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Improving urban run-off quality using iron oxide nanoparticles with magnetic field

Mehdi Khiadani (Hajian)[a,b,*], Maryam Foroughi[b], Mohammad Mehdi Amin[b]

[a]*School of Engineering, Edith Cowan University, Joondalup, WA 6027, Australia*
Email: m.khiadani@ecu.edu.au
[b]*Environment Research Centre, Isfahan University of Medical Sciences, Isfahan, Iran*

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ABSTRACT

Run-off from road surfaces is a major source of pollution in the environment. The aim of this study was to investigate the efficiency of nano iron oxide under a magnetic field to improve urban run-off quality. Experiments were conducted in a 50 mm diameter column made of Plexiglass in which 20 cm deep stainless steel wool was used as the medium bed. A pair of magnets, each with 0.7 T magnetic charge density, was installed around the column. The particle size of the iron oxide was determined by X-ray diffraction (XRD) analysis. Atomic absorption spectroscopy, spectrophotometer, turbidimeter, and pH meter were used to measure heavy metals, nitrate and phosphate, turbidity and pH, respectively. Results from XRD analysis revealed that the average nanoparticle size was 32 nm. The average removal efficiency for turbidity, Pb, Zn, Cd, and phosphate were 41.5, 93.9, 96.2, 88.4, and 87.4%, respectively. However, nitrate was not removed from the column tests. The results of this study showed that nano iron oxide in the presence of magnetic field has the potential to improve urban run-off quality. However, for further reduction of turbidity and nitrate removal other options should be considered.

Keywords: Iron oxide nanoparticles; Magnetic field; Urban run-off

1. Introduction

Roads in urban areas include significant quantities of pollutants such as nutrients, heavy metals, and hydrocarbons which normally originates from traffic activities. Run-offs from these roads are considered a major source of pollution in urban areas. Pollutants in run-offs from roads may exert a serious long-term impact on receiving soils or water-based ecosystems [1].

Heavy metals such as cadmium (Cd), lead (Pb), and zinc (Zn) in stormwater are considered to be of greatest concern as their concentrations often exceed surface water quality guidelines by 10 times or even more [2]. The impact of eutrophication and issues related to phosphate and nitrate ions are also important [3,4].

Magnetically assisted processes are being used in water purification. Magnetism influences the physical properties of contaminants in water. High-gradient

*Corresponding author.

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magnetic separation (HGMS) is a commonly used expression in magnetic separation techniques that comprise a bed of magnetically susceptible wires placed inside an electromagnet [5]. A magnetic field around a column with wires produces large gradient which can attract and trap magnetic particles on the surface of wires. Particle sizes, their magnetic properties, and magnetic field gradients are important factors affecting the capture of particles [6]. The magnetic force attracting particles toward the wires must take over the fluid drag, gravitational, inertial, and diffusion forces.

Several magnetic-based methods have been used for water purification. Fe(III) as a coagulant forms insoluble precipitate which is magnetizable. This property has been used to remove contaminants from paper and steel industries. During this process it was also noticed that algae, biochemical oxygen demand, total nitrogen, and total phosphorus can simultaneously be lowered [5].

Nanomaterials are currently used to treat water. Their combination with magnetism could be an efficient treatment technology. Magnetic nanoparticles have large surface area while maintaining their magnetic property. One of the advantages of this process is that nanoparticles could be eliminated by an external magnetic field.

Magnetic nanoadsorbents, due to their better removal efficiency, were also used to remove metallic ions such as Cr(VI), Cu(II), Co(II), Cd(II), As(V), As(III), and Hg(II) from wastewater [5]. Magnetic nanoabsorbants as a seeding absorbent with HGMS were successfully used to remove phosphorous from wastewater [7]. Arsenic was successfully removed by combining the processes of magnetic seeding flocculation and HGMS [8]. HGMS process assisted with physico-chemical pre-treatment was used to remove heavy metals from industrial wastewaters using iron-oxide particulate matter. This was found to be a cost-effective method [9].

The aim of this study was to investigate the efficiency of nano iron oxide particles in the presence of magnetic field to improve urban run-off quality.

2. Materials and methods

2.1. Run-off synthesis

Run-off used in this study was synthesized and composed of turbidity (60 NTU), Pb (2.37 mg/l), Zn (2.54 mg/l), Cd (0.52 mg/l), PO_4^{-3} (9–10 mg/l), and NO_3^- (4–5 mg/l). Although using natural stormwater has advantages over using synthetic stormwater, maintaining consistency of its concentration and characteristics is difficult [10]. Apart from this, due to rare and dispersed rain events in the city of Isfahan, Iran where this study was conducted, synthetic stormwater was a better choice for this study. The characteristics of synthetized run-off have been illustrated in Table 1.

The chemicals used to synthezis the run-off were purchased from Merck Company. Stock solutions 1 g/l of Pb, Zn, Cd, PO_4^{-3} and NO_3^- were respectively prepared from $PbCl_2$, $ZnSO_4{\cdot}7H_2O$, $(CH_3COO)2Cd{\cdot}2H_2O$, K_2HPO_4 , and KNO_3 using double-distilled water. Standard acid and base solutions (1 M H_2SO_4 and 1 M NaOH) were used to adjust the pH. Turbidity of the solution was adjusted using Kaolin.

2.2. Nanoparticle characteristics

Characteristics of Fe_3O_4 nanoparticles used in this study are presented in Table 2. This product was purchased from Aldrich. Esmaili et al. [11] used Debye–Scherrer equation to determine the particle size for this product. The approximate mean size of nanoparticles using this equation at 454 reflection peak, $2\theta \sim 36^\circ$ and 2.54 °A, was estimated to be 37 nm. This size was different from 60 nm that was given by the manufacturer (Aldrich); however, they acknowledged that this could be due to the difference in NaOH and pH of the solutions used.

Table 1
Characteristics of synthesized run-off

Pollutant	Concentration
Turbidity (NTU)	60
Lead (mg/l)	2.37
Zinc (mg/l)	2.54
Cadmium (mg/l)	0.52
Nitrate (mg/l)	4–5
Phosphate (mg/l)	9–10
pH	6.5–7.5

Table 2
The characteristics of nano iron oxide particles

Scientific name	Iron oxide magnetic nanoparticles
Chemical formula	Fe_2O_3
Purity (%)	99.2
Particles size (nm)	60
Morphology	spherical
SSA (m^2/g)	55
Bulk density (g/m^3)	0.84

Point of zero charge (PZC) for Fe_3O_4 nanoparticles was determined to be around 7 [11]. Different techniques have been used to synthesis iron oxides nanoparticles, so different values of pH_{pzc} (3.8–9.9) have been reported in the literature [12].

2.3. Experimental conditions

Fig. 1 shows an overview of the pilot used in this study. Two magnets, each with 0.7 T magnetic flux density, were installed on the walls of the column. All tests were conducted in a 50 mm diameter (internal) Plexiglass column where 200 mm of its height was filled with stainless steel wool. The total volume of the column was 400 ml in which half of it was occupied by the stainless steel wool. The exposure time (retention time) of 10 min was allowed between run-off and nanoparticles. This optimum time has been experimented using Fe_3O_4 nanoparticles [12].

Synthetic stormwater was flown through the column five times and for each run, 0.5 g/l nano iron oxide was added during an exposure time of 10 min [12], then the samples for further analysis were collected.

Atomic absorption spectroscopy (Perkin-Elmer 2380), spectrophotometer (Hach DR 5000), turbidimeter (Euteoh Instruments TN100), and pH meter (pH-meter CG824) were used to measure heavy metals, nitrate, phosphate, turbidity, and pH, respectively.

3. Results and discussion

The result in terms of removal efficiency has been presented in Fig. 2. The minimum, maximum, and average removal efficiencies for each parameter are given in Table 3.

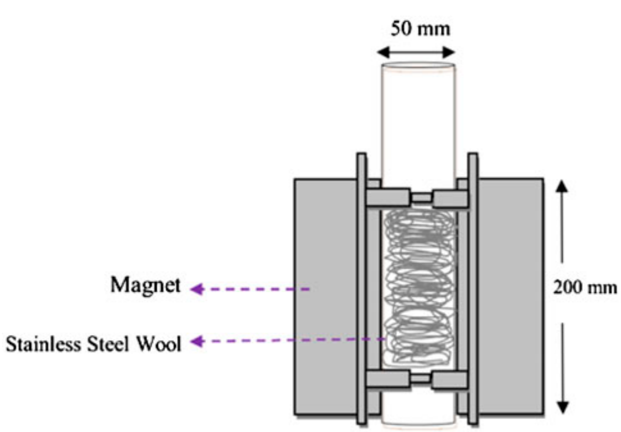

Fig. 1. The scheme of laboratory system.

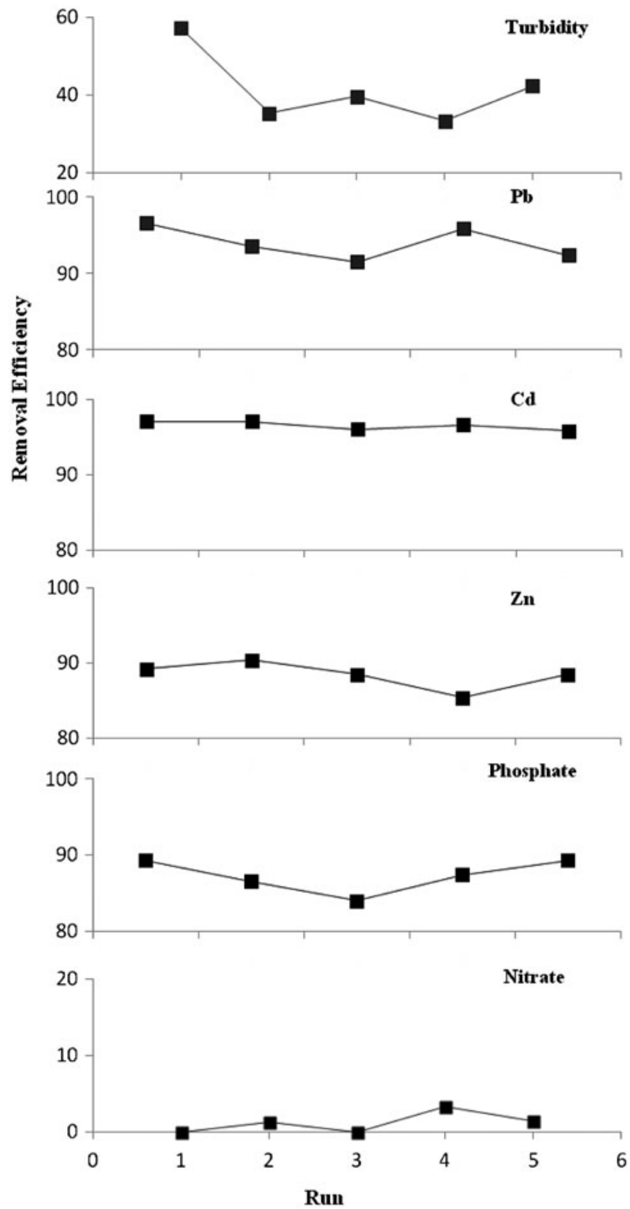

Fig. 2. Removal efficiency of pollutants from the column.

4. Discussion

As indicated in Table 3, the mean removal efficiency for turbidity was 42%, which is not very significant. This may be due to the fact that stainless steel wool media due to its large porosity does not act similar to filter system or settling mechanism. In a sand filtration system, three mechanisms such as filtration, settling, and adsorption are constitute the primary removal process [13]. It has been claimed that zeta potential of sand filter columns reduces in the presence of magnetic field and this leads to particle instability, aggregation, and formation of larger

Table 3
Minimum, maximum, and average removal efficiencies

Parameters	Minimum removal efficiency (%)	Maximum removal efficiency (%)	Average removal efficiency (%)
Turbidity	33.0	57.1	42.0
Pb	91.5	96.5	93.9
Cd	95.7	97.0	96.4
Zn	85.3	90.3	88.4
PO_4^{-3}	84.0	89.3	87.3
NO_3^{-1}	–	–	–

particles, and as such accelerates filtration, and settling [14]. Therefore, it is not surprising that the stainless steel wool column with such large porosity is not able to remove turbidity significantly. In this process, the dominant mechanism to remove turbidity seems to be adsorption only. Nanoparticles are small-sized particles with large surface area and consequently their adsorption capacity is high. Apart from this, surface charges of magnetic nanoparticles are arranged so that atoms in the surface have high reaction capacity and this increase reaction between the nanoparticles and adsorbents [15]. Apart from this the magnetic field entraps iron nanoparticles which maximize the surface area inside the column and help to reduce turbidity.

The average removal efficiency of the column for lead, Zn, and Cd was 93.9, 96.4, and 88.4%, respectively. This indicates that Fe_3O_4 nanoparticles are effective into removing metal ions from the solution. Shen et al. [16] used Fe_3O_4 nanoparticles of 8 nm with a contact time of 24 h to remove metal ions from wastewater. The removal efficiency in their experiments for metal ions Cu, Cr, Cd, and Ni were 99.8, 97.6, 84.7, and 88.5%, respectively. In this study, X-ray diffraction patterns for the sample collected proved that ion-adsorbed nanoparticles were crystalline, suggesting that the adsorption mechanism for removal of the metals is mainly electrostatic attraction [15]. Furthermore, investigations by others have proved that magnetic nano–particles can produce large specific surface areas which can have a higher adsorption capacity and fast adsorption rate for metal removal [16].

The average phosphate removal in the present study was 87.4%, which is consistent with finding from other studies [12]. In this study, Fe_3O_4 nanoparticles was used to remove organic matters from wastewater. They concluded that the Fe_3O_4 nanoparticles are an effective, easy and low-cost method to remove metals and also recover them using a magnetic field. In another study, removal of phosphate from synthesized urban run-off was investigated by authors using sand filter column which was coated with Fe_3O_4 nanoparticles [14]. Removal of phosphate from the sand filter coated with Fe_3O_4 nanoparticles was less when cmpared to that from the current study. This supports that removal mechanism in column with stainless steel wool is mainly due to adsorption. Free Fe_3O_4 nanoparticles have more adsorption capacity than when they are coated on sand.

Nitrate was not removed by the column and this was due the fact that removal mechanism was physical and/or adsorption. This is consistent with findings from other studies where adsorption mechanism is not a suitable method to remove nitrate [10].

5. Conclusions

The study showed that the column with stainless steel wool in the presence of Fe_3O_4 nanoparticles and magnetic field is an effective method to remove heavy metals from urban run-off. However, the column was less effective to remove turbidity. Also, the results indicated that in situations where nitrate is the critical pollutant, this method is not a suitable treatment option.

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