2. The Structure of the Sample
To understand the composition of a series of different NaBH4 using nanosheets, XRD investigations have been carried out in Figure 2. Extremely weak and broad diffraction peaks at 20 values of 35.1° and 63.0° well indexed to the (100) and (110) planes of δ-FeOOH (JCPDS 77-0247) were observed for all the samples [13]. The variations in NaBH4/metal ratio during chemical reduction of nanosheets precursors resulted not significantly change the XRD patterns of a series of FeOOH nanosheets. In addition, the presence of extremely weak and broad diffraction indicates that the samples retain a nearly amorphous state.
3.3. The Physicochemical Property of the Sample the Structure of the Sample

Physical properties were further determined by N2 physisorption. The N2 adsorption–desorption isotherms for the nanosheets samples obtained via different amount of NaBH4 are shown in Figure 3. According to the Brunauer Deming Deming teller classification, from the curve in the figure, we can judge that the shape of the isotherm of these samples is type IV, and the hysteresis loop is type H3, which may be related to the slit like mesopores formed by the special morphology of FeOOH nanosheets.

The textural parameters calculated from these isotherms, such as BET surface areas, total pore volumes and the average pores size, are summarized in Table 1. It is worth noting that the sample NS-1 has a quite large specific surface area (402.5 m²/g) and pore volume (1.5 cm³/g) due to its ultrathin 2D-layered structure. On the contrary, the sample NS-3 possessed an even higher surface area (414.2 m²/g) but exhibited lower pore volume (0.94 cm³/g). According to the results obtained by TEM and Pore size distributions, it seems that nanosheets of sample NS-3 had relatively small lateral dimensions and closely stacked together, thus leading to a narrower pore size between the layers and lower pore volume. In contrast to sample 3B-Fe Ns and 5B-Fe Ns, sample 4B-Fe Ns displayed lowest surface area (204.3 m²/g) and pore volume (0.44 cm³/g), in coincidence with the TEM results. Due to the huge specific

![Figure 2. Effect of different NaBH4/Fe additions on sample structure](image)

**Figure 2.** Effect of different NaBH4/Fe additions on sample structure
a. 3B-Fe Ns; b. 4B-Fe Ns; c. 5B-Fe Ns

![Figure 3. Effect of different NaBH4/Fe additions on physicochemical property](image)

**Figure 3.** Effect of different NaBH4/Fe additions on physicochemical property
a. 3B-Fe Ns; b. 4B-Fe Ns; c. 5B-Fe Ns
Surface area and large pore size of nanosheets, it is very conducive to the adsorption of organic pollutants. This characteristic is beneficial to the treatment of organic dyes.

**Table 1.** Effect of different NaBH4/Fe additions on sample physicochemical property

| Samples | $S_m$(m$^2$/g) | $V_p$(cm$^3$/g) | dp(nm) |
|---------|----------------|-----------------|--------|
| 3B-Fe Ns | 204.3          | 0.44            | 9.1    |
| 4B-Fe Ns | 402.5          | 1.50            | 14.2   |
| 5B-Fe Ns | 414.2          | 0.94            | 9.6    |

### 3.4. Adsorption of Organic Dyes

Owing to the strong adsorption capacity of the FeOOH nanosheets by their large surface area and pore volume, all samples showed excellent adsorption performance for CR. We carried out several experiments on dye adsorption by using different amount of reducing agent. Tests with increased adsorption time were first conducted and results are presented in Figure 4A. It is seen that the NS-1 sample has the highest adsorption capacity for CR dye removal of 48% in comparison of sample NS-3 and NS-2 with removal of 43% and 33.5%, respectively, and all samples could reach at an equilibrium position after 60 min. This result also showed similar trends of nitrogen adsorption results and clearly indicates that high surface area and large pore volume perform significant functions in enhancing the adsorption ability of nanosheets for CR dyes. In the adsorption isotherm in Figure 4B, the relationship between the adsorption capacity of the FeOOH nanosheets and the initial concentration of CR can be found. It is obvious that the FeOOH nanosheets synthesized by this method have a high adsorption capacity for CR, with an adsorption capacity of approximately 1260 mg/g. Finally, it needs to be pointed out that most of the reported adsorption results have the best pH in the literature (usually around 2). This also reflects the fact that under actual conditions, it may not be possible to achieve high adsorption of Congo Red under normal pH. Therefore, we believe that this method can achieve high adsorption capacity in the Congo red adsorption experiment without adjusting the pH value, which shows that this material has a good application prospect in actual water treatment applications.

**Figure 4.** The variations of CR dyes concentration with the addition of B-Fe Ns
(A) Adsorption experiment at 250 mg/L, 100ml CR dye and 10 mg FeOOH Ns; a. 3B-Fe Ns; b. 4B-Fe Ns; c. 5B-Fe Ns
(B) Adsorption experiment at 100ml CR dye and 10 mg 4B-Fe Ns, 6h

### 4. Conclusion

In conclusion, we have developed a novel, green and facile approach for synthesizing high-quality FeOOH nanosheets by chemical reduction method as organic dye adsorbents. By adjusting the molar ratio of the reducing agent to the Fe ions, the ionicity can be adjusted appropriately, and the Congo red organic dye with good water purification effect can be obtained. It has a large specific surface area, large pore volume, excellent chromium adsorption performance, and no need to adjust the pH value. Our work shows that the as-prepared nanosheets have great application potential in wastewater treatment. Because
the preparation reagents all use environmentally friendly solvents and the preparation conditions are mild, which has an ideal and feasible large-scale green chemical process potential.

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References
[1] M.M. Cheng, L.J. Huang, Y.X Wang, Synthesis of graphene oxide/polyacrylamide composite membranes for organic dyes/water separation in water purification, J. Mater. Sci. 54 (2019) 252-264.
[2] X. Jiang, P. Sun, L. Xu, Y. Xue, H. Zhang, W. Zhu, Platanus orientalis leaves based hierarchical porous carbon microspheres as high efficiency adsorbents for organic dyes removal, Chinese J. Chem. Eng. 1 (2020) 254-265.
[3] S.K. Saroj, S. Pal, R. Nagarajan, Polyol intercalation in copper substituted zinc hydroxide acetate and evaluation of its adsorptive role towards Congo red dye, Appl. Clay Sci. 185 (2020) 105411-105420.
[4] I. Aminu, S. M. Gumel, W. A. Ahmad, A. A. Idris, Kinetic Studies of Congo-Red Removal from Waste Water Using Activated Carbon Prepared from Jujube Seed, Am. J. Anal. Chem. 11 (2020) 47-59.
[5] C.R. Wang, J.J. Yin, R. Wang, Facile Preparation of Self-Assembled Polydopamine-Modified Electrospun Fibers for Highly Effective Removal of Organic Dyes, Nanomaterials 9 (2019), 116-120.
[6] A.L. Vega-Negron, L.A. Nole, O.P. Perez, Simultaneous Adsorption of Cationic and Anionic Dyes by Chitosan/Cellulose Beads for Wastewaters Treatment. Int. J. Environ. Res. 12 (2019) 59-65.
[7] A. Boutelba, N. Benhadria, A. Elaziouti, K. Ezziane, Competitive adsorption removal of indigo carmine and Congo red dyes from residual effluents by Zn2Al-LDH prepared by co-precipitation, Desalin. Water Treat. 201 (2020) 404-419.
[8] J. M. Jabar, Y. A. Odusote, K. A. Alabi, I.B. Ahmed, Kinetics and mechanisms of congo-red dye removal from aqueous solution using activated Moringa oleifera seed coat as adsorbent, Appl. Water Sci. 10 (2020) 136-147.
[9] T. Yan, N. Li, Z. Qiao, W. Li, H. Wang, Z. Jing, Z. Jiang, Ultrathin sodium ferric silicate 2D nanosheets: A novel and robust adsorbent for selective removal of cationic dyes in wastewater, J. Alloy. Compd. 784 (2019) 256-265.
[10] J.S. Zou, G. Peleckis, C.Y. Lee, G. G. Wallace, Facile electrochemical synthesis of ultrathin iron oxyhydroxide nanosheets for the oxygen evolution reaction, Chem. Commun.155 (2019) 8808-8811.
[11] C. Liang, B.B. Wang, S.T. Xing, Growth of Iron (Hydr)Oxides on Different Carbon Substrates and Their Fenton-like Performance. Catal. Commun. 107 (2018) 1-4.
[12] H. Chen, X.J. Wu, Two-Dimensional CoII Coordination Polymer for Photodegradation of Organic Dyes and Treatment of Temporary Osteoporosis of the Hip (TOH) by Regulating wnt/β-catenin/PPARγ Pathway, Aust. J. Chem. 73 (2019) 9-15.
[13] V.V. Strykanova, L.B. Gulina, V.P. Tolstoy, E. V. Tolstobrov, D. V. Danilov, I. Skvortsova, Synthesis of the FeOOH Microtubes with Inner Surface Modified by Ag Nanoparticles, ACS Omega 25 (2020) 15728-15733.