ISSN: 2586-7652 (Print) Vol. 03, No. 01, March 2020
ISSN: 2635-7607 (Online)
International Journal of Advanced Engineering
Source: http://ictaes.org
Manuscript received: December 5, 2019 ; Revised: December 31, 2019; Accepted: January 5, 2020

Synthesis and Characterization of Magnetic Commercial Activated Carbon Composite for the Removal of Arsenic

Sahira Joshi[1], Anshu Kumari[2]

[1,2] *Department of Applied Sciences, Pulchowk Campus, IOE, Tribhuvan University, Nepal*

sjoshi61@hotmail.com[2]

Abstract

Recently, magnetic activated carbon (AC) composite, made by dispersing iron oxide on AC, is gaining attention for arsenic removal from aqueous solution. A magnetic iron oxide/AC composite for arsenic adsorption was prepared by facile one-pot hydrothermal treatment of aqueous solution containing commercial activated carbon, iron (III) chloride hexahydrate (of FeCl3.6H2O), polyvinyl pyrrolidone (PVP) and ethanol. To characterize AC and composite, analytical techniques such as scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) were used. The result confirmed the formation of magnetite (Fe3O4) nanoparticles on the surface and pores of AC. Percentage removal of arsenic by the AC and the composite was studied using As2O3 solution and found that it can remove arsenic from aqueous solution far more effectively than the plain AC. It shows that as synthesized composite have a great potential to be used in treatment of arsenic contaminated water.

Keywords: *Activated carbon, Arsenic, Magnetic composite, Hydrothermal treatment.*

1. Introduction

Arsenic (As) contamination of groundwater has been recognized as human health problem affecting millions of people in many parts of the world. The largest population at risk among the 21 countries with known groundwater arsenic (As) contamination is in Bangladesh, followed by West Bengal in India and Nepal (Pal et al., 2009).

About 49 % of Nepal's total population (2.3 million) is living in Terai (Southern plain) region and 90% of them are relying on groundwater from tube wells as sources of water for drinking purposes (Guillot et al., 2015). About 3.5 million people of this region are estimated to have been exposed to As levels between 10 and 50 µg/L and approximately 0.5 million people at risk of consuming water with As concentration above 50 µg/L. (Shrestha R., 2012). The main source of As contamination in Terai region is believed to ben geogenic and its elevated

Corresponding Author : Sahira Joshi
Author's affiliation : Department of Applied Sciences, Pulchowk Campus, IOE, Tribhuvan University, Nepal
Email: sjoshi61@hotmail.com
Copyright © ICT-AES

concentrations is caused by reductive dissolution of ferro-oxyhydroxide (Mueller B. 2017). The permissible value of As in drinking water is 10 μg/l and permissible values of Nepal interim standard is of 50 μg/l (WHO, 2008).

Arsenic exists in organic as well as inorganic forms. Inorganic As is more toxic than organic and exists as arsenite (As (III)) and arsenate (As (V)). As (III) is estimated to be 10 times more toxic than As(V) and 70 times more toxic than the methylated derivatives of As. In ground water, As exists as arsenate (As (V)) or arsenite (As (III)) (Thakur et al. 2011). Continuous exposure to As can cause damage to the central nervous system, kidney, skin, liver and lungs in humans. It can also increase glutathione peroxidase and mitochondrial superoxide dismutase (MSOD) activities in liver and lungs. Arsenic aids the coagulation of protein, aid the formation of complexes with coenzymes and stops the production of adenosine triphosphate (ATP) during respiration (Okereafor et al., 2020). In addition, chronic As toxicity can cause cardiovascular diseases, hypertension and affects vascular system. Due to the health risks are associated with As consumption in drinking water, it is necessary to remove As from groundwater used for drinking purposes. Various techniques such as ion exchange, precipitation- coagulation, oxidation, reverse osmosis, nanofiltration, adsorption etc. have been used to remove As from water. However, adsorption is inexpensive, simple, and effective even at low As concentration in water. A wide range of adsorbent materials have been developed such as active carbon, zeolite, silica gel, alumina, metal oxides etc for As adsorption. Activated carbon is among the most widely used adsorbent in water purification all over the world because it has exceptionally high porosity, surface area and high degree of surface reactivity. These properties can be tailored, making them versatile materials for a range of separation applications such as removal of contaminants from water and gas streams, and as catalyst support (Banasa et al., 1988).The surface area of commercial grade carbons typically vary in the range between 500 and 1500 m2/g or even as high as 3000 m2/g (Saleem et al., 2019). Commercial activated carbons are usually derived from natural materials such as wood, coconut shell, lignite or coal. AC is of two types: Granular activated carbon (GAC) and powdered activated carbon (PAC). Both granular and powdered ACs are used in liquid-phase applications. The granular form is used in continuous processes because it is capable of regeneration, whereas the powdered form is used generally in batch processes (Hao et al., 2018).

AC has great capacity of adsorbing various organic compounds and can be easily modified by chemical treatment to increase its adsorption properties. However, it is difficult to remove and recover the suspended AC powders from water which results in secondary pollution. Techniques such as centrifugation and filtration are usually adopted to separate the used AC powders from liquid solutions (Juang et al., 2018) but, these techniques are expensive. Thus, there is a great environmental interest in developing composite adsorbent incorporating AC to remove organic pollutants. Numerous approaches have been investigated for the development of magnetic carbon adsorbent by integrating magnetic particles with AC. (Jiuhui Q.U., 2008). Hydrous ferric oxide (HFO) is most effective for removing both As (III) and As(V) from aqueous solution because of its high specific surface area and iso-electric point (An et al., 2005). In the last few years, HFO/AC magnetic composites have been synthesized to enhance adsorption capacity for As removal. In these composite adsorbents, hydrous ferric oxide is the active components for As removal whereas AC provides a high surface area and acts as a solid support. Such combination of iron oxide nanoparticles and AC was demonstrated to be a feasible technique to take advantage of the properties of two materials for As adsorption. The objective of this study was to synthesize and characterize the magnetic commercial AC composite for the removal of arsenic (III) from aqueous solution.

2. EXPERIMENTAL

Materials and Method

All the chemical reagents used in this experiment were analytical grade and were used as received without any

further purification. Commercial activated carbon (Fischer Scientific) was used for preparation of magnetic composite. Iron (II) chloride tetrahydrated (FeCl2.4H2O) (Samchun Chemicals), Liquor Ammonia (NH3) (Fischer Scientific) and Polyvinylpyrrolidone (PVP, MW-5800) (Alfa Aesar) were used. All solutions were prepared with distilled water.

Synthesis of magnetic AC composite

The Fe3O4/AC magnetic composite was prepared by one step hydrothermal method. In typical experiment, 400 mg FeCl2.4H2O along with 10 mg of Polyvinylpyrrolidone (PVP) were dissolved in 20 ml of distilled water and 1 ml of ammonia solution was added to this solution. The solution was stirred constantly 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 transferred into the 75 ml Teflon-lined stainless steel autoclave for hydrothermal treatment at 130 oC for 6 hrs. After hydrothermal reaction, the autoclave was cooled down to room temperature and the product was washed with distilled water and ethanol several times. Finally, the prepared composite sample was dried in air oven at 30°C for 12 hrs and at 80°C for 6 hrs afterwards.

Characterization of AC and its magnetic composite

Iodine number of AC was determined according to ASTM D4607-94 method (ASTM Standards, 2006). Methylene blue number of AC was determined by single point adsorption isotherm studies according to Standard Method (Raposo et al., 2009). Surface area of AC was estimated by iodine and methylene blue numbers using multiple regressions (Cleiton and Guerreiro, 2011). The energy dispersive x-ray analysis (EDX) and surface morphology of AC and as-synthesized composite were studied by filed-emission scanning electron microscopy (FE-SEM, S-7400, Hitachi, Japan).

Adsorption experiments

For the adsorption of arsenic, 25 mL of As solution was separately taken in 100 mL plastic conical flask and 0.025 g of AC and the composite were separately added. The suspensions were shaken on an orbital shaker (180 rpm) for 3 hrs at room temperature. After equilibrium, the suspension was filtered and residual As concentrations in the filtrates were analyzed by the molybednum blue method using UV/Vis spectrophotometer (CECIL-CE-100) at absorbance 840 nm. The percentage removal of As adsorbed by AC and magnetic composite was calculated using the following equation:

$$\text{Removal } (\%) = \frac{(C_o - C_e) \times 100}{C_o} \quad (1)$$

Where, Co = initial concentration of fluoride ions (mg/L); Ce = equilibrium concentration of fluoride ions (mg/L).

3. RESULTS AND DISCUSSION

Iodine Number (IN), Methylene blue Number (MBN) and Surface area of the AC

IN and MBN are the most important parameter used for the determination of adsorption capacity of the carbon. Iodine number is the amount of iodine adsorbed (in milligrams) by 1g of carbon (Cleiton and Guerreiro, 2011). In

the same way, methylene blue number is defined as the amount of methylene blue dye adsorbed (in milligrams) by 1g of carbon (Raposo et al, 2009). IN, MBN and surface area of commercial AC are shown in Table: 1.

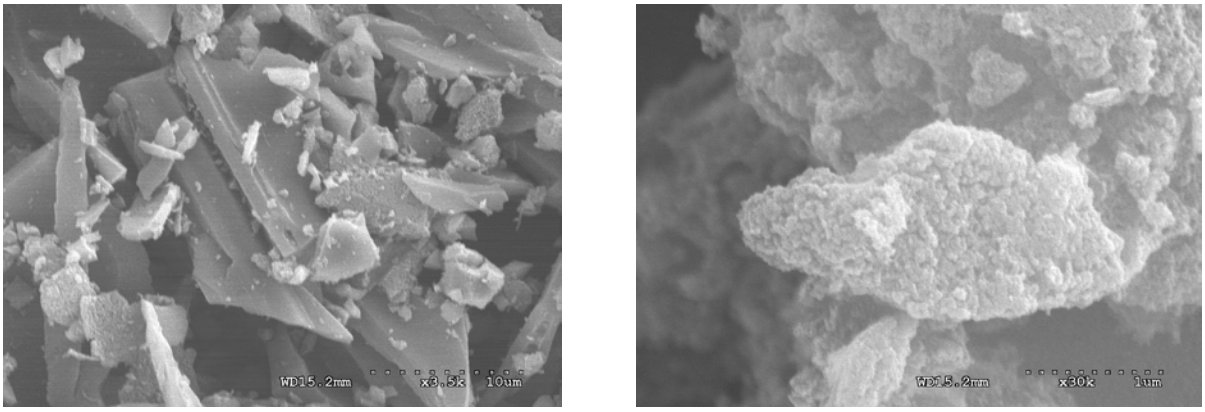
Table 1. Characteristic of Big Data

Iodine No. (mg/g)	955
Methylene blue No. (mg/g)	420
Surface area (m^2/g)	1049

Iodine number (IN) represents the microporous structure (< 2 nm) of the AC relative to the amount of iodine adsorbed from solution. It indicates that, carbon preferentially adsorbs small molecules. Methylene blue number (MBN) measures the mesoporous (2-50 nm) structure and indicates the adsorption capacity of the carbon for medium size molecules. IN and MBN and surface area of AC were found to be higher suggesting that, the commercial AC posses higher microporosity, mesoporosity and surface area.

Scanning electron microscopy (SEM) image

Surface morphology of carbons was studied by scanning electron microscopy (SEM). SEM image also exhibits the nature and size of the pore, depending on the magnification of the image taken. Scanning electron microscopy (SEM) images of AC with its composite are shown in Figure: 1.



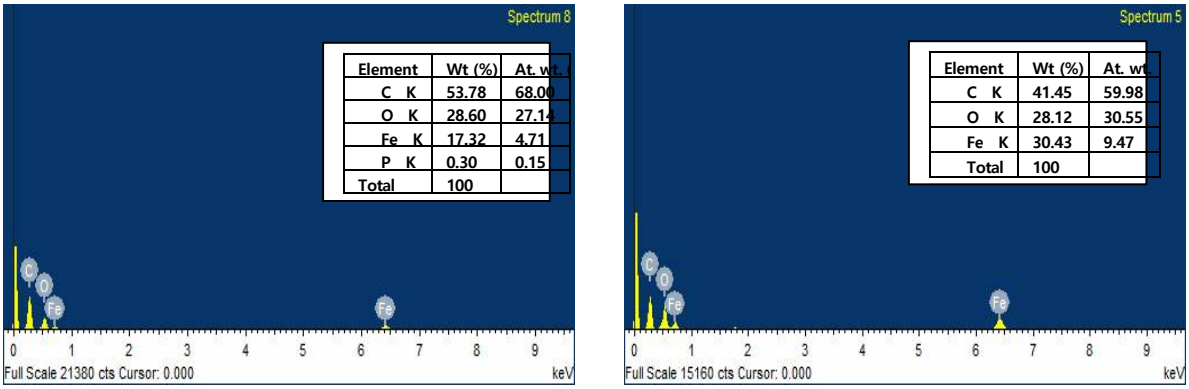
(a) Activated carbon **(b) Fe3O4/AC composite**

Figure 1. Scanning electron microscopy (SEM) images of AC with its composite

As shown in the SEM images (Fig. a and b), the AC shows smooth and porous surface. The composite contains the aggregation of the Fe3O4 particles nanoparticles. These particles are uniformly deposited on AC surfaces or pores in the composite and stuck to each other. The incorporation of Fe3O4 in the carbon matrix partially blocked the porosity of the AC surface. It is suggested that impregnation of AC by the iron oxide has been done effectively.

Energy-dispersive X-ray (EDX) analysis

EDX spectrum and the summary for the elemental composition using energy-dispersive X-ray analysis (EDX) for AC and its composite respectively are shown in the Figure: 2.



(a) Activated carbon **(b) Fe3O4/AC composite**

Figure 2. EDX spectra and the summary for the elemental composition for AC and its composite

The composite spectrum revealed that the carbon content was of 41.45 %, followed by oxygen (28.12 %) iron (30.43 %). It has shown that, the iron content is more in the magnetic composite compared to plain AC. It means iron content of the AC has increased by compositing with Fe3O4. Correspondingly, the oxygen content also increased simultaneously with the iron. The increased amount of iron and oxygen in the composite is due to dispersion of iron oxide nanoparticles on the surface of AC during hydrothermal treatment. Meanwhile, presence of small amount of iron and phosphorus in the AC might due to the contaminants on EDX machine sample's plate. EDX of the composite suggested that, Fe3O4 particles were dispersed uniformly on the active carbon surface. Similar results have been observed for the used tea waste derived AC after Fe3O4 loading (Mahmood et al., 2018).

Adsorption studies

Comparison on percentage of removal of AC and magnetic composite were carried out. The percentage of arsenic removal by AC and magnetic composite is presented in Figure: 3.

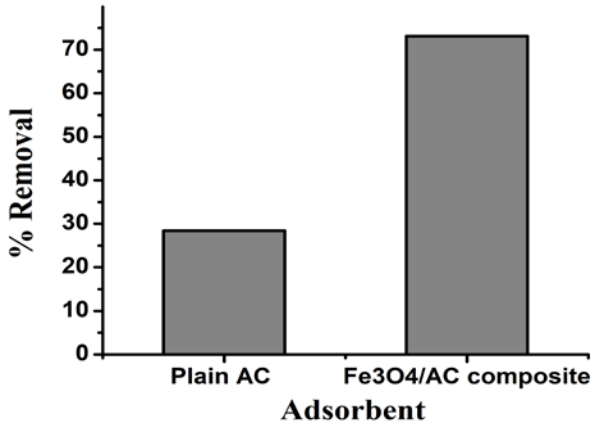


Figure 3. Percentage of arsenic removal by Fe2O3/AC composite and AC

The percentage of As removal by AC is found to be approx.33 %, but the adsorption capacity increased to 74 % by using the magnetic composite. It clearly indicates the synergistic effect of AC for adsorption of As. Thus, the composite of AC is much better magnetic composite than individual components for As removal. The adsorption

of arsenite on magnetic composite may be due to a ligand exchange mechanism. Ligands may be hydroxyl ions or neutral water molecules present in the Fe-coordinated sphere. The adsorption of As (III) takes place by ligand exchange reaction of oxyanions of As such as H2AsO4 or HAsO42- with OH2 and OH−in the coordination spheres of surface of magnetic composite (Baskan and Pala, 2011).

4. CONCLUSION

In summary, we have synthesized Fe3O4/AC magnetic composite by a facile one pot hydrothermal method. IN, MBN and surface area of AC suggested that, the commercial AC has large surface area with well developed porosity. SEM image indicated that iron oxide particles are uniformly dispersed on the surface of composite. The presence of iron oxide in the magnetic composite surface is also confirmed by EDX analysis. The composite showed high adsorption capacities for arsenic as compared to the plain AC. The results of this study show that, Fe3O4/AC magnetic composite can be potentially applied for the treatment of water contaminated by arsenic.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from University Grants Commission (UGC) CRG 73/74-Engg-02, Nepal for this work.

References

[1] An, B., Steinwinder, T.R. and Zhao, D. 2005. Selective removal of arsenate from drinking water using a polymeric ligand exchanger, Water Research, 39, 4993–5004.

[2] Annual Book of ASTM Standards. 2006. Standard test method for determination of iodine number of activated carbon, ASTM D4607-94, Philadelphia PA, United State of America.

[3] Banasa, R.C., Donne, J.B. and Stoeckli H.F. 1988. Active carbon. Marcel Dekker, New York, 27.

[4] Baskan, M.B. and Pala, P. 2011. Removal of arsenic from drinking water using modified natural zeolite, Desalination, 281, 17, 396-403.

[5] Cleiton, N.A. and Guerreiro, M.C. 2011. Estimation of surface area and pore volume of activated carbons by methylene blue and iodine numbers, Quimica Nova, 34(3), 472-476.

[6] Guillot, S., Garçon, M., Weinman, B., Gajurel, A., Tisserand, D., France-Lanord, C. et al. 2015. Origin of arsenic in late pleistocene to holocene sediments in the nawalparasi district (Terai, Nepal), Environmental Earth Sciences, 74, 2571–2593.

[7] Hao, L., Liu, M., Wang, N. and Li, G.A. 2018. Critical review on arsenic removal from water using iron-based adsorbent, RSC Advances, 8, 39545–39560.

[8] Jiuhui, Q.U. 2008. Research progress of novel adsorption processes in water purification: A review, Journal of Environmental Sciences, 20, 1–13.

[9] Juang, R.S., Yei, Y.C., Liao, C.S., din K.S., Lu H.C., Wang, S.F. and Sun A.C. 2018. Synthesis of magnetic Fe3O4/activated carbon nanocomposites with high surface area as recoverable adsorbents, Journal of the Taiwan Institute of Chemical Engineers, 90, 51–60.

[10] Mahmood, T., Aslam, M., Naeem, A. and Siddique, A. 2018. Adsorption of As(III) from aqueous solution onto iron impregnated used tea activated carbon: Equilibrium, kinetic and thermodynamic study, Journal of the Chilean Chemical Society, 63(1), 3855-3866.

[11] Mueller B. 2017. Arsenic in groundwater in the southern lowlands of Nepal and its mitigation options: a review, environmental Reviews, 25(3), 296-305.

[12] Okereafor U., Makhatha M., Mekuto L., Uche-Okereafor N., Sebola T. and Mavumengwana V. 2020. Toxic metal implications on agricultural soils, plants, animals, aquatic life and human health, International Journal of Environmental Research and Public Health, 17, 2204, 2-24.

[13] Pal, P., Sen, M., Manna, A., Pal, J., Pal, P., Roy, S. and Roy, P. 2009. Contamination of groundwater by arsenic: a review of occurrence, causes, impacts, remedies and membrane-based purification, Journal of Integrative Environmental Sciences, 6(4)295-316.

[14] Raposo, F., Rubia, D.L.M.A. and Borja, R. 2009. Methylene blue number as useful indicator to evaluate the adsorptive capacity of granular activated carbon in batch mode: Influence of adsorbate/adsorbent mass ratio and particle size, Journal of Hazardous Materials, 165(1-3), 291–299.

[15] Saleem, J., Shahid, U.B., Hijab, M., Mackey, H. and McKay, G. 2019. Production and applications of activated carbons as adsorbents from olive stones, Biomass Conversion and Biorefinery, 9,775–802.

[16] Shrestha, R. 2012. Arsenic contamination of groundwater in Nepal: Good public health intention gone bad, Student Pulse, 4(09), 1-14.

[17] Thakur, J.K., Thakur, R.K., Ramanathan, A.L., Kumar M. and Singh, S.K. 2011. Arsenic contamination of groundwater in Nepal—An Overview, Water 3, 1-20.

[18] WHO 2008, Guidelines for drinking-water quality, World Health Organization, ISBN 9789241547611, Geneva, 3(1).