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Adsorption and oxidation study on arsenite removal from aqueous solutions by polyaniline/polyvinyl alcohol composite

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ABSTRACT

In this study, the Polyaniline/Polyvinyl Alcohol (PANi/PVA) composite was examined for arsenite (As(III)) removal from aqueous solution. The effect of several parameters including PVA concetration (0–5 g/L), pH (1–13), adsorbent dosage (0.5–6 g/L), contact time (0–120 min), initial As(III) concentration (0.5–100 mg/L), and As(III) oxidation were evaluated on the adsorption efficiency. The results indicated that PVA has an effective role in increasing adsorptive capacity of PANi, by changing its morphology and extending its active surface sites. The adsorption process was pH dependent and As(III) removal consistently improved by increasing solution pH. Adsorption reached equilibrium within 1 h and Kinetics study showed that the adsorption process followed the pseudo-second-order rate model. Maximum arsenite removal efficiency was obtained when 2 g/L of PANi/PVA was added to the solution. The equilibrium adsorption data were well fitted to Langmuir isoterm model, and the maximum adsorption capacity of arsenite was 27.25 mg/g. Furthermore, arsenite oxidation led to 65% adsorption enhancement at the neutral aqueous system and also decreased the sensitivity of adsorption to pH.

1. Introduction

Arsenic is a poisonous metalloid that is widely distributed and its pollution is a serious environmental problem around the world [1]. Recently, arsenic contamination has been reported in several countries including USA, India, China, Taiwan, Vietnam, Mexico, Poland, Canada, Japan, Bangladesh, Chile, Argentina, Hungary and New Zealand [2]. Arsenic is a toxic compound that causes several diseases including skin lesions, cancer of the liver, brain, stomach, and kidney. Arsenic exists in four valency states including −3, 0, +3 and +5. The elemental state −3 and 0 are extremely rare, whereas +3 and +5 oxidation states are commonly found in groundwater systems, depending on the prevailing redox conditions. Arsenite (As(III)) is dominant under moderately reducing anaerobic environment; while Arsenate (As(V)) exists in water with abundant dissolved oxygen levels [3]. Arsenite is 25–60 times more toxic than arsenate [4]. Nevertheless, it has been found at levels of 100–2000 μg/L in groundwater in several countries [3].

The World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) have set the maximum contaminant level (MCL) of 10 μg/L for arsenic in drinking water [5,6]. Therefor8e, efficient treatment methods for arsenic removal are required to meet the standard. Several methods have been studied for removal of arsenic from water, including adsorption, ion-exchange, precipitation, and membrane filtration [7,8]. Among them adsorption is always considered as a potential treatment method for water with arsenic contamination, due to the high efficiency of removal and ease in phase separation [9–12]. There are many solid adsorbents which have been examined for the adsorption of arsenic, including amorphous aluminum hydroxide [13], amorphous iron hydroxide [14], γ-Fe_2O_3-TiO_2 magnetic nanoparticles [15], $MnFe_2O_4$ and $CoFe_2O_4$ nanoparticles [3], activated carbon [16], activated alumina [13,16,17], activated bauxite [16], and hematite [18]. Although some of these adsorbents showed a good potential for arsenate adsorption, arsenite adsorption was

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not always as it expected [2]. Because of the low concentration of the ionic form of As(III) in water solutions, the Van der waal force is the dominant force between the solute and the adsorbent in this case. This makes a very weak bond that does not lead to an efficient adsorption. Therefore oxidation of arsenite to arsenate and then performing the removal of oxidized arsenic by a proper adsorbent has been proposed in many studies [19,20].

Conducting polymers possess unique properties in electrochemical activity. Oxidation of a conducting polymer occurs with anion incorporation from the solution, to keep its electric neutrality, e.g. doping, and vice versa for its reduction, e.g. de-doping. Accordingly, based on doping and de-doping process, a conducting polymer can be utilized for adsorption of metal ions from aqueous systems and then for stripping them from itself [21]. These adsorbents have the ability to use both ion exchange and surface adsorption for heavy metal removal [22]. Polyaniline and its composites have shown strong properties as an adsorbent. High adsorption capacity, versatility [23,24] and environmental stability [25,26] of these composite are some of the benefits which these composites provide as an adsorbent. However, to address the poor processability, polyaniline synthesis in the presence of water soluble polymers such as polyvinyl alcohol, polyethylene glycol and polyvinyl pyrrolidone have been reported [27–29]. Removal of mercury ions by a composite of polyaniline with polystyrene [30], treatment of chromium by polyaniline–poly ethylene glycol composite [28] asorption of Cu(II) and Cd(II) by polyaniline on sawdust [31], removal of Cr(VI) polyaniline/polyvinyl alchohol composite [27], Re(VII) removal using organic–inorganic hybrid of polyaniline/titanium phosphate [32], and arsenate removal by polyaniline modified activated carbon [33] have been reported recently and all have suggested a significant improvement in removal efficiency of heavy metals compared to the traditional removal methods.

In this study arsenite removal by Polyaniline/Poly vinyl Alcohol (PANi/PVA) composite was explored. The effect of several parameters including PVA concentration, pH of the aqueous solution, adsorption time, adsorbent dosage and initial concentration of arsenite were evaluated to find the optimum adsorption conditions. Also adsorption isothermal behavior and equilibrium concentrations were studied. Finally oxidation of arsenite to the less toxic form of arsenate, and removal efficiency in this oxidation form by the composite was studied.

2. Experimental

2.1. Materials

Sulfuric acid, potassium iodate, sodium hydroxide, hydrochloric acid, poly vinyl alcohol (72000MW), arsenic trioxide, potassium permanganate and aniline were obtained from “Merck Chemical Company”. Aniline monomer purification was done by two-stage distillation to complete elimination of its color before starting polymerization process.

2.2. Instrumentation

A magnetic stirrer (MR Hei standard _heidolph), pH meter (827 Lab, Metrohm), and fixed temperature shaker (5082u, Labcon, Flatform) were utilized in this experiment. Total arsenic concentration was measured by atomic fluorescence spectrometer (AF-640 Rayleigh Instruments) at 193.7 wavelengths.

2.3. Chemical synthesis

In order to synthesize PANi/PAV composite, 1.6 g of potassium iodate was added to 200 mL of 1 M H_2SO_4 and fully mixed. Then, based on required PVA concentration, 0–1 g of PVA was added to the solution and the solution was shaken for 2 h. Afterward, 2 mL of pure aniline monomer was added to the solution and the mixture left on the shaker for 5 h. The polymer composite slowly synthesized within this time. The filter paper was used to separate the polymer composite from the solution. To remove impurities, separated polymer was washed with distilled water and acetone. Finally, the synthesized polymer was dried at the oven temperature of 105 °C for 48 h and then grinded to form the composite powder.

2.4. Experimentation

Arsenic solutions were prepared by dissolving arsenic trioxide in NaOH and then neutralizing the mixture by HCl. Required arsenic concentration solution was obtained by adding sufficient amount of deionized water to the arsenic solution. In this study, total arsenic was measured to evaluate the effectiveness of each process. In the experiments including arsenite oxidation, the process was performed by adding 2.8 g $KMnO_4$ per 1 g of As(III), which is about 2 times of stoichiometric ratio according to the following reaction [34]:

$$3H_3AsO_3 + 2MnO_4^- \rightarrow 3H_2AsO_4^- + 2MnO_2 + H_2O + H^+ \qquad (1)$$

Batch sorption experiments were performed by addition of predetermined quantities of PANi/PAV composites to a 50 mL of prepared arsenite solution. A shaker was employed at 160 rpm for mixing to reach equilibrium concentration. pH adjustment was performed by adding 0.1 M HCl and 0.1 M NaOH solutions. When the determined agitation time passed, solutions were filtered using filter paper and the filtrate was analyzed for arsenic concentrations. All the adsorption experiments were performed in duplicate. The efficiency of removal was calculated according to Eq. (2):

$$R = 100\frac{C_0 - C_f}{C_0} \qquad (2)$$

Where C_0 and C_f are initial and final concentrations of arsenic in the solutions (mg/L), respectively. Desorption experiments were also performed in batch mode to evaluate recovery of the adsorbent. The ability of arsenic desorption was studied with 0.2 M HNO_3 and 0.2 M NaOH as desorbents. desorption effectiveness was calculated using Eq. (3):

$$R = 100\frac{C_t}{C_0 - C_f} \qquad (3)$$

Where C_0 is initial concentration of arsenic in solution (mg/L), C_e is the final concentration of arsenic after adsorption (mg/L), and C_t is the concentration of arsenic in desorbent solution (mg/L).

2.5. Scanning electron microscopy (SEM)

A LEO 440i scanning electron microscope (SEM) was utilized to characterize the surface morphology of prepared PANI/PVA composite.

3. Results and discussion

3.1. Effect of PVA concentration

0.1 g of different PANi/PVA composites were added to 50 mL of a solution with As(III) concentration of 10 mg/L and pH of 11, then the solution was agitated for 1 h to evaluate the effect of the PVA concentration on the adsorption capacity of the composite.

Results revealed that all the adsorbents, including PANi without PVA and PANi/PVA, possess a high capability for As(III) removal from the aqueous solution (see Fig. 1). The mechanism of arsenic removal for PANi/PVA composite seems to be surface adsorption. The presence of amine and imine, and hydroxyl functional groups