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Nano fiber composite prepared from disposable food container as a promising solution for removing the arsenate from water

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Abstract: This project has worked on the production of Nano filters using recycled foam form polystyrene enriched by magnetic nanoparticles, as a solution for Arsenic removal from water. Magnetic nanoparticle synthesis was accomplished using co-precipitation and magnetic fiber nanocomposite production was done by an Electrospinning method. Characterization of magnetic nanofiber was carried out using the Scanning Electron Microscopy (SEM), X-Ray powder Diffraction (XRD) and Energy Dispersive Spectrometry (EDAX). In addition, magnetic behavior of nanoparticles was evaluated by magnetization measurements, a pilot was designed and the effect of important parameters was investigated. Inductively Coupled Plasma (ICP) method has been used for determination of the amount of removing arsenic. The results of the pilot showed that the height of the nano filter and the amount of magnetic nanoparticles has the most significant effect on the arsenic removal from water.

Introduction

Nowadays regarding the human population growth and increasing volume of industrial pollution, shortage of drinking water is a serious issue, knowing that water resources are getting depleted and polluted very quickly. The presence of arsenic as pollution in natural waters, especially in underground water is a serious issue [1, 2]. As (III) and As (V) is the main arsenic forms in water, which is dependent on the oxidation – reduction potentials and other solution chemistry. Intake of arsenic would cause various health problems such as cancer, hypertension, angio cardiopathy and skin diseases [3, 4]. In 2001 World Health Organization (WHO), European Committee and also Environmental Protection Agency (EPA) decreased the permitted amount of Arsenic in drinking water from 5 to 1 μg/ l due to the high toxicity of it [5].

Among the methods that address arsenic problem, adsorption offers many advantages, including simple and stable operation, easy handling of waste, and absence of added reagents, compact facilities and generally lower operation costs. Iron oxides and oxy-hydroxides are the most widely used classes of adsorbents for Arsenic removal due to their high removing capacity, strong binding of adsorbed arsenic and their low cost [6]. Generally, adsorption capacity is a function of the surface area and charge. Under this prism, amorphous or nanoparticle forms seem to be more efficient. As compared to the bulky particles, the nanoparticle form, usually presents higher accessible surface area and more active sites for arsenic removal [7–9]. Although iron oxy-hydroxides are usually preferred for their higher surface charge, iron oxide Nano crystals (Fe_2O_3, Fe_3O_4) were also reported as potential adsorbents due to the additional adsorption mechanisms. They activate (ion exchange,

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precipitation) [8]. Moreover, magnetic nanoparticles due to homogeneous dispersion in water, ability of being magnetically separated and collected after their use, can be a good candidate for the water plant setup other than the typical filtration bed [9, 10]. For instance, the pumping power to overcome the high pressure drop in an adsorbent column can be minimized and replaced by the periodical operation of an electromagnet that captures magnetic nanoparticles from the water flow [11]. Furthermore, filtration, problems related to occlusion and fouling of packed columns can also be avoided. According to Yeanet al. [7] Research, the maximum adsorptive capacity of mono-disperse Fe_3O_4 particles by the diameter of 20 nm was around 11.4 mg/g, and it increased to 172 mg/g when the diameters were down to 12 nm. However, it is expected that such ultrafine particles will face great challenges in their practical applications. The first challenge is separation of Fe_3O_4 nanoparticles from bulky solution in an effective and economical manner. As far as, the acting force of the magnetic field on the particles is directly proportional to particle size, it is expected that ultrafine particles (e.g. ~10 nm) cannot be effectively separated in a moderate magnetic field. Due to the presence of Brownian movement [12,13], and employing high magnetic fields would inevitably increase the cost of processing [14,15]. Another problem is the tendency of nanosized Fe_3O_4 particles to aggregation into bulky particles and lead to a significant decrease in adsorption capacity. As a result, developing Fe_3O_4-based adsorbents with high capacity and feasible separation is becoming an interesting topic in the field of environmentally functional materials.

An effective approach to overcome these challenges is loading or coating nanosized Fe_3O_4 particles onto larger-scale carriers like boron nitride nanotube [16] or wheat straw [2], to improve the nanoparticle dispersion in water, and easily separated from the bulky solution due to their larger particle size. In recent years, micro or nano polymeric beads were widely applied as a new host for Fe_3O_4 particles for different applications such as controlled release systems [17, 18] and biosensor systems [19, 20].

Various techniques such as interfacial polymerization, template synthesis and electrospinning can be used for preparation of polymeric beads as a Fe_3O_4 particle carrier. Electrospinning compared to other fabrication methods, is a relatively straightforward and effective technique for fibers fabrication that are long in length, uniform in diameter, and diverse in composition [21]. This technique involves the use of a high voltage to charge the surface of a polymer solution droplet and thus to induce the ejection of a liquid jet through a spinneret. Due to bending instability, the jet is subsequently stretched by many times to form continuous, ultrafine fibers. The diameters of fibers prepared by this method can range from a few nanometers to several micrometers. Nanofibers produced by electrospinning technique have several remarkable characteristics such as a very big ratio of surface area to volume, pore size within nano range, unique physical characteristics, and flexibility for chemical/physical modification and functionalization [22]. These nanofibers prepared by electrospinning are good candidates for a wide variety of applications, including electronic and photonic device fabrication [23–25], composite reinforcement [26], high performance filters [27], delivery carriers [28,29], gas sensors [30], catalysis as well as biomaterial scaffolds for tissue engineering and wound dressings [31–35].

Amorphous polystyrene is one of the most suitable plastics because it is strong, cheap, and with a fine property for getting isolated. However the main application of polystyrene is in reservoir production, wall coating and furniture, but electrospun polystyrene fibers are suitable substance for filter layers or protective clothes. In recent years the use of polystyrene disposable food containers in foam form is rising up dramatically due to its reasonable cost and less detrimental chemical. One of the main problems emerging from this pandemic trend is the impossibility of recycling by re-melting method. As far as, the only way for recycling of this polymer is solvent method which is expensive, using this recycled polymer for a suitable application such as arsenic adsorption can cover this expense.

In this study two different Nano technology methods are used to prepare an economic and feasible composite product.

Results and Discussion

Characterization of magnetic nanoparticles:

As shown in (Figure **1a**), the main XRD peaks of crystalline Fe_3O_4 were observed at 2θ of 19.3 (D 111), 30.9 (D 2 2 0), 35.9 (D 3 1 1), 43.8 (D 4 0 0), 57.7 (D 5 1 1), and 62.9 (D4 4 0), which is an agreement with the standard diffraction spectrum (JCPDS Card No. 19-0629). Broadening of the peaks in the XRD pattern points out the small size of magnetic. The crystal sizes of synthesized Fe_3O_4 were

calculated using the characteristic peaks by Scherer equation as follows:

$$D = K\lambda / (\beta_{1/2} \cos \theta)$$

Where D is the average crystal size; K is a constant (here chosen as1); λ is the wavelength of X-ray radiation (1.542 Å); $\beta 1/2$ is the half width of the diffraction peak (rad); and θ (°) is the Bragg angle [36]. The result of D value using 311 planes is about 20 nm. The SEM micrograph of nano- Fe_3O_4 (Figure **1b**) indicates regular morphology of magnetic nanoparticles in a spherical shape.
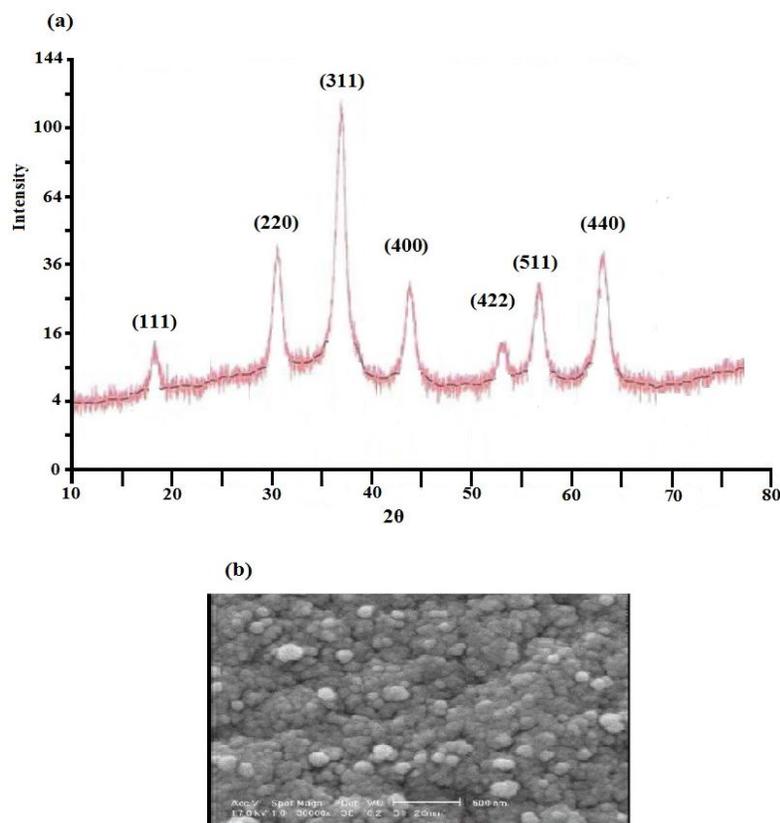

Figure 1: XRD pattern (a) and SEM image (b) of nano-Fe_3O_4

In order to study nanoparticles magnetic behavior, magnetization measurements for Fe_3O_4 was performed. As it can be seen in (Fig ure **2**), it has a hysteresis loop with zero coercivity and remanence value. This means that this is single domains with superpara magnetic characteristic. The saturation magnetization value of magnetic was 56.8 (emu/g).
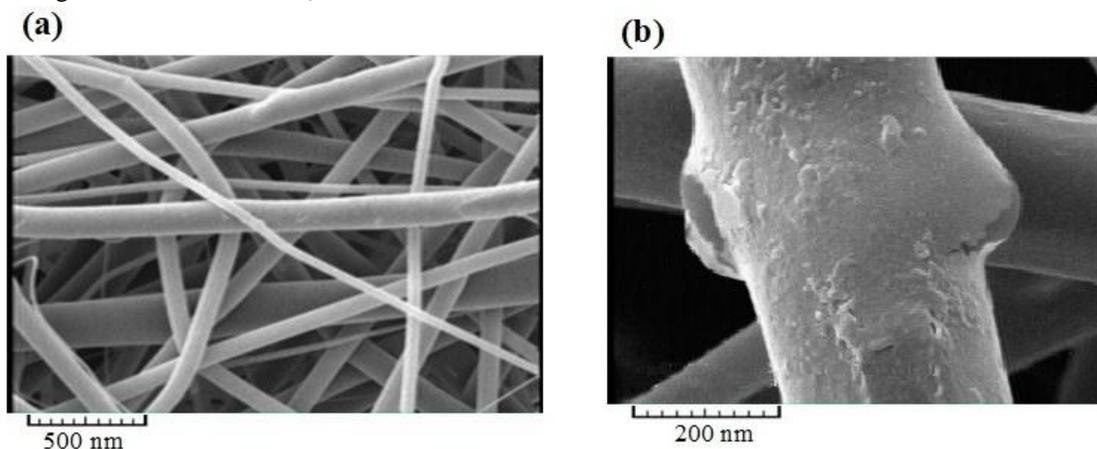
Characterization of magnetic nano fiber composite:

Electrospinning has been actively exploited as a simple and versatile method for generating uniform and ultrafine fibers made of various materials. The morphology of the electrospun fibers is controlled by the experimental design and is dependent upon the solution conductivity, solution concentration, polymer molecular weight, viscosity, and applied voltage, etc. By optimizing the governing parameters that affect electrospinning (not discussed here), uniform polystyrene-Fe_3O_4 nanofibers composite with diameters in the range of 50 to 300 nm were prepared, and the morphologies of them are shown in (Figure **3**). (Figure **3a**) displays that the nanofibers are almost uniform in diameter and aligned in random orientation, which was caused by the bending instability, associated with the spinning jet. The magnified image (Figure **3b**) shows that the surfaces of the fibers are rough and covered by nano magnetic particles.
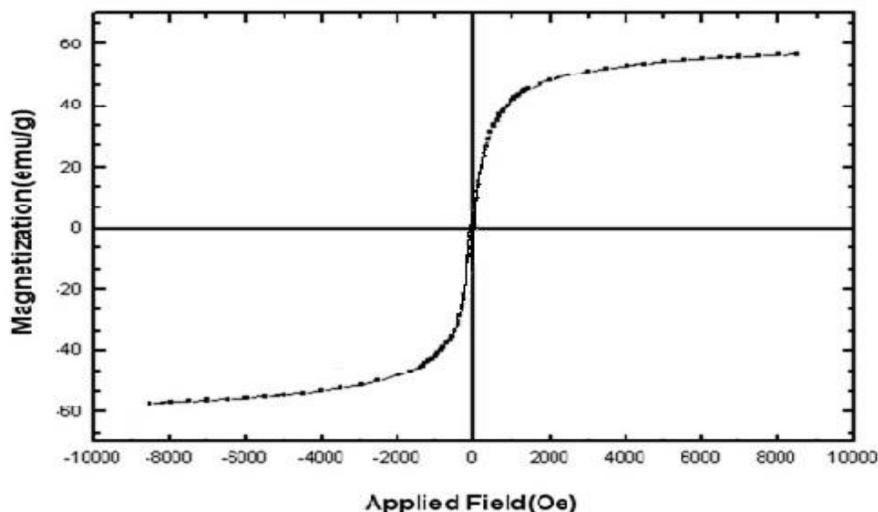
Figure 2: Magnetic curve of nano-Fe$_3$O$_4$

Figure 3: SEM micrographs by two different magnification (a,b) of magnetic nanofiber composite.

EDAX spectrum (Figure **4**) confirmed the presence of iron (Fe), oxygen (O) with iron abundance higher than oxygen.

Evaluation of different parameters effect on arsenic removal:

One parameter in each run:

Analysis of arsenic removal has been performed considering the height of nano filter and the flow rate of passing water through the filter for evaluation of arsenic adsorption capability of filter. Removal process of arsenic from water can be described by adsorption of arsenate as negatively charged ions from aqueous solution by fiber nanocomposite enriched by nanoparticles, Arsenic gets entangled in nanoparticles and the amount of effluent Arsenic is reduced significantly. Our target is to determine the relationship among arsenic removal and the height of magnetic nanofiber and also the water flow rate, according to CCD software result that gives a linear equation; it shows that the amount of arsenic removal equals to 'n' amount of fiber length and 'n' amount of flow rate of water.

At first, flow rate, height of the nano filter, and nano magnetic percent in filter effects on the removal of arsenic were evaluated. As it can be seen in (Figure **5a**), water flow rate that passes through the filter column has no effect on the amount of arsenic

removal. It is completely against the prediction it is expected that increasing flow rate causes to less adsorption and following less arsenic removal. There is a direct relationship between the height of the filter and removal of arsenic (Figure **5b**). The more filter height leads to more arsenic removal. It can be due to the increasing adsorption rate of filter by increasing the height. At the end, direct relationship between magnetic nanoparticles percent and arsenic removal can be observed (Figure **5c**). It can be due to increasing the adsorption capacity of the filter due to increasing the nano magnetite percent.

Two parameters in each run:

Evaluation results of two parameters (out of three) effecting on the amount of arsenic removal are presented in 3D diagram in (Figure **6**).

In (Figure **6a**), the relationship between flow rate and the height of the nano filter on the amount of arsenic removal is shown; this 3D diagram explains that the amount of arsenic removal increases when the flow rate and the height of the nano filter increase. The

relationship between flow rate and magnetic nanoparticles effecting on the amount of arsenic removal is shown in (Figure **6b**). As it can be seen, the amount of arsenic removal increases in response to the rise of flow rate and magnetic nanoparticles percent in filter.

In 3D diagram of (Figure **6c**), increasing the arsenic removal is related to the height of the nano filter and the amount of magnetic nanoparticles percent increasing. In the other word, on the basis of comparison, by the two parameters, height of the nano filter and the amount of magnetic nanoparticles, the removal process enhances significantly that can be based on the data accrued from the experiments and presented in Figure **6**, it is concluded that the height of the nano filter and the amount of magnetic nanoparticles has the most significant effect on the arsenic removal from water that can be due to the better adsorption potential of filter by modification of these two factors.
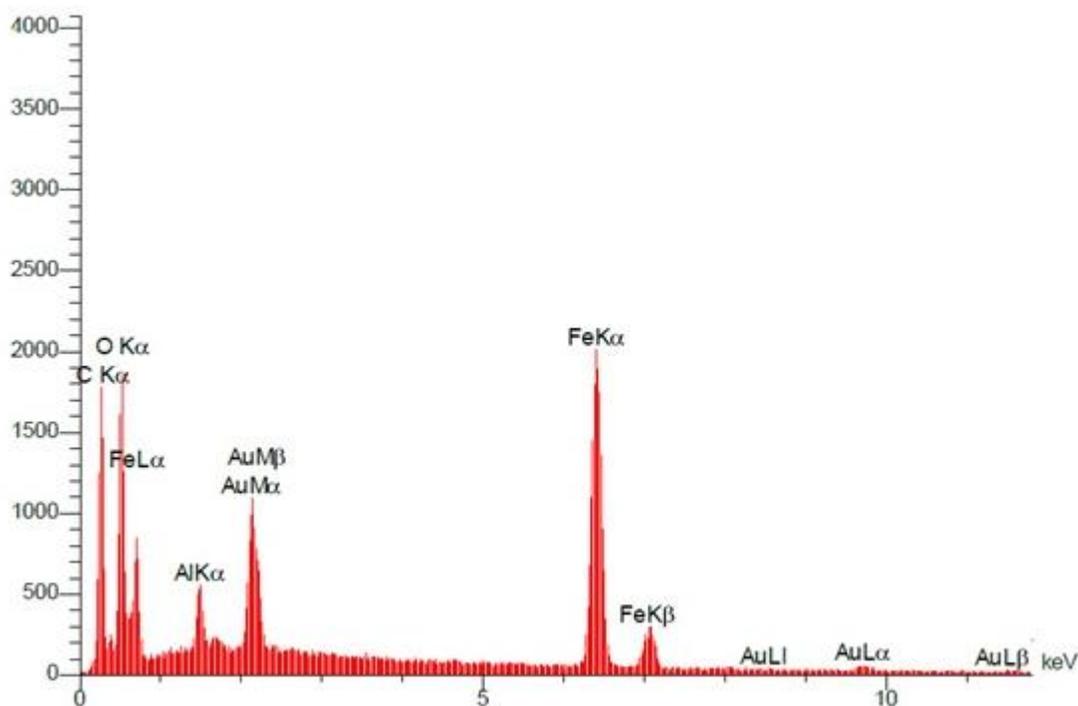
Figure 4: EDAX image of magnetic nanofiber composite
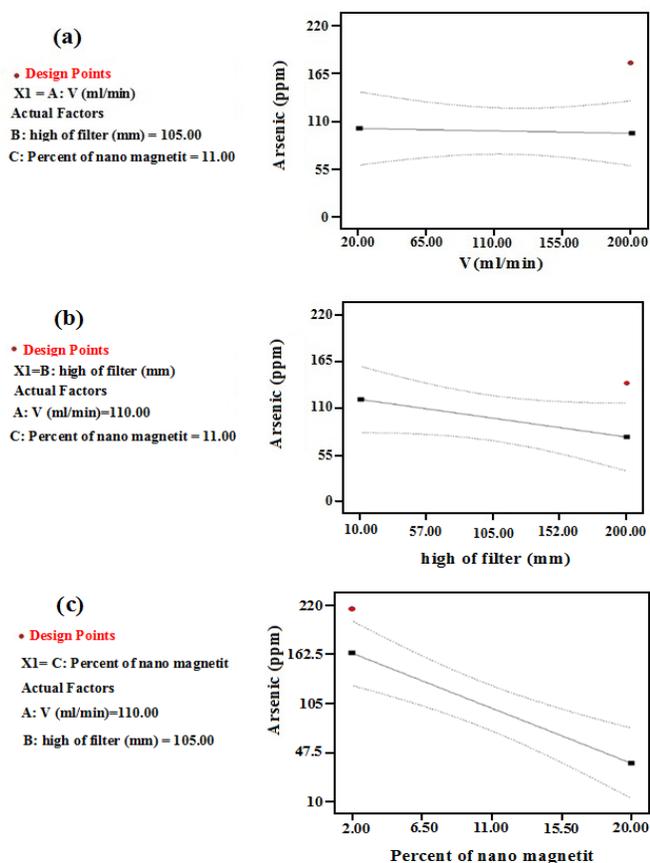
Figure 5: Effect of water flow rate (a), height of nano filter (b) and nano magnetic percent in filter (c) on arsenic removal.

Experimental

Materials:

Ferric chloride hexahydrate, ferrous chloride tetrahydrate, ammonium hydroxide, dimethyl formamide and di sodium hydrogen arsenate were analytical grade and purchased from Merck. They were used without further purification. Styrene was provided in the form of disposable food containers and purchased from local markets.

Preparation of nano -Fe$_3$O$_4$:

Coprecipitation method has been used for the synthesis of nano magnetic particles. Briefly, ferric chloride hexahydrate (FeCl$_3$.6H$_2$O) and ferrous chloride tetrahydrate (FeCl$_2$.4H$_2$O) (molar ratio 2:1) were dissolved in 50 mL of distilled water and the mixture was stirred vigorously under N$_2$ atmosphere. Then, 50 mL NH$_4$OH solution (1M) was added dropwise into the iron solution to maintain pH at 10 under vigorous stirring at 25 °C. Changing color to

black is the sign of Fe$_3$O$_4$ particle formation. In this step, coprecipitation of Fe^{2+} and Fe^{3+} has been occurred, according to the following equation [37]:

$$2FeCl_3+FeCl_2+4H_2O+8NH_3 \rightarrow Fe_3O_4+8NH_4Cl$$

Then, stirring was steadily continued for more than 2 h under N$_2$ atmosphere. The solvent was removed by magnetic decantation. Particles were washed several times with distilled water until the pH reached at 7. Then, the final products were dried in a vacuum oven at 60°C for 10 h. As a dried product were characterized using X-ray powder diffraction (XRD) Siesert Argon 3003 PTC using nickel –filtered XD-3a Cu Kα radiations (λ=0.154 nm) and scanning electron microscopy (SEM) Philips.
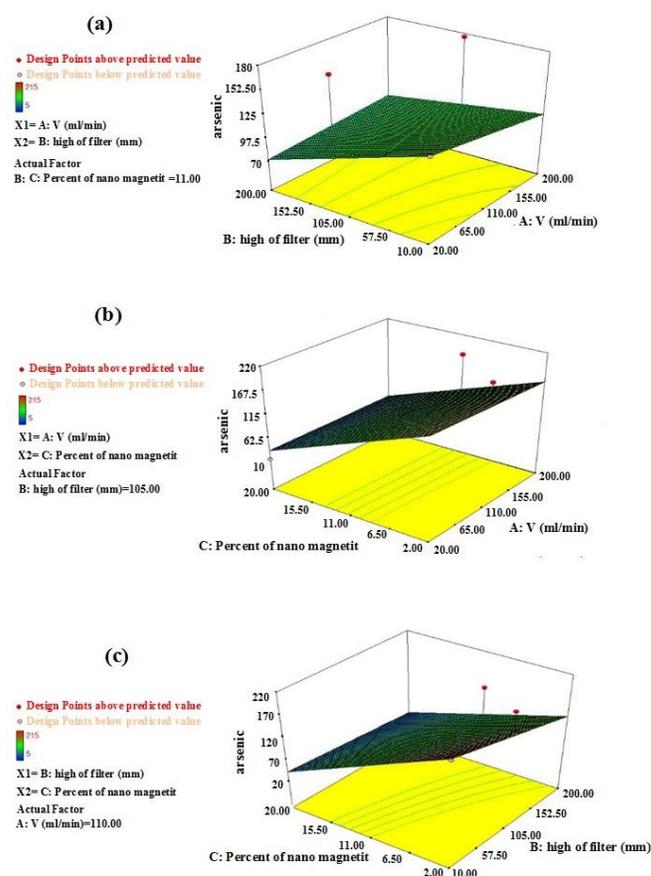
Figure 6: Evaluation results of two parameters (out of three) effecting on the amount of arsenic removal in 3D diagram

Synthesis of Magnetic fiber Nano composite:

At first food containers were chopped in small pieces, and dissolved in dimethyl formamide to give a homogeneous polymer solution by mass fraction 40%. Then, synthesized magnetic nanoparticles were added

and stirred for 24 h till a uniform solution is obtained. Different concentrations of nano magnetic particles (2, 11 and 20 % of polymer weight) have been applied for evaluation of their effect on arsenic removal quantity. For electrospinning, the prepared solution was firstly placed into a 10 ml plastic syringe with the inner diameter of the capillary of 0.5mm. During the electrospinning process, the solution was fed to the tip using a syringe pump (KDS- 100, KD Scientific, Inc. USA) at a flow rate of 20µl/min. A positive voltage of 20 kV was applied to the polymer solution by attaching a clip to the stainless steel needle from the positive lead. The grounded electrode was connected to a metallic plate wrapped with aluminum foil. The electrospun fibers were typically obtained at a tip-to-collector distance of 17 cm. After electrospinning, the non-woven membranes of the fibers were dried in a vacuum oven, at room temperature for 12 h to remove the residual organic solvent before characterization. The morphology of synthesized magnetic fibers was evaluated by SEM and the presence of magnetic nanoparticle in nanofibers confirmed by Energy Dispersive Spectrometry (EDAX) which was connected to SEM equipment.

Design of experiment for Arsenic removal from water:

Pilot which was designed for removal of arsenic from water was a simple U shaped system which contains two glass tubes with 1cm diameter and 30cm height. A plastic tube connects from one side to one glass tube and from the other side to the inlet port of flow meter in order to examine the flow rate of water. Outlet of flow meter connects to a pump via another plastic tube. At the end, third plastic tube connects the pump to the end of the outer glass tube.

According to the Design of experiment, water flow rate and height of magnetic nanofiber are effective parameters on removal of arsenic. Water flow rate through fiber in the range of 20 to 200 ml/min and height of magnetic nanofiber between 10 to 200 mm has been considered. CCD statistical method and Design Expert software have been applied for the determination of water flow rate and height of magnetic nanofiber in each run. For the test, a reference solution of arsenic by concentration of 300 ppm is required. The amounts of applied parameters in the design of experiments are presented in (Table **1**).

The experiment is conducted in the order which at a first arsenic reference solution based on the experimental design passed through the column, then the discharged water which bore arsenic were collected. The quantity of arsenic removal was evaluated by Inductively Coupled Plasma/Optical Emission Spectroscopy (ICP-OES) (Varian-OES 730).

Table 1: Amount of applied parameters in design of experiment.

Type of variable	Name of variables	Range and level		
		-1	0	+1
Numerical	V (ml/min)	20	110	200
	Height of nano filter (mm)	10	105	200
	Perecent of nano magnetic	2	11	20

Conclusions

In this project, by combining few techniques including chemical synthesis of magnetic nanoparticles, and physical production of micro and nano fibers, using recycled polymer via an electrospinning method, a layer of filter was produced that exhibits clear advantages for environmental remediation, Since the characteristics of electrospun PS enriched by magnetic nanoparticles depicts its very high capacity for arsenate removal within a low magnetic field in a reasonably economical kinetics. Arsenic removal from aqueous solutions using this nanofiber provides opportunities for energy saving, environmental protection regards and least side effects, in case of disposals knowing that an Alkaline treatment could regenerate nano filter and leave it reusable for the same repeated operations. It is notable that there has been no evidence of dispatch magnetic nano fibers within the effluent, however, including a sieve part comprised of a magnet bar near the end of filter seems to be cautious just in case.

This project was only aimed for production of the filter, next steps for further studies and thorough assessment are still required to achieve the utmost efficiency and the convenient installation and assembly suggestions within and alongside of the other building blocks of water treatment plants, later on electrospun PS-Fe$_3$O$_4$ could get its scale up promotions for industrial manufacturing prospects.

Acknowledgements

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