INFLUENCE OF TEMPERATURE AND CONTACT TIME ON THE SYNTHESIS OF IRON OXIDE NANOPARTICLES FOR THE REMOVAL OF HEAVY METALS FROM ROOFTOP HARVESTED RAINWATER

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ABSTRACT: Rooftop harvested rainwater is an alternative source of drinking water. But researches from various parts of the world show that roof harvested rainwater is heavily contaminated especially with microorganisms and heavy metals. Iron oxide based nanoparticle is an attractive media for removal of heavy metals contamination from water. But due to practical difficulties they must be coated onto suitable supports like sand, polyurethane, etc. Previous study shows that the iron content in the iron oxide nanoparticle coated sand synthesized using biological methods employing chitosan templates was less, thus affecting the performance efficiency in removing heavy metals. Thus the present study focuses on the effect of two parameters, the temperature during coating and contact time of coating which affect the properties of synthesized iron oxide nanoparticle coated sand thereby improving their performance in the removal of two heavy metals namely lead and cadmium from rooftop harvested rainwater. The optimum removal of lead and cadmium occurs at 500^0C temperature and 60 minutes of contact time and the corresponding percentage removal was 82.66 and 74.74 respectively. An enhanced removal of 12.66% for lead and 24.74% for cadmium was also observed with respect to previous study where the above factors not optimized. Thus the study showed the significance influence of the above parameters on the properties of the synthesized media and their performance in removing heavy metals.

KEYWORDS: Iron oxide nanoparticles, Heavy metals, Rainwater.

INTRODUCTION

Domestic rooftop rainwater harvesting is receiving an increased attention worldwide as an alternative source of drinking water. Rainwater is generally considered as non-polluted, or atleast not significantly polluted, but may be acidic, contain traces of lead, pesticides, etc. depending on the locality and prevailing winds. Researches show that roof harvested rainwater is heavily contaminated microbiologically by a variety of indicator and pathogenic organisms as well as it contain elevated levels of toxic metals in case of metal rooftop. This indicates the need of proper treatment of rainwater if it is to be used for drinking [Appan, 1997; Chang et al., 2004; Meera and Ahammed, 2006].

Though the rainwater is contaminated microbiologically, heavy metals in harvested rainwater have particular interest due to their toxicity, ubiquitousness, etc. The commonly present heavy metals include zinc, lead and cadmium. In order to detoxify heavy metals, various techniques like photo catalytical oxidation, chemical coagulants, ion-exchange resins, adsorption, etc. have been employed [Lee et al., 2012]. Recently, nanomaterials have been suggested as efficient, cost effective and environmental friendly alternative to existing treatment materials, from the standpoints of both resource conservation and environmental remediation [Hu et al., 2006; Xu et al., 2012]. Nanomaterials especially derived from iron oxides is more attractive for removal of heavy metal contamination from the water because of their unique features like small size, high surface area to volume ratio, surface modifiability and magnetic property.

Iron oxide nanoparticles can be synthesized by physical, chemical and biological methods. Of these three methods chemical methods is widely used. But the use of toxic compounds limits their applications. Though several methods are available for the synthesis of nano iron, a definite protocol is not available for their synthesis. Green synthesis of

nanoparticles makes use of environmental friendly, non-toxic and safe reagents [Nidhin et al., 2007; Mahdavi et al., 2013; Patra and Baek, 2014]. The biological method of synthesis prevents the aggregation of particles and improves their stability. Due to practical difficulties, the iron oxide nanoparticles are coated onto some porous supports like sand, polyurethane forms, etc. Since sand is the commonly available filter media, the iron oxide nanoparticles are coated onto sand. Recent study shows that the performance of iron oxide nano coated sand was found to be only slightly superior when compared to iron oxide coated sand in removing heavy metals from roof harvested rainwater [Rasheed and Meera, 2016]. The various factors which affect the quality and quantity of iron oxide nanoparticles during synthesis include pH, reaction time, temperature, method of synthesis, reducing agent, stabilizing/binding material, nature of supporting media, pressure, etc.

MATERIALS AND METHODS

Sampling Site and Sample Collection

This study was carried out in Thrissur district. Metal rooftop harvested rainwater was collected from a house located at Manithara, Thrissur district. The roofing sheets are made up of galvanized iron (GI) sheets. This house is located at 10° 36' 1.22" N latitude and 76° 11' 10.81" E longitude. Many small scale industries like welding units, galvanizing units, forging units and foundry units are located near this site. The age of the roof is 5 years and has an area of 2500 sq. feet. The rainwater was collected in four polyethylene tanks of 2000 litres capacity each and age of the tank is 5 years. No first flush device was employed. The samples were collected during the month of January 2016. The rainwater was collected in the tank during the north east monsoon in Kerala in 2015. Clean and dry plastic containers of 10 litres capacity were used for sample collection and samples were stored at room temperature. Required amount of stored rainwater was withdrawn from the containers after thorough mixing when needed. Since the concentration of lead and cadmium was below detectable limit, the rainwater was spiked with known concentrations of lead and cadmium (2.019 and 0.792 mg/l for lead and cadmium respectively). Zinc was not considered since it is less toxic compared to lead and cadmium.

Media Preparation

River sand of gradation between 2.36 mm and 0.85 mm was taken as the media. The sand was soaked in 8% nitric acid solution for 24 hours, rinsed with de-ionized water to pH 7 and dried at a temperature of about 105^0C for 24 hours. It was then stored for further use.

Iron Oxide Nanoparticle Coating

The iron oxide nanoparticle coated sand was prepared using chitosan templates under different conditions. The factors which affect the synthesis, considered include temperature during coating and contact time of coating.

Chitosan is a natural polysaccharide having features like hydrophilicity, biocompatibility, biodegradability, antibacterial properties, etc. and also it has remarkable affinity for many bio macromolecules. It is mainly composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit).

Temperature

The coated sand was synthesized at 500^0C, 650^0C and 800^0C. The pH during coating was maintained at 7. For synthesis, 94g of chitosan was dissolved in 2% acetic acid. 1M $FeSO_4.7H_2O$ was added followed by 1000g sand. The solution was stirred for 30 minutes. Then the template-iron-sand mixed solution was treated at 500^0C, 650^0C and 800^0C in three sets of coating and maintained at that temperature for 120 minutes, after which it was cooled to room temperature at a rate of 10^0C/minute. Then the coated sand was washed several times with de-ionized water to remove loose precipitates. It was then dried and stored for further use.

Contact Time

The contact time considered were 30, 60 and 180 minutes. In this temperature and pH was maintained constant. 94g of chitosan was dissolved in 2% acetic acid. 1M $FeSO_4.7H_2O$ was added followed by 1000g sand. The pH was adjusted to 7. The solution was stirred for 30, 60 and 180 minutes in three sets. Then the template-iron-sand mixed solution was treated at 500^0C and maintained at that temperature for 120 minutes, after which it was cooled to room temperature at a rate of 10^0C/minute. Then the coated sand was washed several times with de-ionized water to remove loose precipitates. It was then dried and stored for further use.

Batch Study

Batch study was conducted to determine the effect of temperature and contact time during synthesis in the removal of heavy metals from rainwater. It was carried out in 250 ml Erlenmeyer flasks containing 2g adsorbent and 100 ml rainwater spiked with known concentrations of lead and cadmium. The solutions were shaken at 200 rpm in a temperature-controlled shaker at room temperature for 15 minutes. After that, the samples were collected and filtered through whatmann filter paper no.1. Finally, the concentration of lead and cadmium in the collected samples were analyzed using atomic absorption spectrophotometer.

RESULTS AND DISCUSSIONS

Properties of Sand

The bulk density, specific gravity and porosity of iron oxide nanoparticle coated sand and the methods of analysis are shown in Table 1.

Table 1. Properties of sand

Parameter	Iron oxide nanoparticle coated sand	Method of analysis
Bulk Density (kg/m^3)	1760	As per IS 2386 part III 1963
Specific gravity	2.85	
Porosity	0.65	

Influent Characteristics of Rainwater

Table 2 shows the influent characteristics of rainwater after spiking with known concentration of lead and cadmium.

Table 2. Influent characteristics of the sample

Parameter	Value
pH	6.4
Turbidity, NTU	BDL
Alkalinity, mg/l as $CaCO_3$	16.80
Iron, mg/l	0.52
Total Dissolved Solids, ppm	22.00
Lead, mg/l	2.019
Cadmium, mg/l	0.792

Batch Study

Effect of Temperature

Batch study was carried out at three different temperatures namely 500^{0}C, 650^{0}C and 800^{0}C. The pH was maintained at 7. It was conducted for a contact time of 15 minutes and the results are given in Table 4. The effluent samples were collected and analyzed for lead and cadmium.

Table 3. Results of batch study for the effect of temperature

Sl. No.	Media	Lead, mg/l	Cadmium, mg/l
1	Iron oxide nanoparticle at 500^{0}C	0.55	0.22
2	Iron oxide nanoparticle at 650^{0}C	0.57	0.23
3	Iron oxide nanoparticle at 800^{0}C	0.58	0.32

For temperature below 500^{0}C, the coating was found to be not stable. So the experiments were conducted from 500^{0}C to 800^{0}C. Maximum removal of both lead and cadmium was observed for temperature of 500^{0}C. As the temperature during coating of media is increased, the internal energy of the molecules in the system will increase. The internal energy of the molecules may include the translational energy, vibrational energy and rational energy of the molecules, the energy involved in chemical bonding of the molecules as well as the energy involved in nonbonding interactions. Too much heat

can cause the rate of an enzyme catalyzed reaction to decrease because the enzyme becomes denatured and inactive. Thus the removal was less at higher temperature.

Effect of Contact Time

Batch study was carried out at three different contact times namely 30, 60 and 180 minutes. The pH and temperature was maintained at 7 and 500^0C respectively. The results are given in Table 5. The effluent samples were collected and analyzed for lead and cadmium.

Table 4. Results of batch study for the effect of contact time

Sl. No.	Media	Lead, mg/l	Cadmium, mg/l
1	Iron oxide nanoparticle at 30 min	0.55	0.22
2	Iron oxide nanoparticle at 60 min	0.35	0.20
3	Iron oxide nanoparticle at 180 min	0.50	0.26

Maximum removal of lead and cadmium was observed for 60 minutes of contact time. As contact time increases, the removal of heavy metals by nanoparticle coated sand also increases. But increase in time beyond certain value leads to desorption by the adsorbent media.

Comparison with previous study

Characterization

The medium was characterized using energy dispersive spectroscopy (EDS). EDS is a valuable tool for qualitative and quantitative elemental analysis. Fig 1 gives the EDS spectrum of the iron oxide nanoparticle coated sand in the present study and Table 6 and Table 7 shows the elemental composition in the present and previous study.

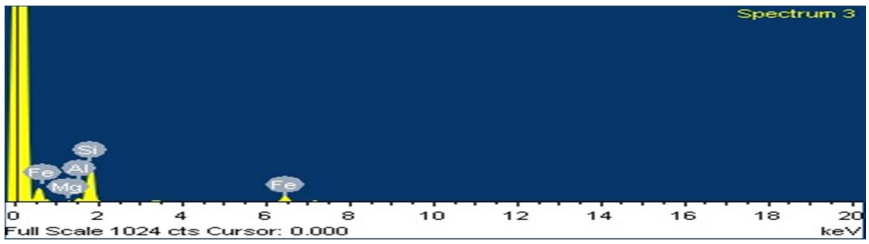

Figure 1. EDS of iron oxide nanoparticle coated sand in the present study

Table 5. Elemental composition of iron oxide nanoparticle coated sand in the present study

Element	Weight %	Atomic %
Mg K	0.59	0.87
Al K	4.31	5.72
Si K	51.25	65.31
Fe K	43.85	28.10
Total	100.00	100.00

Table 6. Elemental composition of iron oxide nanoparticle coated sand in the previous study [Rasheed and Meera, 2016]

Element	Weight %	Atomic %
O K	55.06	70.68
Al K	1.51	1.15
Si K	33.57	24.55
Fe K	9.85	3.62
Total	100.00	100.00

The iron content in the nanoparticle coated sand synthesized at 500^0C and 60minutes was 43.85 by weight percentage and 28.10 by atomic percentage. The iron content in the nanoparticle coated sand synthesized at 800^0C and 30 minutes in the study by Rasheed and Meera (2016) was found to be 9.85 by weight percentage and 3.62 by atomic percentage. Thus

the EDS results showed that, the iron content in the iron oxide nanoparticle coated sand is increased by 34 by weight percentage and 24.48 by atomic percentage.

Efficiency in the removal of lead and cadmium

Table 8 shows the comparison between present and previous study. The optimum removal of lead and cadmium by iron oxide nanoparticle coated sand synthesized at 500^0C and 60 minutes of contact time were obtained as 82.66% and 74.74% respectively. The iron oxide nanoparticle coated sand synthesized at 800^0C and 30 minutes of contact time shows 70% and 50% removal for lead and cadmium respectively. The results show an increase of 12.66% and 24.74% in the removal of lead and cadmium respectively.

Table 8. Comparison of performance efficiency in removal of lead and cadmium

Reference	Source	Media	Pollutant and its initial concentration	% removal
Rasheed (2016)	Rooftop harvested rainwater	Iron oxide nanoparticles coated sand synthesized using chitosan templates at 800^0C and 30 minutes	Lead, 2.0 mg/l	70.00
			Cadmium, 0.7 mg/l	50.00
Present study	Rooftop harvested rainwater	Iron oxide nanoparticles coated sand synthesized using chitosan templates at 500^0C and 60 minutes	Lead, 2.019 mg/l	82.66
			Cadmium, 0.792 mg/l	74.74

CONCLUSION

The iron oxide nanoparticle is a widely used adsorbent for the removal of heavy metals from water/wastewater. On account of high surface energy, naked iron oxide nanoparticles tend to aggregate and flocculate which might reduce the use of these particles. The aim of the present study was to study the influence of two different parameters that affect the property of iron oxide nanoparticle synthesis and their coating on sand in order to stabilize these particles and also to prevent their aggregation. The iron oxide nanoparticles were synthesized using chitosan templates and are coated on sand particles at two different conditions. The effect of temperature during coating and contact time of coating on the properties of synthesized nano iron coated sand and their performance in removing lead and cadmium from rooftop harvested rainwater were studied. The maximum removal of lead and cadmium were occurs at 500^0C and a contact time of 60 minutes. The percentage removal of lead and cadmium were 82.66% and 74.74% respectively for 500^0C temperature and 60 minutes contact time. A 34% increase of iron content and an enhanced efficiency of 12.66% and 24.74% in the removal of lead and cadmium were observed with respect to previous study.

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REFERENCES

[1] Appan A; (1997); Roof Water Collection Systems in some Southeast Asian Countries: Status and Water Quality Levels; Journal of Royal Society of Health; **117**; 319-323.

[2] Chang M., Mcbroom M.W. and Beasley R.S; (2004); Roofing *as a Source of Non-Point Water Pollution*; Journal of Environmental Management; **73**; 307-315.

[3] Hu J., Chen G. and Irene M.C.L; (2006); Selective Removal of Heavy Metals from Industrial Wastewater Using Maghemite Nanoparticle: Performance and Mechanisms; Journal of Environmental Engineering; **132**, **7**; 709-715.

[4] Lee S.M., Laldawngliana C. and Tiwari D; (2012); Iron oxide nano-particles-immobilized-sand material in the treatment of Cu(II), Cd(II) and Pb(II) contaminated waste waters; Journal of chemical engineering; **195-196**;103-111.

[5] Mahdavi M., Namvar F., Ahmad M.B. and Mohamad R; (2013); Green Biosynthesis and Characterization of Magnetic Iron Oxide (Fe_3O_4) Nanoparticles Using Seaweed (Sargassum muticum) Aqueous Extract; Molecules; **18**; 5954-5964.

[6] Meera V. and Ahammed M.M; (2006); *Water Quality of Rooftop Rainwater Harvesting Systems: A Review*; Journal of Water Supply Research and Technology – AQUA; **55.4**; 257-268.

[7] Nidhin M., Indumathy R., Sreeram K.J. and Nair B.U; (2007); *Synthesis of Iron Oxide Nanoparticles of Narrow Size Distribution on Polysaccharide Templates*; Bulletin Materials Science; **31, 1**; 93-96.

[8] Patra J.K. and Baek K.H; (2014); Green Nanobiotechnology: Factors Affecting Synthesis and Characterization Techniques; Journal of Nanomaterials; **2014**, 1-13.

[9] Rasheed R. and Meera V; (2016); Synthesis of iron oxide nanoparticles coated sand by biological method and chemical method; Procedia Technology; **24**; 210-216.

[10] Xu P., Zeng G.M., Huang D.L., Feng C.L., Hu S., Zhao M.H., Lai C., Wei Z., Huang C., Xie G.X. and Liu Z.F; (2012); *Use of iron oxide nanomaterials in wastewater treatment: A review*; Science of the Total Environment; **424**; 1-10.