



Facile Synthesis of Magnetic Activated Carbon Composite for Arsenic Adsorption

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Abstract: Porous activated carbon (AC) and magnetic iron oxide nanoparticles (NPs) are widely used for the removal of arsenic from water body. Fabrication of composite material of iron oxide NPs on the surface of porous AC can further enhance this activity for commercial application. In this research, a magnetic AC composite for arsenic adsorption was prepared by facile hydrothermal treatment of aqueous solution containing activated carbon obtained from lapsi seed stone, iron(II) chloride, polyvinylpyrrolidone (PVP) and ethanol. Several analytical techniques such as scanning electron microscopy (SEM), energy dispersive x-ray (EDX), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) confirmed the formation of magnetite (Fe₃O₄) nanoparticles on the surface of porous AC. The prepared materials were accessed for their arsenic adsorption capacity using arsenic (III) trioxide solution and found that composite Fe₂O₃/AC can remove the arsenic from water far more effectively than activated carbon alone. For 0.5 g/ltr loading of composite sample with contact time of 5 hours, the arsenic content was significantly reduced, which shows that as-fabricated composite can be used potentially for water treatment.

Keywords: Activated carbon, Adsorption, Arsenic, Hydrothermal treatment, Magnetite.

1. Introduction

Arsenic has been creating potentially serious environmental problems for humans as well as other living organisms throughout the world. Coagulation of protein, formation of complexes with coenzymes and inhibition of adenosine triphosphate (ATP) production during respiration are some of the health hazards brought about by arsenic [7]. Most of the reported arsenic problems are found in groundwater water supply systems and are caused by both natural and artificial processes. Mineral weathering and dissolution resulting from a change in the geo-chemical environment to a reductive condition are the possible natural causes for arsenic contamination of water. While human activities like mining wastes, petroleum refining products, sewage sludge, agricultural chemicals,

ceramic manufacturing industries and coal fly ash can be considered as some of the major causes of arsenic contamination [14]. Recently, one of the major challenges in developing countries is the removal of toxic metals from water. The methods such as chemical precipitation [17, 19], solvent extraction [2], ion exchange [8], reverse osmosis and adsorption [18] have been adopted to remove the heavy metal ions from water. Among these techniques adsorption with suitable adsorbent is the mostly used method. Powdered activated carbon has been used as water treatment agent for quite a long time and with great efficiency as it has high adsorption rate and capacity for various organic pollutants and is also inexpensive. But AC alone is not very effective when it comes to removal of arsenic from water. The synthesis of magnetic carbon adsorbent by integrating magnetic particles with powdered activated carbon has gained increasing attention worldwide. Various literatures have shown that the hydrous ferric oxide (HFO)/magnetite nano particles (MNP) form of iron has a high capacity to remove both arsenite and arsenate, compared to other conventional adsorption media in practice [13]. Arsenic adsorption onto iron-tailored AC is considered to be a promising treatment technology because it is economical and easy to set up. AC can also act as a protective structure to support the otherwise fragile granular iron media [12]. There are several methods of arsenic removal techniques that are in practice today. Combination of oxidation and precipitation, nano filtration and ion exchange and adsorption are some of the popular methods for removal of arsenic from water.

The most frequently used magnetic particle is iron oxide, especially magnetite [15]. Iron (III) has a great affinity toward inorganic arsenic species and it is very selective in the sorption process [6]. The aqueous oxyanions (such as H_2AsO_4 or HAsO_4^{2-}) undergo a ligand exchange reaction with iron speciation on the carbon surface and form an inner-sphere mono-dentate or bi-dentate surface complex [9,11]. The amount of arsenic removed is closely related both to the amount of iron loaded, and to the dispersion and surface accessibility of this iron within the activated carbon [5]. Therefore, we have developed a simple strategy to decorate Fe_2O_3 NPs on the surface of porous AC carbon by facile hydrothermal treatment of iron oxide precursor solution. Hydrothermal processing can be defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and recrystallize materials that are relatively insoluble under ordinary conditions [4]. Due to its various advantages in processing of nano materials for wide range of applications, hydrothermal technique is becoming one of the major tools for advanced material processing [22]. Various composites like Ag-iron oxide/fly ash [16], Ag-ZnO/g- C_3N_4 [1] and Ag-ZnO/reduced graphene oxide [20] have been successfully synthesized using simple one pot hydrothermal approach

2. Experimental

2.1 Materials

The activated carbon prepared from lapsi seed powder [21] was used for the fabrication of composite material. Iron chloride tetra hydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) (Samchun Chemicals), ammonium hydroxide (NH_4OH , 25% NH_3 in water) (Fisher Scientific), arsenic trioxide (As_2O_3) (G.S. Chemical Testing Lab and Allied Industries), potassium hydroxide (KOH) (Fisher Scientific), sulphuric acid (H_2SO_4) (Fisher Scientific) and polyvinylpyrrolidone (PVP, MW-5800) (Alfa Aesar) were used as received for this study.

2.2 Preparation of Fe/AC Composite

A one step hydrothermal approach was followed for the fabrication of magnetic activated carbon composite. The sample was prepared by dissolving 400 mg of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 10 mg of PVP in 20 ml of distilled water and 1 ml of ammonia solution was added to this solution with constant stirring for 45 minutes using magnetic stirrer. The solution containing 50 mg AC in 10 ml of distilled water and 5 ml of ethanol was added to the former solution. The mixture was then transferred to autoclave for hydrothermal treatment at 130°C for 3 hours. After cooling at room temperature, the obtained product was filtered and washed repeatedly with distilled water and ethanol and was dried in oven at 30°C for 12 hours and at 80°C for 6 hours. The process was repeated for different weight proportions of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

2.3 Characterization

The surface morphology and composition of as-synthesized particles were studied by field-emission scanning electron microscopy (FE-SEM, S-7400, Hitachi, Japan) and energy dispersive x-ray analysis (EDX). Information about the crystallographic structure of as-synthesized composite and pristine AC was obtained using Rigaku x-ray diffractometer (XRD, Rigaku, Japan) with $\text{Cu K}\alpha$ ($\lambda = 1.540 \text{ \AA}$) radiation over Bragg angles ranging from 5 to 90° . Fourier transform infrared (FT-IR) spectra of different samples were recorded by using an ABB Bomen MB100 spectrometer (Bomen, Canada).

2.4 Preparation of Arsenic Stock Solution

500 ppm stock solution of arsenic was prepared by using arsenic trioxide (As_2O_3). 15% potassium hydroxide (KOH) solution was prepared by dissolving 1.6 g of KOH pellets in 9 ml distilled water and 0.165g of As_2O_3 was added to it and allowed to dissolve. The solution was then neutralized with 1N sulphuric acid (H_2SO_4) and 3 ml excess of H_2SO_4 was added to make the solution acidic. The solution was then diluted to 250 ml. The solution was then diluted to adjust the concentration to 2 ppm by serial dilution which was then treated with the prepared AC and its composite.

2.5 Arsenic Adsorption Test

The standard silver diethyldithiocarbamate/(SDDC, 3500-As, C) method as defined by American Public Health Association (APHA) was deployed to know the concentration of arsenic in water before and after treatment with the prepared composite sample. In this method, inorganic arsenic present in sample was reduced to arsine (AsH_3) by zinc in acid solution in an arsenic generator. The arsine was passed through a delivery tube containing filter paper impregnated with lead acetate solution and into an absorber tube containing silver diethyldithiocarbamate dissolved in chloroform. In the absorber, arsenic reacts with the silver salt, forming a soluble red complex whose photometric determination was conducted at 510 nm using UV/visible spectrophotometer (CECIL CE2041).

3. Results and Discussion

3.1 Characterization of the Composite Particles

The surface morphologies of pristine activated carbon and iron oxide nanoparticles doped activated

carbon were investigated using FE-SEM analysis. Fig.1 shows the respective morphologies of pristine AC and iron oxide/AC composite. The FE-SEM images of composite demonstrate that rod shaped magnetite nanoparticles of diameter of about 50 nm have been formed on the surface of porous activated carbon.

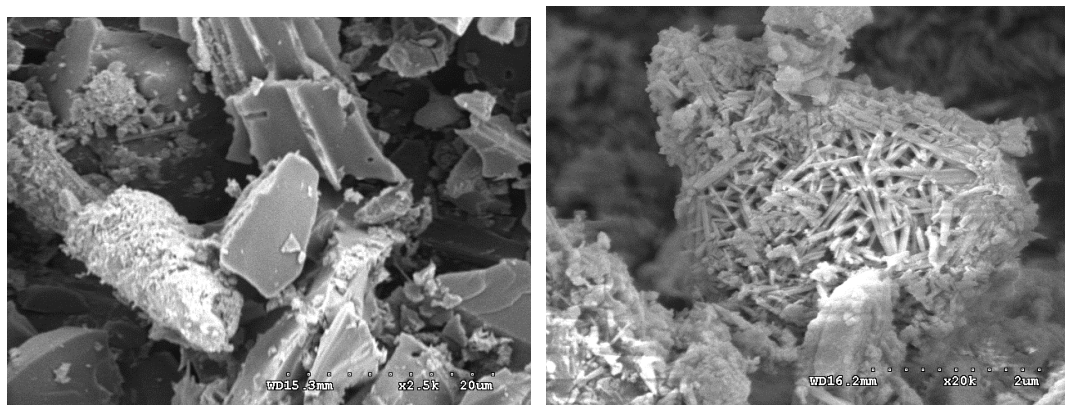


Fig. 1: FE-SEM image of pristine AC (a) and iron oxide/AC composite (b)

SEM-EDX analysis was performed to examine the composition of the fabricated composite material which confirmed that the nano particles deposited were of iron oxide as shown in Fig.2. The formation of composite was further confirmed by FT-IR spectroscopy. Fig. 3 shows the FTIR spectra of pristine AC and iron oxide/AC composite. The composite sample showed a wide band at 3300 cm^{-1} which can be assigned to stretching mode of adsorbed water molecules [16, 10]. The corresponding band is not visible in pristine AC sample which can be accounted for the presence of more hygroscopic magnetite particles. Another adsorption band can be seen in the IR spectra of composite material at 570 cm^{-1} which can be assigned as the analytical band of magnetite [3, 16]. Hence from the IR spectroscopy it can be concluded that the nano particles of magnetite have grown on the surface of AC after hydrothermal treatment.

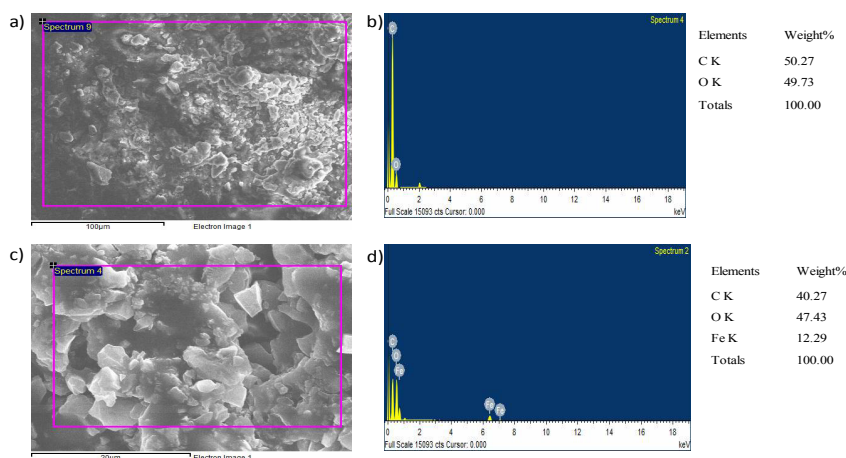


Fig. 2: SEM-EDX of pristine AC (a, b) and $\text{Fe}_3\text{O}_4/\text{AC}$ composite (c, d)

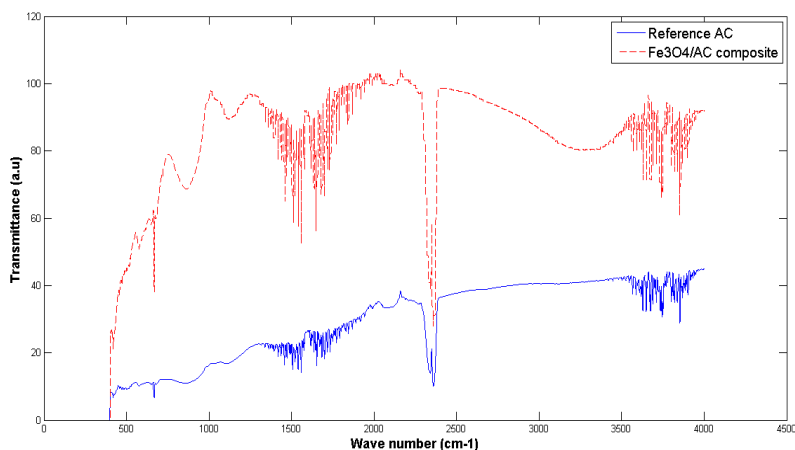


Fig. 3: FT-IR spectra of pristine AC and $\text{Fe}_3\text{O}_4/\text{AC}$ composite

Furthermore, XRD analysis was performed to determine the crystal structure of the synthesized composite. Fig. 4 shows the XRD pattern of pristine AC and the prepared iron oxide/AC composites with corresponding 2θ values. The XRD graph for the composite sample shows strong and sharp peaks indicating that the synthesized product has well developed crystallinity when compared to XRD graph of pristine AC sample. The XRD pattern for pristine AC sample shows broad peak at diffraction angle (2θ) 25° . This peak can be indexed to amorphous carbon [20]. Similarly, the main peaks at diffraction angle of 35.80° , 43.50° , 53.70° , 57.30° and 74.20° are of Fe_3O_4 [16]. Hence XRD analysis shows that the hydrothermal treatment resulted in the growth of magnetite nano particles on AC also increasing the crystallinity of the composite.

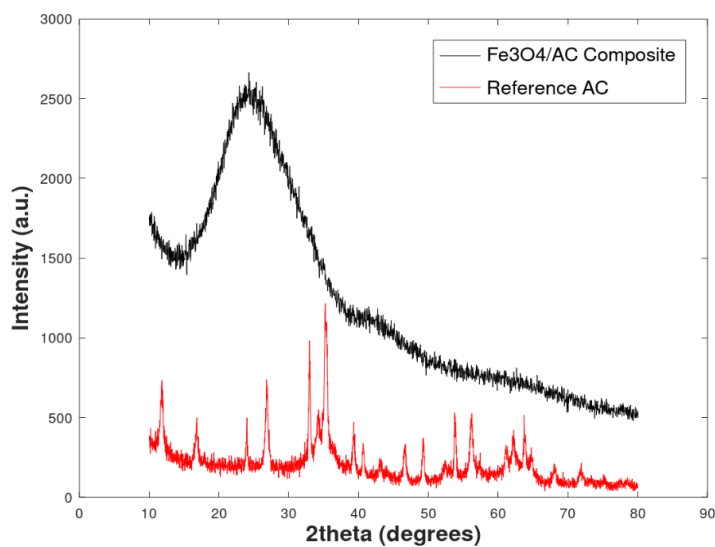


Fig. 4: XRD patterns of pristine AC and $\text{Fe}_3\text{O}_4/\text{AC}$ composite

3.2 Arsenic Adsorption

The prepared 500 ppm arsenic stock solution was diluted to 2 ppm by serial dilution. The prepared 2 ppm solution was then distributed in two glass bottles with 100 ml each. The pH of the solution prepared was measured to be 2.3. 50 mg of pure AC was added into one bottle and 50 mg of $\text{Fe}_3\text{O}_4/\text{AC}$ composite was added to another bottle and stirred for 5 hours. Each solution was then filtered and the filtrate was collected in clean glass bottles and tested for arsenic content. The result obtained after SDDC test is shown in Fig. 5. The result showed that after 5 hours treatment with 50 mg of synthesized composite in 100 ml of arsenic the arsenic concentration was reduced to 690ppb from 2000 ppb while the concentration in the solution treated with AC was dropped down to just 1420 ppb. The result indicates that $\text{Fe}_3\text{O}_4/\text{AC}$ composite is far more superior in removal of arsenic from water than the conventional AC alone because its high isoelectric point (IEP=8.1) and selectivity for arsenic [13].

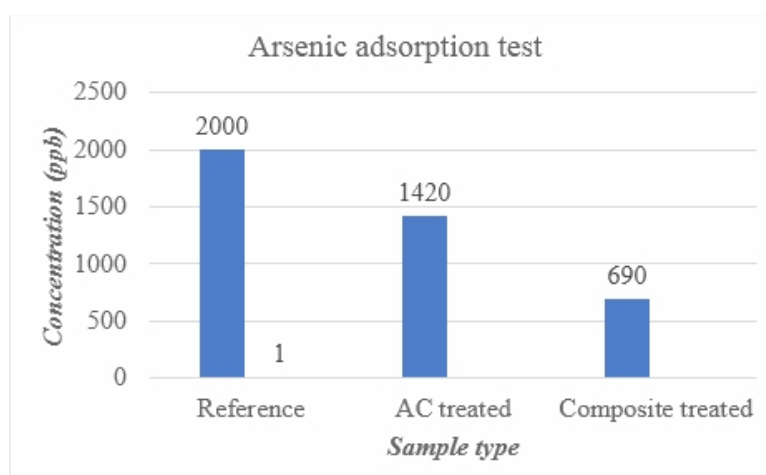


Fig. 5: Arsenic adsorption test of pristine AC and $\text{Fe}_3\text{O}_4/\text{AC}$ composite

4. Conclusion

In summary, a magnetically separable and stable $\text{Fe}_3\text{O}_4/\text{AC}$ composite was synthesized using one pot facile hydrothermal treatment. Furthermore, it is reported that the temperature of the hydrothermal treatment was significant in determining the grown of nano iron oxide particles. Activated carbon (AC) obtained from agricultural waste materials are potential for cost effective adsorption media. Macro and meso pores in activated carbon can serve a suitable adsorption site and also provided large surface area for the deposition of magnetite nano particles. The $\text{Fe}_3\text{O}_4/\text{AC}$ composite displayed excellent efficiency in removal of arsenic from water. The presented protocol for the synthesis of the composite product is simple, fast, environmentally friendly, cheap and yet very efficient and effective.

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