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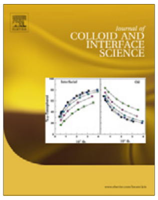

Multifunctional kaolinite-supported nanoscale zero-valent iron used for the adsorption and degradation of crystal violet in aqueous solution

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ABSTRACT

Kaolinite-supported nanoscale zero-valent iron (K–nZVI) was successfully synthesized as a multifunctional composite and used for the degradation of crystal violet (CV). The presence of kaolinite not only decreased the aggregation of zero-valent iron nanoparticles (nZVI) with maintenance of reactivity, but also facilitated reaction by increasing the local concentration of CV in the vicinity of nZVI as an adsorbent. This was confirmed by scanning electron microscopy (SEM) and batch experiments, which showed that 97.23% of CV was removed using K–nZVI, while only 78.72% and 39.22% of CV were removed using nZVI and kaolinite after 30 min, respectively. Different factors impacting on degradation of CV were investigated as well. On the basis of these results, a removal mechanism was proposed including: (i) prompt adsorption of CV to the K–nZVI phase, and (ii) reduction of CV by Fe^0 on K–nZVI. Furthermore, different adsorption and reduction kinetics were employed to examine the removal process of CV, where a better fit with the pseudo-second-order model for adsorption and pseudo-first-order model for reduction process was observed, and reduction was the rate limiting step. In addition, isotherm and thermodynamic parameters were evaluated for a specific study of the important adsorption step. Finally, the application of K–nZVI to treat wastewater showed the removal efficiency higher than 99.9%.

1. Introduction

Dyes from textile or dyestuff industries have aroused much concern for the impact they have on the quality of water resources [1]. Most of the dyes and their degradation products are toxic and carcinogenic [1]. Of the broad range of the triphenylmethane dyes, crystal violet (CV) is usually difficult to degrade due to its complex structure containing aromatic rings [2]. Many techniques involving physical, chemical, and biological methods have been exploited to apply in treating the dye wastewater [1]. These methods can remove dyes from wastewater, but they are often expensive, inefficient, and produce secondary waste products [1–3].

Nanoscale zero-valent iron (nZVI) has recently been used in groundwater treatment and site remediation due to its larger surface area and higher intrinsic reactivity of surface sites [4,5]. For dye wastewater treatment, a few reports have been documented on using nZVI for degradation of dyes such as anthraquinone and triphenylmethane dyes [1,4]. Compared to the conventional methods, nZVI can reduce dye molecules to products that are more amenable to mineralization in biological treatment processes. However, nZVI tend to agglomerate or react with surrounding media and thus form oxide layers on the particle surface, resulting in significantly reducing reactivity [6]. To address this issue, many porous materials have been proposed to disperse nZVI particles such as resin, kaolinite, and bentonite [7–9]. In our previous study, we found the use of kaolinite and bentonite as a support for nZVI could effectively reduce the aggregation of nanoparticles, thereby enhanced their reactivity and stability in removing Pb(II) [8], Cr(VI) [9,10] and methyl orange [5], where the simultaneous adsorption and degradation demonstrated that this was a promising remediation method for both metal ions and dyes. Other reports on resin-supported, carbon-supported nZVI had been documented as well for remediation of heavy metals or chlorinated organic compounds and nitroaromatics [11,12].

Nevertheless, to date, (1) though most of the studies on supported nZVI confirmed a simultaneous or consecutive adsorption and degradation mechanism [1,7,12,13], only a few of them identify the adsorption and reduction process, respectively. For instance, the adsorption and simultaneous dechlorination of 2-ClBP on GAC/Fe/Pd have only recently been reported [14]. Further

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studies to understand the specific adsorption or reduction behavior in a removal process involving both adsorption and reduction are necessary. (2) Despite increasing research efforts to gauge the removal efficiency of supported/capped nZVI [11,13,15], the detailed adsorption mechanism of the support material is still unknown. However, an understanding of the adsorption behavior including isotherm and dynamic studies could provide useful information for selecting a proper support material in designing effective wastewater treatment materials. (3) Kaolinite is a naturally abundant, low-cost and easily available material, and coupled with its chemical and mechanical stability, strong adsorption capacity and unique structural properties, these make it a great support material for removing crystal violet from wastewater. Moreover, kaolinite has been studied as the supporting material for catalyst, photocatalyst, and adsorbent [16]. Although kaolinite itself can use as the adsorbent to remove various contaminants, the adsorbed contaminants may be released into the environment and pose another kind of potential risk [3].

In this paper, we elucidate the mechanistic aspects of the multifunctional K–nZVI system when it removes CV in aqueous solution from the kinetic and dynamic studies. The following are reported in this study: (1) synthesis and characterization of K–nZVI; (2) evaluation of various parameters affecting the degradation of CV; (3) kinetic studies of the adsorption and reduction processes, respectively; (4) the corresponding isotherms and thermodynamic parameters of the adsorption process; and (5) a suggested possible degradation mechanism and the potential application of K–nZVI in remediation of dyes wastewater.

2. Experimental

2.1. Materials and reagents

Kaolinite used in this study was supplied by Taojingfeng New Materials Co., Ltd., Fujian, China, and its chemical composition was as follows: SiO_2 50.67%, Al_2O_3 44.02%, Fe_2O_3 0.10%, TiO_2 0.21%, CaO 0.00%, MgO 0.17%, K_2O 0.21%, and Na_2O 0.00%. After being dried at 70 °C for over 12 h, kaolin was ground and sieved with a 200 mesh screen prior to the experiment. $FeCl_3{\cdot}6H_2O$ was obtained from Tianjin Chemical Reagent Co. (Tianjin, China). $NaBH_4$, NaOH, HCl, and crystal violet ($C_{25}H_{30}N_3Cl$) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All the chemicals used in this study were analytical grade and applied without further purification. Deionized water was used throughout this experiment.

2.2. Synthesis of nZVI and K–nZVI

nZVI and K–nZVI were synthesized using the liquid-phase reduction method with kaolinite acting as a support material, which has been previously reported [8,10]. Briefly, the preparation of K–nZVI had a Kaolin/Fe^0 mass ratio of 1:1. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) (4.84 g) was dissolved in 50 mL of miscible liquids, followed by the addition of 1.00 g treated kaolinite. The mixture was stirred for 15 min, and then, 0.47 M $NaBH_4$ solution (100 mL) was added at the speed of 1–2 drops per second into this mixture and vigorously stirred under a nitrogen atmosphere. Black particles were gradually produced as the mixture's color turned from red brown to light yellow and then eventually to black [8,10]. Vacuum filtration was employed to collect the K–nZVI, and they were quickly rinsed three times with absolute ethanol. Then, it was dried at 333 K under vacuum overnight and kept in a nitrogen atmosphere prior to use. Unsupported nZVI and K–nZVI with different mass ratios of kaolinite versus nZVI, theoretically calculated to be 0:1, 1:1, 2:1, 3:1 and 4:1, were then prepared by varying the initial kaolinite loading at the beginning of the procedure.

2.3. Characterization

Scanning electron microscopy (SEM) images of kaolinite, nZVI and K–nZVI before, and K–nZVI after reacted with CV were obtained using a Philips-FEI XL30 ESEM-TMP (Philips Electronics Co., Eindhoven, Netherlands). The specific surface areas (SSAs) of kaolinite, nZVI and K–nZVI (1:1) were tested using the BET-N_2 adsorption method (Brunauer–Emmett–Teller isotherm). This was made possible employing Micromeritics' ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer (Micromeritics Instrument Corp., GA).

2.4. Batch experiments

To compare the degradation of CV in aqueous solution, experiments were carried out using kaolinite (1.00 g), nZVI (1.00 g), and K–nZVI (2.00 g with the mass ratio of 1:1) added to 30 mL CV solution at an initial concentration of 100 mg L^{-1}. Mixed solutions were left at their initial pH level stirred at 60 rpm at 303 K to the desired time intervals. They were then filtered through 0.45 μm membranes to measure the residual concentration of CV. Various parameters affecting the degradation of CV using K–nZVI were investigated, such as solution of pH, dosage of K–nZVI, initial concentration, temperature of the CV solution, and speed of the shaker.

To explore the feasibility of CV, wastewater collected from a textile printing and dyeing company based in Fuzhou, China, was tested. The wastewater was centrifuged at 3000 r/min for 10 min to remove any insoluble impurities, prior to determining the initial pH and concentrations of CV. It contains approximately 4.18 mg L^{-1} of CV, and then, the performance of K–nZVI was investigated by adding an extra 100 mg L^{-1} of CV under optimal conditions.

The residual concentration of CV solution was measured using a UV-Spectrophotometer (722 N, Shanghai, China) at λ_{max} = 592 nm. The degradation efficiency of CV was calculated using the following equation [8,10]:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

where $R(\%)$ is the degradation efficiency of CV, C_0 (mg L^{-1}) is the initial concentration of CV in the solution, and C_t (mg L^{-1}) is the concentration of CV at t min.

3. Results and discussion

3.1. Removal of CV using various materials

To evaluate the degradation of CV in aqueous solution by various materials, the removal of CV using kaolinite, nZVI, and K–nZVI (1:1) was investigated (Fig. 1). K–nZVI demonstrated the highest removal efficiency despite it had a lower surface area (19.84 m^2/g) than nZVI (35.16 m^2/g). Furthermore, 39.22% CV was rapidly adsorbed onto kaolinite, which was a relatively high rate of efficiency for adsorption concerning the kaolinite's low surface area (6.03 m^2 g^{-1}).

It is noteworthy that equilibrium for CV removal from the aqueous solution was reached promptly within the first 2 min using kaolinite, demonstrating a process of adsorption, while more than 30 min was required for nZVI caused by a much slower process of chemical redox reactions. Meanwhile, an immediate sharp increase in the removal efficiency followed by a much slower decrease