Preparation of Highly Cross-linked Magnetic Polymer Composite Particles and Application in the Separation of Arsenic from Water

M. K. Sharafat*, H. Ahmad, M. A. Alam and M. M. Rahman

Depratment of Chemistry, University of Rajshahi, Rajshahi 6205, Bangladesh.

*Corresponding author: *mksharafat10@gmail.com*

Abstract

Iron oxide magnetic particles have become a promising research field in separation technology because of their easy separation by external magnetic field and can be applied for the removal of toxic metals from waste water. Highly cross-linked Fe_3O_4/P(S-DVB) particles were prepared in this research by suspension polymerization of styrene (S) and divinylbenzene (DVB) in presence of nanosized Fe_3O_4 particles. At first Fe_3O_4 nanoparticles were prepared by co-precipitation of Fe^{2+} and Fe^{3+} from their alkaline aqueous solution. To stabilize the magnetic particles, the surface of the particles was modified with oleic acid. The morphology and surface structure were characterized by Fourier Transform IR(FTIR), Transmission Electron Microscope (TEM), Scanning Electron Microscope(SEM), and light microscope.The adsorption behavior of As(III) on composite polymer particles was evaluated and a comparative study with reference copolymer particles revealed that composite polymer particles possessed better adsorption capacity.

Keywords: Styrene;Divinylbenzene; Suspension polymerization;Highly cross-linked polymer.

INTRODUCTION

The contamination of daily used water by toxic metal ions is a worldwide environmental problem. Since the degradation of toxic metal ions does not occur naturally, they have a tendency to accumulate in organisms and enter the food chains [1]. Among the different toxic metals, arsenic (As) is a common and toxic pollutants[2,3] which is mobilized by natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities. However, mining activities, combustion of fossil fuels, use of As pesticides, herbicides, and crop desiccants and use of As additives to livestock feed create additional impact. As shows different oxidation states −3, 0, +3 and +5 [4]. Inorganic forms of As present in water is more toxic than organic form [5]. Arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), referred to as As(III) and As(V) are two common form of As in natural water. Pentavalent species predominate and are stable in oxygen rich aerobic environments whereas trivalent species in moderately reducing anaerobic environments such as groundwater [6]. Drinking As contaminated water over a long period causes skin, lung, bladder, and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis) neurological disorders, muscular weakness, loss of appetite, and nausea [7,8]. Since exposure to toxic metals, even at trace level, is believed to be a risk for human beings [9-11], thus, removing of undesirable metals from water system has become a challenging task. Recently adsorption technique is used in large scale which offers flexibility in design and operation, and in many cases it will generate high-quality treated effluent [12]. Among different types of adsorbents nano-sized metal oxides (NMOs), including ferric oxides, manganese oxides, aluminum oxides,

68

Rajshahi Univ. j. sci. & eng.
Vol. 44: 67-74, 2016

titanium oxides, magnesium oxides and cerium oxides, are highly used for removing toxic metals from aqueous systems [13-15] where iron oxide particles show recycling advantages because of its magnetic nature [16]. In this research iron oxide (Fe_3O_4) nanoparticles are coated with divinylbenzene (DVB) cross-linked polystyrene (PS), the magnetic NMOs-based composite adsorbents also allow easy isolation by an external magnetic field from aqueous solutions for recycling or regeneration [17].

EXPERIMENTAL

A.   Chemicals and instruments
Styrene of monomer grade, purchased from Fluka, Chemika, Switzerland, was distilled under reduced pressure. Crosslinking agent DVB from Sigma-Aldrich, Chemie (80% grade) was purified with aqueous 10% NaOH solution and subsequently dehydratd by stirring with anhydrous $CaCl_2$. Benzoyl peroxide (BPO) from BDH Chemicals Ltd. UK was recrystallized from methanol and preserved in the refrigerator before use.Polyvinyl alcohol (PVA) from Thomas Baker (Chemicals) Limited, India, of molecular weight 1.4×10^4 $gmol^{-1}$ was used as polymeric stabilizer. As_2O_3 from May & Baker, UK, ferric chloride ($FeCl_3$), ferrous sulphateheptahydrate ($FeSO_4.7H_2O$), NH_4OH, Oleic acid and other chemicals were of analytical grade. Deionized water was distilled using a glass (Pyrex) distillation apparatus.

TEM was performed with a JSEM-1230 microscope (JEOL, Tokyo, Japan) operating at a voltage of 100 kV, and optical image was obtained by a fluorescence microscope (IX71 Olympus, Japan) to see the particle morphology and size distribution. IR spectrophotometer, FTIR (Perkin Elmer, FTIR-100, UK), Double beam UV-visible spectrophotometer (Shimadzu, UV-1650pc), and microprocessor pH meter from Mettler Toledo (MP 220, Switzerland) Instruments were used in this study. Homogenizer (T 18 Digital Ultra Turrax, IKA, Germany) is used to homogenized the particles.

B.   Preparation of Fe_3O_4 nanoparticles
Nano-sized Fe_3O_4 particles were produced by co-precipitation of Fe^{2+} and Fe^{3+} from their aqueous solutions (molar ratio1:2) containing 25% NH_4OH[18]. The reaction was carried out in a three necked round flask under a nitrogen atmosphere for 2h. Oleic acid was used as a stabilizer. The produced Fe_3O_4 particles were repeatedly washed by magnetic separation and subsequent redispersion in deionized distilled water to remove the residual electrolyte and excess oleic acid.

C.   Preparation of reference P(S-DVB) particles
Styrene (5.3 g), DVB (0.4 g), PVA (1.25 g), toluene (1.50 g) were taken in 50 mL distilled water, homogenized at 10,000 rpm sonication for 3 min in ice-water bath to form monomer droplets. The homogenized mixture was polymerized in presence of BPO (2.6% w/w) based on monomer) at 75°C.

D.   Preparation of Fe_3O_4/P(S-DVB) composite particle
Styrene (5.3 g), DVB (0.4 g), toluene (1.5 g) and 0.88 g (65% solid in *n*-octane) magnetic fluid were mixed to form the oil phase. PVA (1.25 g) and NaCl (1.5 g) were dissolved into 50 mL deionized water to form the water phase. Then the two phases were mixed together with ultrasonic treatment at 5,000 rpm sonication for 3 min prior to the polymerization in presence of BPO at 75°C.

E.Porosity measurement

Bulk density (loose) a property of particulate materials is the mass of many particles of the material divided by the volume they occupy. The occupied volume includes the space between particles as well as the space inside the pores of individual particles. This was measured at 26°C using a 5 mL graduated cylinder. Oven dried P(S-DVB) polymer and Fe_3O_4/P(S-DVB) composite particles were poured separately into the cylinder for each measurement. The weight and volume of the powder of copolymer and composite particles were recorded and the bulk density of them was obtained using the equation (1).

$$\text{Bulk Density of Particles} = \frac{\text{Weight of dry particles (g)}}{\text{Volume of dry particles (cc)}} \qquad (1)$$

The particle density or true density is the density of the particles that make up the powder. This density was measured using a densimetric bottle at 26°C. The volume of the densimetric bottle was first calculated using the appropriate density value of water. Then, 0.2 to 0.3 g of oven dried P(S-DVB) polymer and Fe_3O_4/P(S-DVB) composite particles were taken separately in the bottle for each measurement. Distilled water was added and the contents in the bottle were gently boiled for 10 min to remove any entrapped air. The increase in weight over the polymer powder and composite particles powder was used to obtain the volume of water in the bottle. The volume of the powder of polymer and composite particles in the bottle was obtained by subtracting the volume for each from the total volume of densimertic bottle. Equation (2) was used to calculate the particle density of P(S-DVB) polymer and Fe_3O_4/P(S-DVB) composite particles respectively.

$$\text{Particle density of Particles} = \left(\frac{\text{Weight of dry particles (g)}}{\text{Volume of water displaced particles(cc)}}\right) \qquad (2)$$

Both bulk density and particle density were measured in once and the values are reported in **Table 1**

The amount of pore space or porosity for P(S-DVB) polymer and Fe_3O_4/P(S-DVB) composite particles was measured by density measurement using equation (3).

$$\text{Porosity of particles} = 1 - \left(\frac{\text{Bulk density of particles}}{\text{Particle density of particles}}\right) \times 100 \qquad (3)$$

TABLE1: EXPERIMENTAL VALUES OF PHYSICAL PARAMETERS OF P(S-DVB) POLYMER AND Fe_3O_4/P(S-DVB) COMPOSITE PARTICLES

S. No.	Parameter	Value for P(S-DVB) polymer Particle	Value for Fe_3O_4/P(S-DVB) composite particle
1	Bulk density (loose), g/cc	0.3945	0.4728
2	Particle density or true density, g/cc	3.3143	1.6607
3	Porosity, %	88.10	71.53

70

Rajshahi Univ. j. sci. & eng.
Vol. 44: 67-74, 2016

F.Adsorption behavior of arsenic

The absorption behavior of arsenic on both polymer and composite particles were measured using UV-Vis spectrophotometer. For each measurement, a mixture of 30 mL of 40 ppm As(III) solution was prepared from 10.94 g purified particle solution (0.1g solid) and 1000 ppm arsenic stock solution. The mixture of arsenic-particle emulsion was allowed to stand for specific time at 25°C and pH was maintained at 9 with occasional stirring. Magnetic composite polymer particles were then separated applying external magnetic field followed by centrifugation at 12000 rpm whereas reference P(S-DVB) particles were separated only by centrifugation at 12000 rpm. The supernatant was transferred to arsenic generator and 5 mL conc. HCl, 2 mL KI solution and 0.5 mL $SnCl_2$ were added in it. The content of the flask was swirled and then allowed to stand for about 15 minutes to ensure complete reduction of arsenic to +3 state. The absorber tube was charged with 4.00 mL of the silver diethyldithiocarbamate. 5.0 g pure granulated zinc was added to the solution in the flask and then the hydrogen sulphide scrubber was immediately inserted. The evolution of arsine (AsH_3) was 99% completed within 40 min and additionally the mixture was heated for another 5 min in water-bath at 75°C to complete the reaction. The absorber solution was transferred and its absorbance was measured at the wavelength of 535 nm by a UV-visible spectrometer. The amount of arsenic adsorbed was calculated by subtracting the concentration in the medium from that of initial concentration. Calibration constant was used for this purpose. The separation of As by magnetic particles is schematically shown in Figure 1.
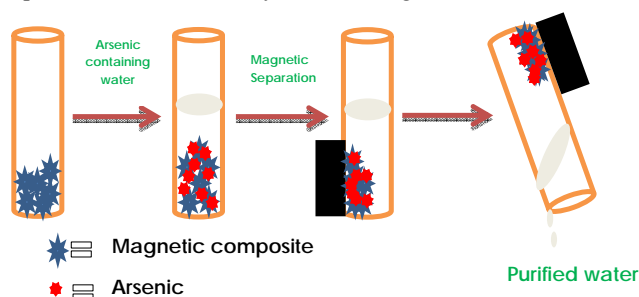

Fig.1. Separation of arsenic using an external magnate.

RESULTS AND DISCUSSION

The particle size and particle distribution of Fe_3O_4 nanoparticles are illustrated in illustrated in TEM images (Figure 2).Before the observation magnetic particles were separated by means of an external magnetic field from the dispersion and washed repeatedly using the same technique using water. The advantage of this magnetic separation is to separate only magnetic particles. The average size of Fe_3O_4 is about 6-8 nm.
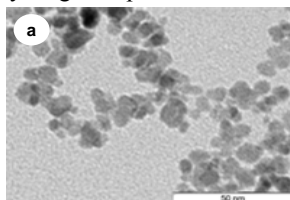

Fig. 2.TEM image of Fe_3O_4 nanoparticles. Magnification scale represents 50 nm.

The SEM photograph andoptical microscopicimagesof Fe_3O_4/P(S-DVB) composite polymer particles prepared at 5,000 rpm sonication speed are illustrated in Figure 3. The average diameter is 14.22 µm for Fe_3O_4/P(S-DVB) composite particles. The particle size distribution is pretty broad as indicated from high coefficient of variation (45%). The nonhomogeneous surface structure is attributed to presence of Fe_3O_4nanoparticles as well as high crosslinking density. It is to be mentioned that many authors observed such surface structure for crosslinked polymer particles [19, 20]. The particle size of the composite particles in the dispersion state characterized by light microcopy is (15.23 µm)to the dry state taken by SEM. This resultalso suggests the formation of highly cross-linked hydrophobic composite particles.
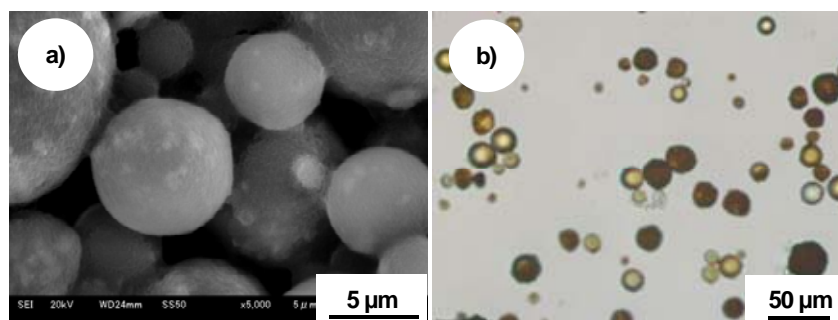

Fig. 3. SEM (a) and optical microscopic (b)images of P(S-DVB)/Fe_3O_4 composite particles prepared at sonication 5000 rpm.

FTIR is a useful tool to characterize the structural composition of the colloidal particles [21]. A comparative plot of FTIR spectra of P(S-DVB), Fe_3O_4 and Fe_3O_4/P(S-DVB) composite Particles is shown in Figure 4. Fe―O bonds appear at 583 and 382 cm^{-1} in Fe_3O_4 particles weakened in Fe_3O_4/P(S-DVB) composite particles. The new peaks that appear in the region 2848–2916 cm^{-1} represent aliphatic ―CH stretching vibrations of aliphatic chain.In the spectrum of Fe_3O_4/P(S-DVB) composite particles C-H and C=C stretching vibrations of the aromatic ring appear at around 3000 cm^{-1}. These results suggest that most of the Fe_3O_4 particles have successfully been encapsulated.
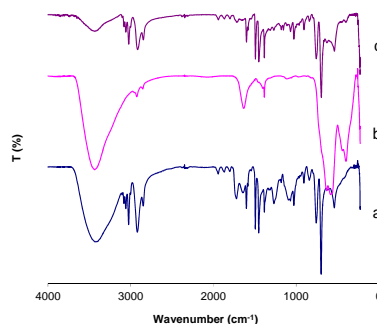

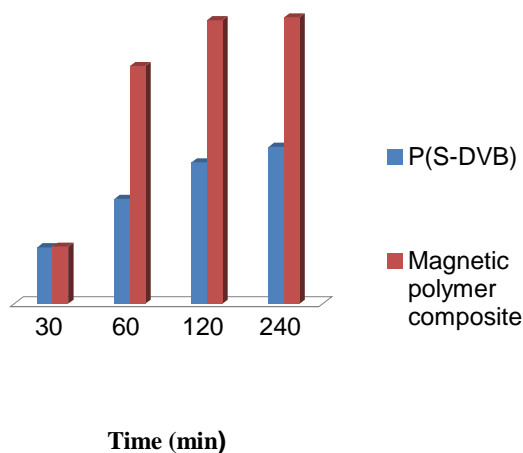Fig. 4. FTIR spectra of a) P(S-DVB) particles, b) Fe_3O_4 and c) Fe_3O_4/P(S-DVB) composite particles recorded in KBr pellets.

Time (min)

Fig. 5. Magnitude of adsorption of arsenic (As) on P(S-DVB) polymer particles and Fe_3O_4/P(S-DVB) composite particles both prepared at 5,000 rpm sonication at 25 C and pH 9.

The adsorption magnitude of As in mass per unit area of the particle surface is shown in Figure 5. The higher adsorption capacity on Fe_3O_4/P(S-DVB) composite polymer particles is due to both porosity[22,23] and chemicalinteraction [24-26]with magnetic nanoparticles dispersed in polymer matrix.

CONCLUSIONS

Highly cross-linked magnetic polymer composite particles were prepared by a novel suspension polymerization of styrene and DVB in presence of nanosized Fe_3O_4 particles. The removal of As by magnetic composite particles was driven by both porosity and interaction with magnetic nanoparticles.

Acknowledgment

References

[1]   WangJ, ChengC, YangX, ChenC, LiA, "A new porous chelating fiber: preparation, characterization, and adsorption behavior of Pb(II)," Ind. Eng. Chem. Res., vol. 52, pp. 4072-4082, 2013.

[2]   Kyzas G-Z, Siafaka P-I, Kostoglou M, Bikiaris D-N, "Adsorption of As(III) and As(V) onto colloidal microparticles of commercial cross-linked polyallylamine (Sevelamer) from single and binary ion solutions," J. Colloid Interface Sci., vol. 474, pp. 137–145, 2016.

[3]   Wang S, Gao B,Zimmerman A-R, Li Y, Ma L, Harris W-G, Migliaccio K-W, "Removal of arsenic by magnetic biochar prepared from pinewood and natural hematite," Bioresour. Technol., vol. 175, pp. 391–395, 2015.

[4]   Smedley P-L, Nicolli H-B, MacdonaldD-M-J, BarrosA-J, TullioJ-O, "Hydrogeochemistry of arsenic and other inorganic constituents in ground waters from La Pampa, Argentina," Appl. Geochem., vol. 17, pp. 259–284, 2002.

[5]   BodekI, LymanW-J, ReehlW-F, RosenblattD-H, Environmental Inorganic Chemistry: Properties, Processes and Estimation Methods, Pergamon Press,USA, 1998.

[6]   GreenwoodN-N, EarnshawA, Chemistry of Elements, Pergamon Press,Oxford, 1984, Chapter 13.

[7]   JainC-K, AliI, "Arsenic: occurrence, toxicity and speciation techniques," Water Res., vol. 34, pp. 4304–4312, 2000.

[8]   KipingM-D, LenihanJ, Fletcher W-W(Eds.), Arsenic, the Chemical Environment, Environment and Man, vol. 6, pp. 93, 1997.

[9]   KhanS, CaoQ, ZhengY-M, HuangY-Z, ZhuY-G, "Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China," Environ. Pollut., vol. 152, pp. 686-692, 2008.

[10]   SinghA, SharmaR-K, AgrawalM, MarshallF-M, "Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India," Food Chem. Toxicol., vol. 48, pp. 611-619, 2010.

[11]   JamilM, ZiaM-S, QasimM, "Contamination of agro-ecosystem and human health hazards from wastewater used for irrigation," J. Chem. Soc. Pak., vol. 32, pp. 370-372, 2010.

[12]   PanB-J, PanB-C, ZhangW-M, LvL, ZhangQ-X, ZhengS-R, "Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters," Chem. Eng. J., vol. 151, pp. 19-29, 2009.

[13]   VanbenschotenJ-E, ReedB-E, MatsumotoM-R, McGarveyP-J, "Metal removal by soil washing for an iron oxide coated sandy soil," Water Environ. Res., vol. 66, pp. 168-174, 1994.

[14]   CostonJ-A, FullerC-C, DavisJ-A, "Pb^{2+} and Zn^{2+} adsorption by a natural aluminum- and iron-bearing surface coating on an aquifer sand," Geochim. Cosmochim. Acta, vol. 59, pp. 3535-3547, 1995.

[15]   AgrawalA, SahuK-K, "Kinetic and isotherm studies of cadmium adsorption on manganese nodule residue," J. Hazard. Mater., vol. 137, pp. 915-924, 2006.

[16]   MandavianA-R, MirrahimiM-A-S, "Efficient separation of heavy metal cations by anchoring polyacrylic acid on superparamagnetic magnetite nanoparticles through surface modification," Chem. Eng. J., vol. 159, pp. 264-271, 2010.

[17]   ZhaoX, LvL, PanB, ZhangW, ZhangS, ZhangQ, "Polymer-supported nanocomposites for environmental application: A review," Chem. Eng. J., vol. 170, pp. 381-394, 2011.

[18]   Ahmad H, Waesmin M-A, Rahman M-M, Miah M-A-J, Tauer K, "Preparation of Hydrophobic Polymer Particles by Radical Polymerization and Subsequent Modification into Magnetically Doped Particles," J. Appl. Polym. Sci., vol. 127, pp. 620-627, 2013.

[19]   KimJ-W, Lee C-H, Jun J-B, Suh K-D, "Monodisperse micron-sized crosslinked polystyrene particles. VII. Importance of monomer-diffusible surface characteristics of growing particles", Colloids and Surfaces A; Physicochem.Eng.Ascpects, vol. 194, pp. 57-64, 2001.

[20]   Kim J–W, Suh K–D, "Highly monodispersecrosslinked polystyrene microparticles by dispersion polymerization", Colloid Polym.Sci., vol. 276, pp. 870-878, 1998.

[21]   HuX, WangY, PengB, "Chitosan-capped mesoporous silica nanoparticles as pH-responsive nanocarriers for controlled drug release,"Chem. Asian J., vol. 9, pp. 319-327, 2014.

[22]   Samiey B, Cheng C-H, Wu J,"Organic-inorganic hybrid polymers as adsorbents for removal of heavy metal ions from solutions: A review" Materials,vol. 7, pp. 673-726, 2014.

[23]   Tan M-X, Sum Y-N, Ying J-Y, Zhang Y,"A mesoporous poly-melamine-formaldehyde as a solid sorbent for toxic metal removal,"Energy Environ. Sci., vol. 6, pp. 3254-3259, 2013.

[24]   Doctoral thesis, Arsenic (V) Adsorption on Iron Oxide, Implications for Soil Remediation and Water Purification, Ivan Carabante, Lulea University of Technology, SE- 971 87 Lulea, Sweden, 2012.

[25]   Chowdhury S-R, Yanful E-K, "Arsenic and chromium removal by mixed magnetite-maghemite nanoparticles and the effect of phosphateon removal," J. Environment. Manag. Vol. 91, pp. 2238-2247, 2010.

[26]   Wang S, Gao B, Zimmerman A-R, Li Y, Ma L, Harris W-G, Migliaccio K-W, "Removal of arsenic by magnetic biochar prepared from pinewood and natural hematite,"Bioresour. Technol. Vol. 175, pp. 391-395, 2015.