Palygorskite-supported nano zero-valent iron – a bisphenol A degradation study

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Abstract:
Novel palygorskite-supported nano zero-valent iron composite materials prepared by evaporative and centrifuge methods were tested for the degradation of bisphenol A in an aqueous medium. Pristine nano zero-valent iron has little effect on bisphenol A degradation. However, when hydrogen peroxide was added, some percentage of bisphenol A removal (~20 %) was achieved; with the aid of dissolved air, the percentage removal can be significantly increased to ~99 %. Compared with pristine nano zero-valent iron and commercial iron powder, The composite materials have much higher reactivity towards bisphenol A and these materials are superior as they have little impact on the solution pH, which is a key factor in maintaining high bisphenol A removal. The optimum conditions were obtained based on a series of batch experiments.

Keywords: zero-valent iron; bisphenol A; palygorskite; composite material.

Introduction

Bisphenol A [2,2-bis-(4-hydroxy phenyl) propane] denoted as BPA is one of the world's most widely-manufactured chemicals, and it is prevalently used in plastic products [1]. However, it was found in recent years that BPA may exhibit hormone-like properties and act as an endocrine disruptor [2]. Some states and countries have banned the use of BPA in baby bottles. However it is still used in many other products and its widespread use has resulted in its ubiquitous existence in the environment. At present, there are only a few methods developed for the removal of BPA from aqueous. For example, adsorption, biochemical oxidation and wet chemical oxidation [3-8], but all of these methods have suffered from some disadvantages such as long reaction times, high cost and low efficiency. Among these methods, advanced oxidation processes have been explored and found to be a promising mechanism. Fenton reaction mechanism in particular follows a radical reaction and can theoretically account for the degradation of most refractory organic contaminants. It also benefits from the fact that no UV or visible light is needed to initiate the reaction. But the traditional Fenton reaction needs a continuous feed of ferrous ions, and after the reaction, there is a large amount of iron precipitate sludge which is a big issue in practical applications [9]. It could therefore be more practical if ferrous ions are generated in situ [10-12]. In recent years, zero-valent iron (denoted as ZVI) has been successfully used as permeable reactive barrier for groundwater contaminants; ZVI prepared on the nano size, shows much higher reactivity and greater efficiency attributed to its small particle size and high surface area [13]. However, ZVI material is not effective on phenolic compounds such as BPA. In literature, there are some studies which investigated the use of ZVI via Fenton reaction as in situ ferrous ions can be generated under acidic conditions which offers an effective means of replacing continuously added of ferrous ions [14]. To the best of our knowledge, there are only a few reports on BPA degradation using commercial ZVI [15], and no research using nano ZVI (nZVI) especially palygorskite-supported nano ZVI. This work aims to assess the feasibility of nZVI/H_2O_2 technology on the degradation of BPA compound. The influence of dissolved air was deliberately investigated and it was found that with the aid of air bubbles, the removal percentage can be significantly increased.

Materials and methods

Palygorskite supplied by the Clay Minerals Society as source clay palygorskite PF1-1(denoted as PF) was processed by acid-leaching under stirring at room temperature. $FeCl_2 \cdot 4H_2O$ was dissolved in a mixture of 95 % ethanol and deoxygenated de-ionised water under stirring. Then, acid-leached PF or unmodified PF was added to this ferrous solution under stirring over night, afterwards the following two different preparation procedures were applied: A) the suspension above was concentrated through rotary evaporation at 40 °C at 40 mbar. Then, $NaBH_4$ solution was added drop by drop to the slurry obtained above in a fume hood under stirring for 2 h. The final solid was centrifuged, washed three times with 200 ml of 95 % ethanol and dried in a 50 °C oven and stored in a desiccator (sample obtained using acid treated PF was denoted as 1HPF-Z-E;

sample prepared with PF was denoted as PF-Z-E); B) Similarly, the suspension was centrifuged at 3000 rpm and room temperature for 15 min in order to wipe off the excessive Fe^{2+}, then, samples were treated using $NaBH_4$ solution in a similar way as mentioned above (sample obtained is denoted as 1HPF-Z-C). The pristine nZVI was prepared by a similar procedure as described above, except that no PF or 1HPF was added. This nano ZVI was denoted as nZVI-Lab and the purchased commercial ZVI was denoted as ZVI-Com. BPA removal measurements were carried out by a batch technique at room temperature. In a typical experiment, sample was weighed and added to a beaker containing 100 ml of BPA solution of known concentration and pH. The initial pH of the working solution was adjusted to a desired value with HNO_3 or NaOH solution. The working solution was stirred using a magnetic stirrer at room temperature for pre-set time and agitated using an air pump with aerator stone at about 500 ml/min air flow rate. After reaction, the solid was separated by a centrifuge (4000 rpm) using a glass centrifuge tube. Aliquots of 1 mL supernatant were withdrawn using glass pipettes. The concentration of the target BPA was freshly quantitatively analysed using an Agilent HP1100 HPLC equipped with a Luna 5μ C18 column and a UV absorbance detector. A mobile phase of methanol-water (70: 30) at a flow rate of 1 ml/min and 40 μL of injection volume was used for this experiment and the analysis wavelength was 278 nm.

Results and discussion
The morphology of nZVI-Lab is very different from that of the ZVI-Com. nZVI shows chain-like morphology; it is likely that this type of chain is connected with pieces of iron particles, and the chain can be as long as several tens of microns while each spherical iron particle has a diameter at about 40 nm. When nZVI particles are loaded onto the surface of PF, it is observed that the most obvious changes come from the individual nano Fe^0 particles on the surface of clay minerals. Fig. 1 shows an image of nZVI particles on palygorskite, which demonstrates that the particle sizes vary, with both bigger and smaller particles being observed. When evaporative method is used for grafting, larger sized iron particles (70-80 nm in diameter) are observed; when centrifuging method is applied, however, smaller iron particles at about 40-50 nm in diameter are observed (figure not shown). It is concluded that elevated temperature favours the larger sized particle growth on clay surface.

nZVI-Lab was first tested for BPA degradation, this material usually has much higher efficiency compared with bigger sized commercial ZVI, but neither of the two materials show noticeable direct degradation towards BPA which is at variance with the result that reported in a literature [15]. Unmodified palygorskite and acid-leached palygorskite absorb negligible amounts of BPA. However, with the addition of hydrogen peroxide solution, it was observed that some percentage of BPA was removed. With the aid of air bubbles, the increase in the level of dissolved oxygen level led to significant improvement of BPA degradation, resulting in which up to 5-fold BPA removal percentage compared to the result obtained by using hydrogen peroxide only. The enhancement of adsorption in the presence of air bubbles is more prominent especially when lower sample amount is used. For example, for nZVI-Lab at 0.025 g, the BPA removal percentage increased from close to 0 % in the presence of H_2O_2 only to about 74 % in the presence of H_2O_2 and air bubbles. For ZVI-Com and nZVI/palygorskite composite materials, air bubbles significantly enhance the removal from 3.4 % to up to 95 %. Fig. 1 also shows a schematic diagram of the possible reaction pathways of nZVI/palygorskite composite material. The enhanced degradation with the aid of air bubbles is due to the presence of O_2 in a solution which enhances the oxidation of organo-radicals as the radicals can react with dissolved O_2 in faster and irreversible reactions [16]. Fe^0 also reacts with O_2 in acidic condition to form H_2O_2.

The pH value is one of the most important factors in the traditional Fenton process and the optimum pH is around 3 [9]. In this study, the effect of initial pH on the removal of BPA on nZVI-Lab, ZVI-Com and nZVI/palygorskite composites were examined at 25 °C by equilibrating 0.2 g of samples (except for nZVI-Lab in which 0.1g was used) with 100 mL of 50 mg/L BPA solutions with pH values varying from 2 to 5.36 (natural pH of 50 ppm BPA aqueous solution). The BPA removal percentage (%) varies significantly with the change of initial pH. The acidic condition is favourable for BPA removal on ZVI or nZVI/palygorskite composites. With the decrease of solution pH, the oxides coatings on ZVI particles would dissolve and thus enhance the accessibility of BPA to fresh reaction sites on Fe^0. pH at about 2.36 is the optimized condition for all investigated samples, where the highest removal percentage of BPA on 1HP-Z-C (nZVI supported onto acid-leached palygorskite using centrifuge method), 1HP-Z-E (nZVI supported onto acid-leached palygorskite using evaporative method), nZVI-lab and ZVI-Com is over 99 % for the first three samples and 90 % for the last sample. It is also observed that for nZVI-Lab, even slightly excess amount of this sample increases the pH of the working solution dramatically and thus, will reduce the degradation reaction rate,

which is also a disadvantage of pristine nZVI. For composite materials, under current conditions, when the initial pH is set at about 2.36, the pH can stay low for the entire procedure which is important as it will help maintain the high reactivity of the Fenton reaction, as at higher pH, the iron precipitates can form and thus, stop the reaction.

Figure 1. A schematic diagram of the possible reaction pathways

Figure 2. Effect of catalysts amount on the degradation of BPA using nZVI-Lab, ZVI-Com, and nZVI/palygorskite composites (initial pH: 2.36; concentration of BPA working solution: 50 mg/L; volume of BPA solution: 100 ml; reaction time: 5h).

The effect of catalysts amounts on BPA removal percentage is shown in Fig. 2. Generally, the BPA removal % increases with the increase of the sample dosage from 0.02 g to 0.2 g. The removal percentages of 0.2 g of ZVI-Chem, 1HP-Z-E and 1HP-Z-C (in 100 mL suspension, initial BPA concentration at 50mg/L) reaches 90.1 %, 99.6 % and 99.2 %, respectively, which corresponds to about 22.5, 24.9 and 24.8 mg BPA/g of the materials. However, this is not applicable for nZVI-Lab, which shows increased removal percentage when the amount is increased from 0.02 to 0.1 g, but it decreases dramatically when the amount is increased further to 0.2 g; this is due to the significant increase of pH as discussed above. In conclusion, the optimum amount of both ZVI-Com and palygorskite/ZVI composites were set at 0.2 g. For ZVI/Palygorskite composite materials, the increase of sample amount can bring increased removal as these materials make little change on the optimum pH of BPA solution. However, nZVI-Lab can increase the pH of the working solution dramatically depending on sample amount. This drawback makes pristine nZVI difficult to use outside the laboratory where accurately controlled reaction condition is difficult to achieve.

In this study, the effect of H_2O_2 dosage on the BPA removal is also examined. Thus, the H_2O_2 dosage was varied from 0.1 ml to 2 ml for all the samples. It can be observed that for nZVI/palygorskite composite materials prepared using evaporative and centrifuge methods, similar excellent results (about 99 % removal) are obtained even when only 0.1 ml of H_2O_2 was added. But for nZVI-Lab, BPA removal rate% was increased from 8 % (when 0.1 ml H_2O_2 was used) to 31 % (0.2 ml) and finally to 99 % (when 0.5 ml or over was used). In this study, the amount of H_2O_2 was kept at 2 ml for all experiments to make sure sufficient amount of H_2O_2 was provided for the reaction. This observation again confirms that compared with nZVI-Lab and ZVI-Com, nZVI/palygorskite composites are superior. The high efficiency of these two composite materials is attributed to the well distributed individual spherical nano ZVI particles on clay's surface.

The relationship between reaction time and removal percentage of BPA by ZVI-Com, nZVI-Lab and nZVI/palygorskite composite materials were also investigated. For ZVI-Com, the reaction rate is apparently the lowest among all other materials, with the increase of reaction time, the removal percentage increases slowly, and finally it reaches about 90 % in 5 h and no further removal happens afterwards. The larger particle size (micron scale) and smaller surface area may cause the slower reaction of this commercial material. For 1HP-Z-E and 1HP-Z-C, the BPA removal curves look similar and their reaction rates are faster. The BPA removal percentage on these two samples can reach over 90 % in about 120 min and 180 min, respectively, and it finally can achieve its maximum at 99 % in 300 min. For nZVI-Lab, BPA is rapidly removed within 20 min (> 90 %), then, it slowly reaches its maximum in 5 h (99 %).

Conclusion

The spherical nano zero-valent iron particles were successfully supported onto acid-leached palygorskite by two routes which also brought different nZVI particle sizes and reactivity. NZVI/palygorskite composite materials together with nZVI-Lab and ZVI-Com have been investigated for BPA degradation using H_2O_2 with the aid of air bubbles, which can significantly enhance the degradation of BPA. Though 1HP-Z-C contains less iron, it has even higher efficiency compared with 1HP-Z-E, and though both samples, have much less iron compared with that in nZVI-Lab, they showed comparable efficiency which can be attributed to the highly reactive spherical nano ZVI particles on clay mineral's surface. nZVI/palygorskite composite materials have clear advantages over nZVI-Lab and ZVI-Com. Optimized reaction time which indicates that solution pH at around 2.36 is the best for BPA degradation was also obtained. Finally, the catalysts amount of nZVI-Lab has to be carefully controlled, as it can greatly affect the solution pH during the degradation process and reduce the removal efficiency significantly.

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