original article

Treatment of synthetic urban runoff using manganese oxide-coated sand in the presence of magnetic field

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ABSTRACT

Aims: The purpose of this study was to investigate the efficiency of manganese oxide-coated sand in the presence of magnetic field to treat urban runoff.
Materials and Methods: A flow-through column having a diameter of 50 mm was filled with coated sand and used to conduct the experiments in this study. Atomic absorption, turbidimeter, pH meter, and spectrophotometer DR5000 were used to measure heavy metals, turbidity, pH, phosphate, and nitrate, respectively. The surface of coated sand was assessed by SEM. Energy dispersive X-ray analysis (EDAX) analysis was used to determine percentage of sand components.
Results: SEM and EDAX analyses confirmed that the sand has been coated with manganese oxide successfully. Results indicated that turbidity, Pb, Zn, and PO_4 removal efficiency by the coated sand in the presence of magnetic field were 89.6%, 65.9%, 81.1% and 67%, respectively. The results indicated that the coated sand is not able to remove NO_3.
Conclusion: Manganese oxide-coated sand filter in the presence of magnetic field improve the quality of urban runoff significantly. Authors believe that this approach is simple, economical and efficient as in comparison to other existing methods. This could be a promising treatment technology that can enhance quality of urban runoff and industrial wastewaters.

Key words: Magnetite field, manganese oxide, sand filter, urban runoff

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INTRODUCTION

Pollutants from an urban area are transported to receiving streams during a rainfall event, causing quality impairment of the waters. They play a critical role in degrading receiving water bodies and ecosystems. The pollutants can pose risks to humans, animals, and plants. In high concentrations, they cause technical and aesthetic problems.[1] Within receiving waters, the exposure of aquatic macro-organisms to metals depends not only on the concentrations of contaminants in the water but also on their bioaccumulation throughout the food chain.[2]

The most frequently reported metals in stormwater are cadmium (Cd), lead (Pb) and zinc (Zn), and concentrations of these ions in stormwater commonly exceed surface water quality guidelines by 10 times or more.[3]

If stormwater contaminated with heavy metals is discharged directly into natural water bodies, the non-biodegradable metals will be able to accumulate in the environment,

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causing both short-term (e.g. acute toxicity) and long-term (e.g. carcinogenic damages) adverse effects on human life. For example, chronic exposure to cadmium is known to enhance lipid peroxidation by increasing the production of free radicals in the lungs, which leads to tissue damage and cellular death, and chronic lead toxicity affects gastrointestinal, neuromuscular, renal, and hematological systems.[4] Phosphorus (P) that in the aqueous environment is most commonly present as orthophosphate (PO_4–P) has been the target compound for several treatment technologies. Excessive concentrations of this element, primarily as PO_4–P, are identified as a principal source of freshwater eutrophication. A main effect of eutrophication is the significant growth of algae and cyanobacteria that reduces dissolved oxygen content leading to the loss of aquatic biodiversity, odor production, and water quality problems related to prevailing anaerobic conditions. In addition to the potentially toxic health implications related to consumption of such water, cyanobacteria blooms may also result in significant economic losses related to decreased recreation, tourism, and freshwater commercial fisheries.[3,5]

Moreover, excess N has led to N saturation, eutrophication and associated water-quality problems, and contamination of major drinking-water supplies.[6]

Manganese oxides are typically the most important scavengers of aqueous trace metals in soil, sediments, and rocks because of their sorptive behavior. They have a large surface area, microporous structure, and high affinity for metal ions. Usually, the surface charge of manganese oxides is negative, and they can be used as adsorbents to remove heavy metals from wastewater. However, pure manganese oxide as a filter media is not favorable because of economic reasons and unfavorable physical and chemical characteristics, but coating manganese oxide to a media surface can provide an effective surface and may be a promising media for heavy metal removal from wastewater.[7]

Magnetic has been applied to remove heavy metals, color, phosphates, and oil from wastewater. For example Johan-Sohaili *et al.* acclaimed that this technology is a promising treatment process which enhance the separation of suspended particles from the sewage.[8] Also Tai *et al.* revealed that magnetized water prevents uptake of harmful metals, such as lead and nickel, by roots.[9] Some researchers reported that magnetic field affects water properties, such as light absorbance, pH, zeta potential, and surface tension.[10]

The objective of the research presented here was to investigate the efficiency of manganese oxide-coated sand (MOCS) in the presence of magnetic field to treat runoff from urban area.

MATERIALS AND METHODS

Materials used in this study were products of Merck Company. $PbCl_2$, $ZnSO_4.7H_2O$, (CH_3COO) 2Cd. $2H_2O$, KNO_3, and K_2HPO_4 were used for lead, zinc, cadmium, nitrate, and phosphate stock solutions, respectively. The solutions were used to prepare synthetic runoff solution. Kaolin was used to adjust turbidity of synthetic runoff. The pH of synthetic runoff was adjusted using 1N HNO_3 and NaOH. The characteristics synthetic runoff used in this study are represented in Table 1.

Media preparation

Sand filter media was mixed size of 2.36-0.85 mm sand obtained from a local quarry.[15] The sand was soaked in an 8% nitric acid solution overnight, rinsed with deionized water to pH 7.0, and dried at 105°C to make it ready for coating.

The acid-washed sand (500 ml volume) was coated using two moles of concentrated hydrochloric acid (37.5%) which was added over a 20 min period to a boiling solution of 0.5 M potassium permanganate in 1 L of deionized water and vigorously stirred before adding HCl. The sand was boiled for an additional 10 min, then filtered and washed to pH 7.0 using deionized water before let it to dry at room temperature of about 25°C.[11]

Column experimental

Columns used in this study were made of plexi glass with internal diameters, heights, and medium bed depth 5, 35, and 20 cm, respectively. Because the columns were operating in downflow mode, an overflow valve was provided to maintain 8 cm water above medium to avoid flow channelization.

Two magnets of 20 cm height with 0.7 T (Tesla) magnetic charge density were mounted around one of the columns to investigate the effects of magnetic field on the removal efficiency of the pollutants from the synthesized runoff. The optimum retention time in bed was considered to be 20 min.[9] Therefore, the effluent rate based on 0.4 L bed volume was estimated to be 20 cm^3/min. Before operation, once more the sand in the columns was rinsed with deionized water to remove any unbound metallic oxide.

Each column was operated for 60 h during which over 10 samples, each repeated three times, was collected. The pH of those samples was collected for measuring their nitrate and heavy metals were reduced to 2 by adding sulfuric and nitric acids, respectively.

Table 1: The concentrations of pollutants used to synthesis of runoff in this study

Pollutant	Concentration	Reference
Turbidity (NTU)	60	[11,12]
Lead (mg/l)	2.37	[13]
Zinc (mg/l)	2.54	[13]
Cadmium (mg/l)	0.52	[14]
Nitrate (mg/l)	4-5	[13]
Phosphate (mg/l)	9-10	[13]

Chemical analyses

Concentrations of lead, zinc, and cadmium in collected samples were measured using the Perkin Elmer 2380 atomic absorption spectrometer. Nitrate and phosphate were determined using the UV-Vis spectrophotometer (HACH DR5000). Turbidimeter (Euteoh Instruments TN 100) was used to measure turbidity. The Schott pH meter model CG-824 was used for pH analysis. The point of zero charge (pH_{PZC}) of manganese-modified natural sand was defined as the pH value at which the surface carries net zero charge. Hence, to evaluate the pH_{ZPC}, the acid and base titrations were carried out by taking 5 g of the solid sample in 500 mL of distilled water and titrated against the 0.1 mol/L of HNO_3 or NaOH solutions. The corresponding pH was recorded using a pH meter. The titration data were further utilized to evaluate the pH_{ZPC}.[16]

The characteristics of the coated sand were determined using scanning electron microscope (SEM), and energy dispersive X-ray analysis (EDAX) was used for identifying the elemental composition of sand.

RESULTS

Figure 1 shows the SEM image of sand before and after coating with manganese oxide. SEM images of acid washed sand [Figures 1a and b] shows that the uncoated sand have smooth surface, but the surface of the coated one [Figures 1c and d] appeared to be rough because of the deposited metal oxide particles. So the coated sand has more micropores and higher specific surface areas. EDAX analyses in Figure 2 show the elemental composition of sand before and after coating. The EDAX spectrum of sand before coating showed only the signals of Si and O, C, and Al. After coating, the peak of manganese in the figure is representing the presence of manganese oxide deposit. The removal efficiency of the sand filter media for turbidity, lead, zinc, cadmium, phosphate and nitrate are presented in Figures 3-8. The characteristics of the media both before and after coating are given in Table 2.

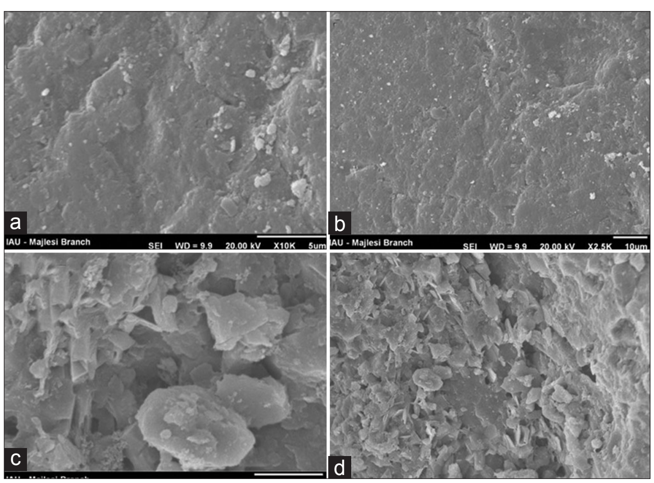


Figure 1: SEM images of sand: (a, b) before coating with manganese oxide and (c, d): after coating with manganese oxide

DISCUSSION

The average removal efficiency of colloidal particles from the synthetic runoff by the coated sand was 88.7%. The performance of the column to remove turbidity was improved over time as indicated in Figure 3. This could be due to the development of "dirty layer" similar to the one develops in biosand/slowsand filters.[11] The removal mechanisms in the column are filtration, settling, and adsorption.[17] A removal effeciency of 87.5% of colloids from the coated sand filter (sand size of 0.8-0.3 mm) without magnetic field has been reported.[11] However, in this study the sand size was 0.85-2.36 mm and with the presence of magnetic field the removal efficiency of colloidal improved slightly.

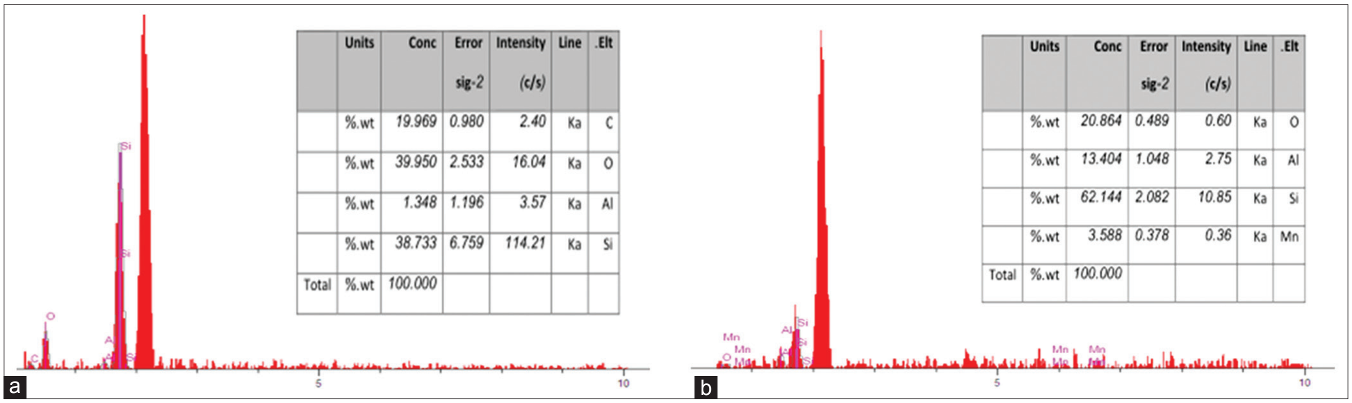
Colloidal stability is influenced by the application of magnetic field, possibly indicating a reduction in charge density within the Stern layer. It has also been proposed that a reduction in zeta potential of turbidity particles lead to instability, aggregation, and consequently sedimentation of particles.[10]

In this study, the removal efficiency of lead and zinc were 64% and 81%, respectively. Previous studies reported an average removal efficiency of 54% and 29% for lead and zinc, respectively.[11,14] It is evidence that sand coated with manganese oxide has improved the adsorption of heavy metals. Metal oxides increases the numbers of adsorption sites and with the presence of water, oxide surfaces such as Mn and Fe are covered with surface hydroxyl groups, protons, and coordinated water molecules. These mineral surfaces are amphoteric, with protons and hydroxyl ions coexisting at the surface in relative populations determined by solution pH. The amphoteric behavior of the surface leads to a point of zero charge (PZC) definition. The point of zero charge of MOCS is 6.4, which is generally below or in the range of pH of natural waters. This implies that MOCS has a net negative charge in the normal range of natural waters pH. Powder X-ray diffraction (XRD) analysis and infrared (IR) spectroscopic analysis showed that manganese oxide coating consists of a mixture of birnessite

Table 2: Column media characteristics

Media	Specific gravity	Bulk density (kg/m^3)	Point of zero charge (PZC)*	Specific surface area (m^2/g)
Uncoated sand	2.60	1620	6.8	0.22
Manganese oxide-coated sand	2.49	1500	6.4	1.51

*The PZC is the pH at which the net surface charge is zero.



	Units	Conc	Error sig-2	Intensity (c/s)	Line	.Elt
	%.wt	19.969	0.980	2.40	Ka	C
	%.wt	39.950	2.533	16.04	Ka	O
	%.wt	1.348	1.196	3.57	Ka	Al
	%.wt	38.733	6.759	114.21	Ka	Si
Total	%.wt	100.000				

	Units	Conc	Error sig-2	Intensity (c/s)	Line	.Elt
	%.wt	20.864	0.489	0.60	Ka	O
	%.wt	13.404	1.048	2.75	Ka	Al
	%.wt	62.144	2.082	10.85	Ka	Si
	%.wt	3.588	0.378	0.36	Ka	Mn
Total	%.wt	100.000				

Figure 2: EDAX spectra of sand: (a) before coating with manganese oxide and (b) after coating with manganese oxide

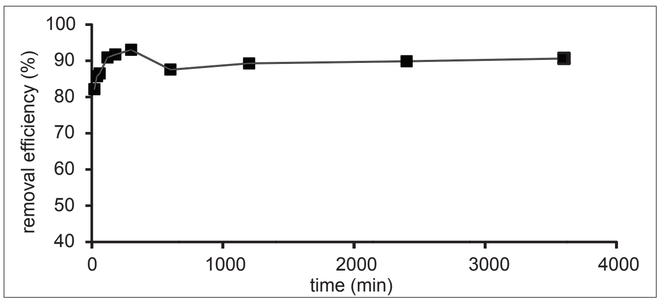


Figure 3: Removal efficiency of turbidity by the column in different operation times

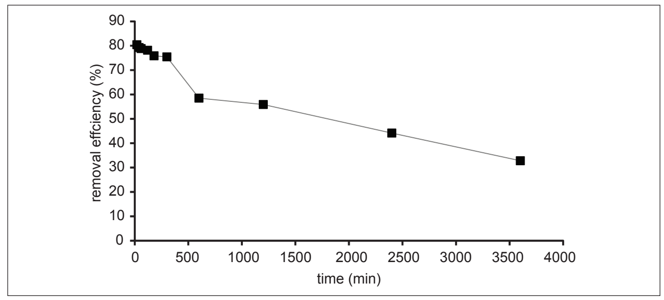


Figure 4: Removal efficiency of lead by the column in different operation times

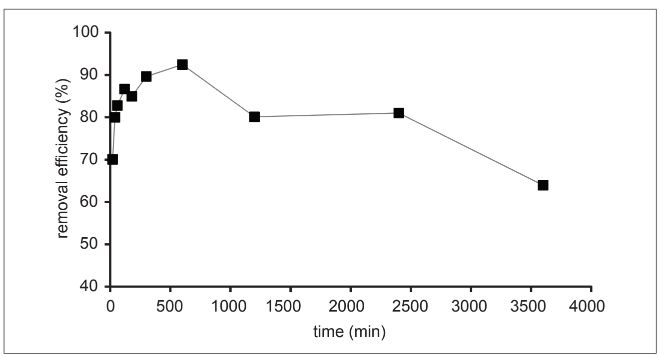


Figure 5: Removal efficiency of zinc by the column in different operation times

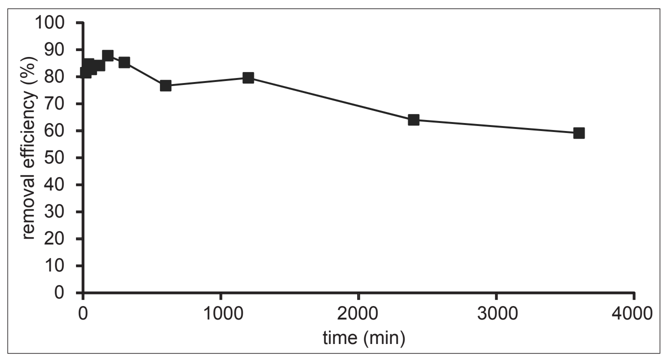


Figure 6: Removal efficiency of cadmium by the column in different operation times

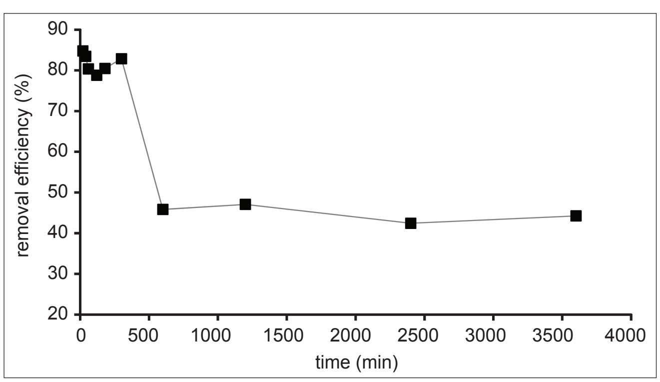


Figure 7: Removal efficiency of phosphate by the column in different operation times

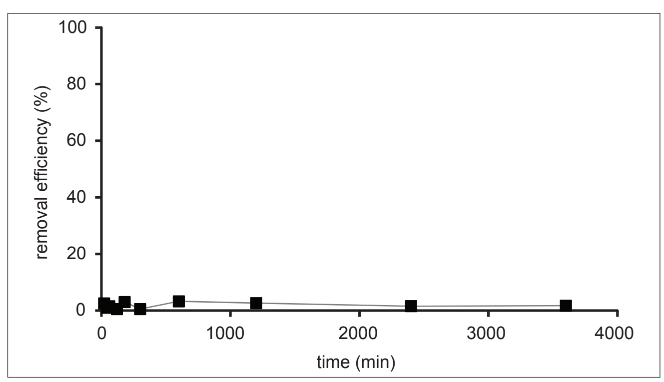


Figure 8: Removal efficiency of nitrate by the column in different operation times

and cryptomelane. At pH 7, pure cryptomelane (-MnO_2) had a negative charge of 4 μmol/m^2, and birnessite (-MnO_2) had a negative charge of 18 μmol/m^2. These characteristics explain the high efficiency of MOCS in removing heavy metals.[11]

Hatt *et al*. reported that sand filters are not a suitable treatment option for phosphate removal.[14] However, in this study a removal efficiency of 67% was attained which is in coordinate with study by Achak *et al.* and Boujelben *et al.* for removing phosphate using sand filters.[18,19] Scholes *et al.* reported that adsorption is a physico-chimical adherence that controlled by factors such as particulate surface area and surface composition.[17] Moreover, Achak *et al.* emphasize that ions are well retained by the cations of the sand such as iron and manganese oxides, etc.[18]

The results of this study show that the effect(s) of magnetic field on removal of the heavy metals and phosphate are consistent with results of Alkhazen *et al.*[10] There is no information about the mechanisms of magnetic field on the solution ions. But increasing of removal efficiencies can be attributed to the magnetic force that breaks hydrogen bonds between water molecules. So the ions separate and combine with elements and precipitate.

In this study, nitrate was not removed by the coated sand. A similar result was obtained by Hatt *et al.* who suggested biochemical modification may improve nitrate removal.[14] However, a high removal efficiency of nitrogen in the Achak *et al.* study was attributed to the development of biofilm that allowed oxidation of all nitrogen forms in the filter.[18]

Results of this study indicated that MOCS has a significant efficiency in improving urban runoff quality. Furthermore, magnetic field increased removal efficiencies of pollutant from runoff. Therefore, MOCS in the presence of magnetic field could be a promising system for treatment of urban runoff. It seems that this approach is easier, economical, and efficient as in comparison with other existing methods. One limitation with this study is that synthesis runoff was used and more tests on real runoff are needed.

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REFERENCES

1. Jang Y-C, Jain P, Tolaymat T, Dubey B, Singh S, Townsend T. Characterization of roadway stormwater system residuals for reuse and disposal options. Sci Total Environ 2010;408:1878-87.
2. Ancion PY, Lear G, Lewis GD. Three common metal contaminants of urban runoff (Zn, Cu and Pb) accumulate in freshwater biofilm and modify embedded bacterial communities. Environ Pollut 2010;158:2738-45.
3. Okochi NC, McMartin DW. Laboratory investigations of stormwater remediation via slag: Effects of metals on phosphorus removal. J Hazard Mater 2011;187:250-75.
4. Wu P, Zhou Y. Simultaneous removal of coexistent heavy metals from simulated urban stormwater using four sorbents: A porous iron sorbent and its mixtures with zeolite and crystal gravel. J Hazard Mater 2009;168:674-80.
5. Rosenquist SE, Hession WC, Eick MJ, Vaughan DH. Variability in adsorptive phosphorus removal by structural stormwater best management practices. Ecol Eng 2010;36:664-71.
6. Collins KA, Lawrence TJ, Stander EK, Jontos RJ, Kaushal SS, Newcomer TA, *et al.* Opportunities and challenges for managing nitrogen in urban stormwater: A review and synthesis. Ecol Eng 2010;36:1507-19.
7. Han R, Zou W, Li H, Li Y, Shi J. Copper (II) and lead (II) removal from aqueous solution in fixed-bed columns by manganese oxide coated zeolite. J Hazard Mater 2006;137:934-42.
8. Johan S, Fadil O, Zularisham A. Effect of Magnetic Fields on Suspended Particles in Sewage. Malaysian J Sci 2004;23:141-8.
9. Tai CY, Wu CK, Chang MC. Effects of magnetic field on the crystallization of CaCO3 using permanent magnets. Chem Eng Sci 2008;63:5606-12.
10. Alkhazan MMK, Saddiq AA. The effect of magnetic field on the physical, chemical and microbiological properties of the lake water in Saudi Arabia. Evol Biol Res 2010;2:7-14.
11. Ahammed MM, Meera V. Metal oxide/hydroxide-coated dual-media filter for simultaneous removal of bacteria and heavy metals from natural waters. J Hazard Mater 2010;181:788-93.
12. Annadurai G, Sung SS, Lee DJ. Simultaneous removal of turbidity and humic acid from high turbidity stormwater. Adv Environ Res 2004;8:713-25.
13. Haijian Nejad M, Vahid Dastjerdi M, Yarahmdi M, Shahsavani A. Investigation of urban runoff quality in isfahan hezar jarib area. Report Number 285009, Isfahan University of Medical Science, 2010.
14. Hatt BE, Fletcher TD, Deletic A. Treatment performance of gravel filter media: Implications for design and application of stormwater infiltration systems. Water Res 2007;41:2513-24.
15. Liu D, Sansalone JJ, Cartledge FK. Comparison of sorptive filter media for treatment of metals in runoff. J Environ Eng 2005;131:1178-1186.
16. Tiwari D, Laldanwngliana C, Choi CH, Lee SM. Manganese-modified natural sand in the remediation of aquatic environment contaminated with heavy metal toxic ions. Chem Eng J 2011;171:958-66.
17. Scholes L, Revitt DM, Ellis JB. A systematic approach for the comparative assessment of stormwater pollutant removal potentials. J Environ Manage 2008;88:467-78.
18. Achak M, Mandi L, Ouazzani N. Removal of organic pollutants and nutrients from olive mill wastewater by a sand filter. J Environ Manage 2009;90:2771-9.
19. Boujelben N, Bouzid J, Elouear Z, Feki M, Jamoussi F, Montiel A. Phosphorus removal from aqueous solution using iron coated natural and engineered sorbents. J Hazard Mater 2008;151:103-10.

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