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The study of mercury removal using synthesized copper ferrite nanofiber in laboratory scale

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ABSTRACT

Mercury (Hg) as a toxic and prohibitive compound is of great concern in wastewater treatment. This study evaluated the Hg removal efficiency using synthesized copper ferrite ($CuFe_2O_4$) nanofiber. We calcined $CuFe_2O_4$ nanofiber in 500 °C, 600 °C and 700 °C. The nanofibers characterized by scanning microscopy (SEM), X-ray diffraction (XRD), vibrating sample magnetometer (VSM) and Brunauer–Emmett–Teller (BET) analysis. The average diameter of $CuFe_2O_4$ nanofibers before calcination varied between 400 nm to 500 nm. After calcination at 700 °C, the average diameter reached to 95 nm. The evaluated specific surface area was 21.03 m^2/g. The value of pH, which adsorption could happen, was 7.5 (pH_{pzc}). The effect of pH in the removal of Hg in a fabricated wastewater containing 30 g/l of Hg and 0.05g $CuFe_2O_4$ nanofiber was studied. The minimum Hg removal was 25%, which elevated by increasing of pH. The maximum Hg removal efficiency was 99.98%, which observed at pH of 10. At pH of 7.5, the various amounts of calcined $CuFe_2O_4$ nanofibers at 700 °C were used in a fabricated wastewater to eliminate Hg in the concentrations of 5 mg/l, 10 mg/l, 30 mg/l, 250 mg/l and 500 mg/l. The empirical data indicated the aptness of Freundlich isotherm in describing of Hg eliminations (R^2 = 99.99% and IA = 97.99%,). The performance of adsorption in Langmuir isotherm (R_L) was satisfactory.

1. Introduction

Mercury (Hg) as a toxic and prohibitive compound is of great concern in wastewater treatment (Asyhar, 2014). Mercury (II) is soluble in water and can be converted to methyl mercury in the presence of microorganisms which is a highly toxic compound (Erhayem et al. 2015). The highest and allowable level of mercury in drinking water is 0.002 mg/l (USEPA, 2001).

To remove Hg from wastewater and water, various approaches such as ion exchange, adsorption, chemical precipitation, reverse osmosis, coagulation and solvent extraction were developed (Zabihi et al. 2009, Zhang et al. 2010). Zabihi et al. (2009), Mohamadi Landi et al. (2012) and Erhayem et al. (2015) studied activated carbon method in removing of Hg in wastewater. Zhang et al. (2009) studied mercury adsorption process using nanocomposite polyaniline/humic acid. The results indicated pH of solution had a significant impact on Hg (II) adsorption. Nano-size materials with unique properties of specific surface area, adsorption capacity and high surface to volume ratio has been introduced as an effective technique in breaking down of heavy metals and organic pollutants in water and wastewater (Mamalis, 2007). The OH^- ions and consequently pH can affect the specifications absorptive surface of nano-particles and hydrolyze metal cations (Roonasi, 2007). The removal efficiency of heavy metals decreases with increasing pH. In high pH, OH^- occupies active sites of the adsorbent. Therefore, the accessed surface area and consequently adsorption of mercury ions can be decreased. In pH_{pzc}, the absorbent surface charge is zero (James et al. 2003; Roonasi, 2007; Tu et al. 2013).

Magnetic ferro-spinals with the general formula of AFe_2O_4 [where A could be iron (Fe), cobalt (Co), nickel (Ni), and zinc (Zn)] are regarded for the removal of heavy metal contaminants. Magnetic ferro-spinals are nanofibers, which coated by with superparamagnetic. The coating increases the surface to volume ratio and the desire for combination with a great variety of chemical compounds and pollutants. Through a magnetic field, these nanoparticles can easily be collected from the flow. Consequently, the recovery of the pollutants and re-use of the nanoparticles are accessible. Copper ferrite ($CuFe_2O_4$) nanoparticles with tetragonal and cubic structures, is a super-magnetic nanoparticle. The nanofibers can be synthesized through several techniques, which electrospinning regarded as an applicable and convenient method (Ponhan and Maensiri, 2009). The produced nanofibers are steady and

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uniform (Huang et al. 2003).

Ponhan and Maensiri (2009) produced copper ferrite nanofibers tetrahedron ($CuFe_2O_4$) using electrospinning method. They used polyvinyl Pyrrlidone (PVP) and ferric and copper nitrates as a source of metal. $CuFe_2O_4$/PVP composite nanofibers (fiber size of 89 nm ± 12 nm in diameter) at 500 ℃ in air for 2 h were calcined. The results were nanofibers in diameter of 66 nm ± 13 nm and well-developed tetragonal structure.

The production of copper ferric nanofibers was studied by Zhao et al. (2012) and Nilmoung (2014).

Fan et al. (2011) studied the removal of silver (Ag +) from water using Fe_3O_4, which coated by thiourea-chitosan. The highest adsorption capacity was noticed at pH 5 and temperature 30 °C, which was 4.93 mmol/g. The Equilibrium adsorption was gained within 50 min.

Ozmen et al. (2010) investigated the adsorption of Cu (II) from water by adsorption. They modified surface of Fe_3O_4 nanoparticles by 3-aminopropyltriethoxysilane and glutaraldehyde. The results showed that modified ferroferric oxide (Fe_3O_4) could be effectively removed Cu (II) from water. Adsorption equilibrium occurred at 15 min. The maximum removal rate was observed at pH between 4 to 5.3.

Pan et al (2012) examined the effect zinc substitution on morphology and magnetic properties of copper ferrite nanofiber. They used the solution containing polyvinyl pyrrolidone (PVP MW ≈1,300,000), copper and zinc nitrates as a source of metal. The voltage was 12.5 KV and the distance between the tip of the needle of syringes and collecting tool was 14 cm. It was calcined for 3 h at 650 °C. The copper ferrite diameter of the nanofibers reached to 110 nm.

Akin et al. (2012) studied the removing of Arsenic (V) from underground water by Fe_3O_4 nanoparticles, which modified by waste red mud (bauxite residue). The results indicated that modified Fe_3O_4 nanoparticles was capable of As (V) adsorption, particularly at low equilibrium arsenate concentrations.

Sezgin et al. (2013) investigated the removal of heavy metals using nanofibers of $CuFe_2O_4$ and $NiFe_2O_4$. They obtained removal efficiencies of Cu (II), Ni (II), and Zn (II) by applying $NiFe_2O_4$ nanoparticles equal to 83.5%, 95.85%, and 99.8%, respectively. Dixit et al. (2016) worked on Hg (II) removal using Titania nanofibers. The results showed a very high adsorption capacity (95.5%). Adsorption process follows Freundlich adsorption isotherm more closely than Langmuir isotherm and the adsorption kinetics follows a Pseudo-second order kinetics.

The main objective was to study the removal efficiency of Hg from wastewater using the synthesized $CuFe_2O_4$ nanofiber. In this regard, the influence of various values of pH and concentrations of the nanofiber was assessed. We produced copper ferrite ($CuFe_2O_4$) nanofiber using olyvinyl Pyrrlidone (PVP), ferric nitrate [$Fe(NO_3)_3$] and copper nitrate [$Cu(NO_3)_2$] via electrospinning technique. The characteristics of nanofiber were assessed using X-ray Diffraction (XRD) analysis, Scanning electron microscope (SEM), and vibrating sample magnetometer (VSM). The specific surface area of the nanofibers was analyzed using Brunauer–Emmett–Teller theory.

2. Material and methods

2.1. Experimental set-up

The schematic of electrospinning set up is indicated in Fig. 1, which is based on Ponhan and Maensiri (2009). The primary elements of the setup were: a high voltage power supply, two electrodes, syringes containing the polymer solution and a collector separated at a specific distance. The syringe pump provided the polymer solution at a steady and manipulated flow rate. To charge the polymer solution, one electrode connected the needle with a spinning solution to power supply. The current and maximum voltage of power supply were 0.01 mA and 30 kV, respectively. Another electrode attached the power supply to the collector plates, which made of aluminium foil. The changes of voltage in the inlet affected the outlet voltage. When the high voltage is

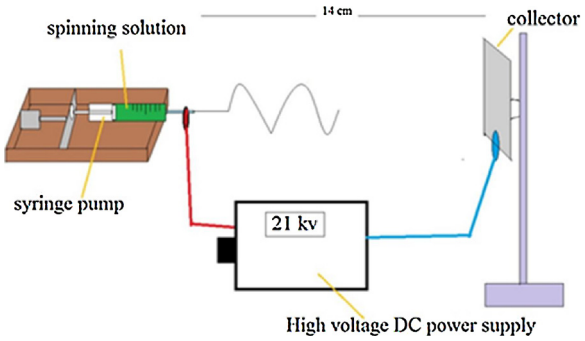

Fig. 1. The schematic of electrospinning set up for making copper ferrite ($CuFe_2O_4$) nanofiber.

applied, the electrostatic forces affected surface tension of polymer solution and the liquid jet started dropping and elongating. By overcoming the electrostatic forces against tension surface, the liquid jet kept to be extended in a constant manner. By evaporation of solvent, a randomly oriented, non-woven mat of thin polymeric fibers on the collector would be formed (Ju et al. 2008).

The required inorganic compounds were copper (II) nitrate nonahydrate [$Cu(NO_3)_2 9H_2O$] with a purity of 98%, iron (III) nitrate monohydrate [$Fe(NO_3)_3.9H_2O$] with a purity of 99%. Dimethyl formaldehyde (C_3H_7NO) was the inorganic and polymeric solvent. The inorganic compounds and 10 ml of solvent were mixed by stirrer in the speed of 300 rpm for 4 h. The used compounds and solvent were produced by Merck, Germany.

The organic compound was polyvinylpyrrlidone (PVP) with the chemical structure of $(C_6H_9NO)_n$. We used PVP K-30 and K-90 polymers were used. Ethanol (C_2H_5OH with a purity of 100%) was as the polymeric solvent. To adjust pH, hydrochloric acid (HCl) of 0.1 M and sodium hydroxide (NaOH) of 0.1 M was employed. For measurement of pH_{pzc}, sodium chloride of 0.1 M was applied. These chemical compounds were provided by Merck, Germany.

In the electrospinning process various amounts of organic and inorganic compounds along with solvent were mixed to gain a stable liquid jet. After several attempts, the following combination was opted for the experimental works: 15 g of PVP was added to 100 ml of a combination of the C_3H_7NO and C_2H_5OH (as the solvent) in the ratio of 3 to 1. They were mixed with the speed of 200 rpm for 12 h. Afterwards, 6 ml of inorganic compounds was added to 50 ml of polymeric solvent and mixed for 6 h (Nalwa 2006, Ponhan and Maensiri 2009). The prepared solution was poured in a plastic syringe with a needle of 10 mm and afterwards added to the syringe pump. The pump in the speed of 0.5 ml/h injected the polymeric solution toward the collector, located in the distance of 14 cm. The voltage was adjusted in 21 kV to keep a continuous and even stream of fibre. The spun fibers was gathered in the collectors and calcined in the temperatures of 500 ℃, 600 ℃ and 700 ℃ for 2 h. The heating rate of the furnace was 5 ℃/*min* (Carbolite Model CWF 12/23). To evaluate the structure of the nanofibers, XRD was applied. The diameter of nanofibers before and after calcination was analyzed using SEM. To understand the magnetic specification of calcined nanofibers, VSM was employed. The specific surface area of the nanofibers was analyzed using Brunauer–Emmett–Teller (BET) theory, which is based on the physical adsorption of Hg on the nanofiber surface. In the high specific area, the nanofiber shows better performance in adsorbing of pollutants.

Through the hysteresis loop, which describes the relation between the magnetization (M) and the applied field (H), specifications of magnetic media can be attained. The saturation magnetization (Ms), remnant magnetization (Mr), coercively (Hc), the squareness ratio (SQR), and the switching field distribution (SFD) are the parameters to indicate characteristics of magnetic media. A large and sufficient magnetic field is introduced to nanofibers, which triggers the spins