Supplementary Information (SI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2025

Supplementary Information

Adsorption of ammonium nitrogen in water by modified bentonite compounded with carboxymethyl-β-cyclodextrin

Yuhan Hu, Renjing Li, Shanshan Lu, Qi Zhu*

School of Chemistry and Materials Science, Heilongjiang University,
Heilongjiang Provincial Key Laboratory of Environmental Nanotechnology,
Harbin 150080, China

*Corresponding author. Email: hdzhuqi@126.com

1.1. Materials

Na-bentonite (bent) was purchased from Hebei province. Carboxymethyl-β-cyclodextrin (CMCD) was produced by aladdin. Ethyl orthosilicate (TEOS) was obtained from Fu Chen (Tianjin) Chemical Reagent Co. Epichlorohydrin (EPI) was supplied by Tianjin Damao Chemical Reagent Factory. Potassium iodide (KI) was provided by Tianjin Komeo Chemical Reagent Co. Mercury iodide (HgI) was provided by Tianjin Beilian Fine Chemicals Development Co. Hydrochloric acid (HCl) was provided by Tianjin Yaohua Chemical Reagent Co. Sodium hydroxide (NaOH) was provided by Tianjin Continental Chemical Reagent Factory. Potassium sodium tartrate was provided by Tianjin Tianli Chemical Reagent Co. Ammonium chloride (NH_4Cl) was provided by Xilong Chemical Co. All the above reagents used in this experiments were analytical grade.

1.2. Preparation of modified materials

First of all, 5.00 g of bentonite was put into a crucible and placed in a muffle furnace and calcined at 500℃ for 2h. The bentonite used in the following preparation experiments were roasted bentonite.

1.2.1. Synthesis of Acidified Calcined Bent/SiO_2

Calcined bent/SiO_2 was prepared in accordance with the method described

previously Wang Junyi's method[1]. 2 g of calcined bentonite was added to 10 mL of deionized water and 150 mL of ethanol. Then the mixture was sonicated for 30 minutes. After that, 2 mL of ammonia water was added to the solution and stirred for 10 minutes. Then, 12.5 mL of TEOS was added slowly to the solution and stirred for 8 hours. Finally, calcined bent/SiO_2 was centrifuged several times with deionized water until pH was neutral. The resulting material was dried and grinded. 2 g of calcined bent/SiO_2 was added to 100 mL of 0.1mol/L hydrochloric acid solution, stirred for 12h. Then it was centrifuged several times with deionized water until pH was neutral and dried. It was used for subsequent experiments.

1.2.2. Synthesis of Acidified Calcined Bent/SiO_2/CMCD

Acidified calcined bent/SiO_2/CMCD was prepared in accordance with the method described previously Zheng Shengyang's method[2]. The acidified calcined bent/SiO_2 was complexed with CMCD. 0.36 g EPI and 1 g CMCD were added to 50 mL of 0.1 mol/L NaOH solution and stirred at 25 ℃ for 6 h, and then 1.5 g of acidified calcined bent/SiO_2 was added and stirred for 5 h. The product was centrifuged, dried, and ground to obtain the final sample.

1.3. Characterization methods

The crystalline phases present in composite were determined by means of X-ray diffraction (Bruker-D8 advance, Germany) using α-ray light sources for Cu and K. SEM (Scanning electron microscopy) images of adsorbents were obtained with a Hitachi S-4800 instrument. Specific surface area and the plot of the pore-diameter distribution of adsorbent were determined on Brunner-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) method from N_2 adsorption/desorption isotherm on a ASAP2460 physical adsorption instrument of Mack in the United States. To demonstrate the presence of CMCD on the adsorbent, Fourier-Transform Infrared Spectroscopy (FTIR, Perkin Elmer's Spectorn One system, United States) was applied in the wave numbers ranging of 400 cm^{-1} to 4000 cm^{-1}. The surface charges of modiefied adsorbent at pH 3 - 11 were analyzed using a Zeta potential analyser (Malvern Zetasizer Nano, ZS90, United Kingdom). A Thermo Scientific with K-Alpha was selected to verify the data of X-ray photoelectron spectroscopy (XPS).

Reference

[1] Wang, J. *et al.* Construction of novel graphene-based materials GO@SiO_2@C@Ni for Cr(VI) removal from aqueous solution. *Journal of Colloid and Interface Science* **557**, 254-265, doi:10.1016/j.jcis.2019.09.021 (2019).

[2] Heydari, A., Khoshnood, H., Sheibani, H. & Doostan, F. Polymerization of β-cyclodextrin in the presence of bentonite clay to produce polymer nanocomposites for removal of heavy metals from drinking water. *Polymers for Advanced Technologies* **28**, 524-532, doi:10.1002/pat.3951 (2016).