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#### Improving urban runoff quality using iron oxide nano particles with magnetic field

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## Abstract

Runoff from roads surface 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 runoff quality.

Experiments were conducted in 50 mm diameter column made of plexiglass in which 20 cm deep stainless steel wool was used as 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 nanoparticles 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 presence of magnetic field has potential to improve urban runoff quality. However, for further reduction of turbidity and nitrate removal other options should be considered.

Keywords: Iron Oxide Nanoparticles, Magnetic Field, Urban Runoff

## 1. Introduction

Roads in urban areas include significant quantities of pollutants such as nutrients, heavy metals, and hydrocarbons where normally originate from traffic activities. Runoff from these roads is considered a major source of pollution in urban areas. Pollutants in runoff from roads may exert a serious long term impact on receiving soils or water-based ecosystem [1].

Heavy metals such as cadmium (Cd), lead (Pb) and zinc (Zn) in stormwater are considered to be of greatest concern as their concentration 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 magnetic separation (HGMS) is a commonly used expression in magnetic separations that comprises 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 gradient 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 magnetisable. 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 (BOD), total nitrogen (T-N), and total phosphorus can simultaneously be lowered [5].

Nanomaterials are currently practiced 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 nano-adsorbents, 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 as a seeding absorbent with HGMS was 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-chamical 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 presence of magnetic field to improve urban runoff quality.

# 2. Materials and methods

## 2.1 Runoff synthesis

Runoff used in this study was synthetised 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  $NO_{3}^{3}$  (4- 5 mg/l). Although using a natural stormwater has advantages over using synthetic stormwater, however, maintaining consistency of its

concentration and characteristics is difficult [10]. Apart from this, due to rare and dispersed rain events in city of Isfahan, Iran which this study was conducted, synthetic stormwater was a better choice for this study. The characteristics of synthetised runoff have been illustrated in Table 1.

The chemicals used to synthesis the runoff 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<sub>2</sub>, ZnSO<sub>4</sub>.7H<sub>2</sub>O, (CH<sub>3</sub>COO)2Cd.2H<sub>2</sub>O, K<sub>2</sub>HPO<sub>4</sub> and KNO<sub>3</sub> using double-distilled water. Standard acid and base solutions (1 M H<sub>2</sub>SO<sub>4</sub> and 1 M NaOH) were used to adjust pH. Turbidity of the solution was adjusted using Kaolin.

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	
рН	6.5-7.5	

Table 1. Characteristics of synthesized runoff

### 2.2 Nano particle characteristics

Characteristics  $Fe_3O_4$  nano particles 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 nano particles using this equation at 454 reflection peak,  $2\theta \sim 36^{\circ}$  and  $2.54^{\circ}A$ , was estimated to be 37nm. This size was different from 60 nm that was given by the manufacturer (Aldrich), however, they acknowledged that this could be due to difference in NaOH and pH of the solutions was used.

Scientific name	Iron oxide magnetic nano particles		
Chemical formula	Fe <sub>2</sub> O <sub>3</sub>		
Purity (%)	99.2		
Particles size (nm)	60		
Morphology	spherical		
SSA $(m^2/g)$	55		
Bulk density (g/m <sup>3</sup> )	0.84		

Table 2. The characteristics of nano iron oxide particles

Point of zero charge (PZC) for  $Fe_3O_4$  nano particles 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 literatures [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 50 mm diameter (internal) plexiglass column which 200 mm of its height was filled with stainless steel wool. The total volume of the column was 400 ml which half of this was occupied by the stainless steel wool. The exposure time (retention time) of 10 min was allowed between runoff and nano particles. This is an optimum time has been experimented using  $Fe_3O_4$  nano particles [12].

Synthetic stormwater was flow through the column five times and for each run, 0.5 g/l nano iron oxide was added during exposure time of 10 min [12], then samples for further analysis was 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 and phosphate, turbidity and pH, respectively.



Fig. 1. The scheme of laboratory system

# 3. Results and discussions

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

Parameters	Minimum removal	Maximum removal	Average removal
	efficiency (%)	efficiency (%)	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 <sub>3</sub> <sup>-1</sup>	-	-	-

Table 3. Minimum, maximum and average removal efficiency



Fig. 2. Removal efficiency of pollutants from the column

#### 4. Discussion

As indicated in Table 3, turbidity mean removal efficiency 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 of filtration, settling and adsorption are primary removal process [13]. It has been claimed that zeta potential of sand filter columns reduces in presence of magnetic field and this leads to particle instability, aggregation and formation of larger 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. Nano particles are small size particles with large surface area and consequently their adsorption capacity is high. Apart from this, surface charges of magnetic nano particles are arranged so that atoms in the surface have high reaction capacity and this increase reaction between the nano particles and adsorbents [15]. Apart from this the magnetic field entrap iron nano particles 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  $Fe_3O_4$  nano particles are effective to remove metal ions from the solution. Shen (a) et al. [16] used  $Fe_3O_4$  nano particles of 8 nm with a contact time of 24 hours 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, XRD patterns for the sample collected proved that ion-adsorbed nano particles 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  $Fe_3O_4$  nano particles was used to remove organic matters from wastewater. They concluded that the  $Fe_3O_4$  nano particles 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 runoff was investigated by authors using sand filter column which was coated with  $Fe_3O_4$  nano particles [14]. Removal of phosphate from the sand filter coated with  $Fe_3O_4$  nano particles was less than current study. This supports that removal mechanism in column with stainless steel wool is mainly due to adsorption. Free  $Fe_3O_4$  nano particles 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 finding from other studies which adsorption mechanism is not a suitable method to remove nitrate [10].

#### 5. Conclusions

The study showed that the column with stainless steel wool in presence of  $Fe_3O_4$  nano particles and magnetic field is an effective method to remove heavy metals from urban runoff. 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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