



Preparation of a novel manganese oxide-modified diatomite and its aniline removal mechanism from solution



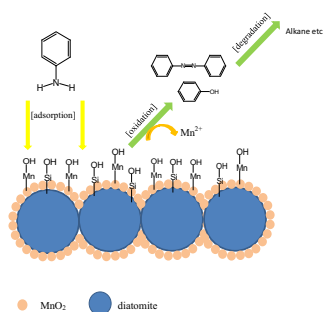
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HIGHLIGHTS

- Diatomite was modified with synthesized manganese oxide after calcination.
- Maximal aniline removal efficiency and capacity is 85.9% (42.9 mg/g).
- Study of the mechanism of aniline removal by manganese oxide-diatomite composites.
- Azobenzene and phenol were the main intermediates.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel modified diatomite was prepared by chemical treatment by impregnating diatomite into an acidic permanganate solution after calcination to remove aniline. Material characterization by Brunauer–Emmett–Teller (BET) and scanning electron microscopy (SEM) and X-ray diffraction (XRD) revealed the presence of manganese dioxide (MnO₂) on the diatomite surface with an increased surface area. Various adsorption conditions, such as contact time, adsorbent dosage, pH and interaction effect were investigated. It was shown that the equilibration removal capacity of aniline from solution for MnO₂ coated-diatomite (Mn-D) was 42.9 mg/g. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) results revealed that aniline was adsorbed by O–H (such as Si–OH and Mn–OH) on the diatomite surface and then oxidized by MnO₂. Oxidation and adsorption therefore existed during MnO₂ removal. Products obtained during removal were studied by gas chromatography–mass spectroscopy (GC–MS) to confirm that azobenzene and phenol were the main intermediates and to propose a possible degradation pathway for aniline. MnO₂ on the Mn-D surface played a role in oxidation and adsorption to degrade aniline. Mn-D can be used as a low-cost adsorbent to remove aniline under mild conditions.

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1. Introduction

Aniline is an important organic chemical raw material and intermediate that is widely present in effluents from pharmaceutical, pesticide, dyestuff, petrochemical and agrochemical industries

[1,2]. Aniline can harm general health and environmental quality because of its high toxicity and environmental accumulation after entering the environment through air or water. Strict limits have been established for its release and it has been listed as a priority pollutant in China. Traditionally, aniline-containing wastewater is treated by photodecomposition [3–5], electrolysis [6], adsorption [7,8], oxidation [9,10], biodegradation [11] and other processes. Of these approaches, adsorption is still the most versatile and

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widely used method to treat organic polluted wastewater because of its high efficiency, simple operation conditions, the fact that it does not generate harmful byproducts, and its regeneration ability [2,12]. Various adsorbents, such as active carbon [13], polymeric resins [14,15], surfactant-modified zeolites [16], organo-clays [17] and porous polymeric adsorbents [18] have been applied to adsorb aniline in aqueous solution.

Diatomite is a relatively new adsorbent that has shown great potential for removing heavy metal ions and organic matter because of its favorable physical properties such as high porosity (25–65%), small particle size, low thermal conductivity, light weight, large surface area and high adsorption capacity [19]. These characteristics present great potential for its utilization in environmental pollution treatment. Diatomite is approximately 500 times cheaper and therefore has the potential of being used as a cost-effective alternative to commercial activated carbon [20]. However, raw diatomite contains many impurities, which disfavors adsorption in aqueous solution. It is therefore necessary to modify diatomite to obtain better adsorption capacity. Suitable diatomite surface modification can improve its surface characteristics and make it amenable for adsorption over raw diatomite [21]. Conventional modification methods include chemical [22] and physical modifications [23]. Calcination has a remarkable effect on the type, distribution and content of surface hydrated species (water, H-bonded silanols and isolated silanols); it influences key reactive sites for various surface reactions, including adsorption [24] and photocatalysis [25]; and it also causes the removal of volatile and organic admixtures [26]. Chemical modification using traditional acid [27] or alkaline treatment, and some inorganic compounds [28] has been used more widely. Increased attention has been given to manganese dioxides as potential modifiers of diatomite because of their adsorption properties and oxidation ability. Khraisheh and co-authors reported that the specific surface area of modified diatomite is 2.4 times that of raw diatomite and reaches its highest performance at a loading of $0.06 \text{ g oxide g}^{-1}$ diatomite [29]. Du et al. reported that wire-like MnO_2 -coated diatomite (Mn-D) yield higher surface areas ($144.2 \text{ m}^2/\text{g}$) than raw diatomite ($25.0 \text{ m}^2/\text{g}$), and a maximal Cr(VI) adsorption capacity with 101 mg/g [30]. Zhang et al. synthesized Mn-D, which exhibited excellent performance for methylene blue (MB) solution degradation (0.02 g/L , 100 mL) by oxidation within only 5 min in acidic solution (pH 2) [31].

Although the use of MnO_2 -modified diatomite composites for metal ions and organic compound cleaning has been reported widely, the focus has mainly been on the adsorption effect but the oxidation role of MnO_2 in the adsorbent has been ignored. To date, few studies have dealt with aniline adsorption by MnO_2 -diatomite and work is still lacking on the removal mechanism of aniline onto modified diatomite. The main objectives of this research were: (1) to prepare a MnO_2 -coated diatomite adsorbent from environmentally friendly and low-cost raw materials for effective aniline removal; (2) to characterize the adsorbent using a variety of techniques and (3) to evaluate its aniline adsorption capacities and examine the mechanism toward MnO_2 on the surface of modified diatomite and during the reaction process.

2. Experiments

2.1. Materials

Raw diatomite (83.3% SiO_2 , 0.8% Al_2O_3 , 5.0% CaO , 0.4% Fe_2O_3 , 0.02% K_2O , 0.4% MgO and 0.1% Na_2O) was from Sigma-Aldrich (St. Louis, MO, USA). All stock solutions were prepared using reagent grade chemicals from Shanghai Zhenxin Reagent Co. (Shanghai, China), and deionized water.

2.2. Adsorbent preparation

Mn-D was prepared using a new method that involves calcination diatomite (C-D) impregnation with permanganate (MnO_4^-) through slow addition of HCl as described by Dang et al. [32]. By controlling the ratio of MnO_4^- ions to diatomite, diatomite surface coating is controlled, and its effect on aniline adsorption is monitored. Several samples with different mass ratios of KMnO_4 to diatomite (ρ) (0.16–3.2) were prepared to study the controllability of the MnO_2 coating on the diatomite surface. C-D was obtained by calcination of raw diatomite at 300°C , 450°C , 600°C , 900°C and 1000°C for 3 h after passage through a 100 mesh sieve. The materials were activated at 105 – 110°C for 1 h, dried in an oven and stored at room temperature. A control experiment was also performed, which consisted of a mixture of 0.1 M KMnO_4 and 6 M HCl without diatomite to produce MnO_2 at room temperature with an average yield of $\sim 0.11 \text{ g}$ total solids. Before further investigation, all samples were pulverized in a mortar with a pestle.

2.3. Characterization

N_2 adsorption/desorption analysis was performed on each adsorbent using a Micromeritics ASAP 2010 surface area analyzer (Norcross, GA, USA). The specific surface areas were determined using the Brunauer–Emmett–Teller (BET) method. Diatomite sample surface morphology and nanostructure were determined by scanning electron microscopy using a Philips XL-30 scanning electron microscope, and energy-dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD) analysis was carried out on an X'Pert PRO diffractometer (PANalytical Co., Almelo, The Netherlands) coupled to a copper anode X-ray tube, at a wave length K, with a diffracted beam monochromator, at 35 kV and 40 mA . The zeta potential of diatomite samples was measured using a Zetasizer 2000 (Malvern Co., UK). Aqueous sample suspensions were dispersed using an ultrasonic bath and an average of three measurements was taken to represent the measured potential. Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Nicolet 6700 Fourier Transform IR spectrophotometer Spectrum (Thermo, USA) to identify functional groups on the diatomite surface after modification and adsorption. FTIR spectra from 400 to 4000 cm^{-1} were obtained with 15 scans for each spectrum recorded at a resolution of 4 cm^{-1} . Modified diatomite chemical compositions before and after aniline adsorption were probed using X-ray photoelectron spectroscopy (KRATOS AXIS ULTRA, DLD) with Al $K\alpha$ radiation and Al/Mg radiation at 450 W and $3.0 \times 10^{-10} \text{ Pa}$. Data were analyzed using X-ray photoelectron spectroscopy (XPS) peak software. To identify intermediates, a gas chromatography–mass spectroscopy (GC–MS) system was used with a gas chromatograph coupled to the mass spectrometer (Agilent GC–MS 7890, USA).

2.4. Bath adsorption experiments

Mn-D (0.5 g) was equilibrated with 250 mL of 25 mg aniline. The pH was adjusted to 5.0 in a conical flask at 25°C for a fixed period of time (2, 5, 10, 15, 30, 45, 60, 120, 240, 480, 720, 1440 min) to investigate the sorption kinetics. pH studies were carried out to determine the optimum pH at which maximum aniline removal capacity could be achieved. R-D, C-D and Mn-D adsorbents (0.2 g) and 100 mL of 100 mg/L aniline solutions were added to a 250 mL conical flask with initial pH adjustment to 3 – 9 with dilute 0.1 M NaOH and HCl , and shaken until equilibrated at 25°C . Supernatant was filtered using a $0.45 \mu\text{m}$ filter and concentrations of aniline in the supernatant were determined by high performance liquid chromatograph 1200Series (Agilent Technologies, USA). Sorption capacity was calculated using Eqs. (1) and (2):

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