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RE-USABILITY STUDIES OF ADSORPTIVE REMOVAL OF SOME HEAVY METALS BY MAGNETITE NANOPARTICLES FROM AQUEOUS SOLUTION

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Abstract

The ecosystem and public health and safety may be at risk if untreated industrial wastewater effluent is released into the natural environment. The rate of water-borne illnesses is extremely concerning, according to records that are currently available from many health centers in most developing countries. Elevated physicochemical and biological properties concentrations in industrial wastewater effluent have the potential to cause problems for the [redacted]

Keywords: *Re-usability, adsorption, pollutant, nanoparticles, removal, analysis*

environment and public health (Dydo et al., 2005; Fujita et al., 2005). In light of this, treating wastewater effluent is crucial before releasing it into the environment. In light of this, wastewater effluent must be cleared of all biological and physico-chemical impurities before being released into the environment. The goal of this study is to compare the biological and physico-chemical

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characteristics of industrial wastewater effluent with the W.H.O. standard discharge limit. Furthermore, the study used a standard operating procedure and technology to remove the pollutants from the waste water by using magnetite nano-particles as an adsorbent. The aim of the study is to investigate the re-usability potential on the adsorptive removal of some heavy metals from Aqueous Solution by magnetite nanoparticles. The result shows the as the time progresses the removal percentage increases with decrease in the filtrations cycles across all the contaminants. The first cycle shows higher ($p < 0.05$) of efficiency of the contaminant removal with the last cycle having the least. The treated effluent was analyzed, and a substantial removal was achieved with 94.21%, 89.62%, 77.26%, and 74.39% at 250 minutes contact time, in the removal efficiencies of copper, zinc, turbidity and boron respectively.

Introduction

Nanoparticles play a vital role in the removal of metals from wastewater. There are several adsorbents being employed for heavy metal removal. Magnetite nanoparticles have received significant attention due to its multifunctional properties including, Nano size, magnetic separation capability, high adsorption, simple synthesis and coating technique and surface modification(Al-Jabri et al., 2018). Furthermore, an efficient, economic, scalable and non-toxic synthesis of Fe_3O_4 nanoparticles is highly desired for practical applications and fundamental research (Giraldo et al., 2013). Generally, adsorption of heavy metals by magnetic nanoparticle (Fe_3O_4) is associated to the surface chemistry of the adsorbate (heavy metals) and the adsorbent (magnetite) due to electrostatic attraction between heavy metals cations and negatively charged adsorption site. This is mainly related to ionic radii of the heavy metals. In general, the pH of the aqueous solution is an important parameter in the heavy metal ion adsorption process.

The cations removal is dependent on proton concentration in the solution. Magnetite surface has a positive charge at pH below 7.0 and a negative charge at pH higher than 7.0 (Hou et al., 2003). It should also be noted that magnetite is an amphoteric solid, which can develop charges in the protonation, ($Fe -$

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$OH + H^+ \rightarrow Fe - OH^{2+}$) and deprotonation ($Fe - OH \rightarrow Fe - O^- + H^+$) reaction of FeOH sites on surface (Wang et al., 2011). The surface could charge differently and behave as an anion or cation exchanger according to the pH of the solution. It is very critical to realize that negative, positive and neutral functional groups can coexist on the surface of magnetite. At pH less than point zero charges (pH < pH_{zpc}, the $FeOH^{2+}$ groups predominate over FeO^-) groups, but notwithstanding the surface may still have a net negative charge. The number of $FeOH^{2+}$ groups is equal to FeO^- groups at pH_{zpc}. As the pH increases, the number of FeO^- equally increases. Magnetite particles may either adsorb negatively or positively charged species by electrostatic attraction depending on pH. Liu et al. (2019) investigated the application of magnetic ferrite nanoparticles for the removal of Cu (ll) from copper ammonium wastewater. The result shows that copper adsorption capacity of 124.80 mg/g was achieved under optimum condition of pH 8. Similarly, Luo et al., (2015) utilizes magnetic chitosan/cellulose (c-Fe_2O_3 nanoparticles) to remove Cu^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution and recorded a Cu^{2+} adsorption efficiency of 92 % followed by Cd^{2+}, (89%) and Pb^{2+} (85 %). Giraldo et al. (2013) equally reported removal efficiencies of Cu (80 %), Zn(ll) 70 %, Mn(ll) 70 %, while Pb(ll) adsorption efficiency increases to 92.3 % at optimum pH. Furthermore, Castro et al. (2018) was able to record removal efficiencies of 97.7 %, 20.1 % and 60 % for Cu, As, Cr and Zn from the open-pit lake using the biogenic iron compound. In contrast, Al-jabri et al., (2018) was able to remove copper from aqueous solution using magnetic nanoparticles and recorded a slight reduction in removal efficiency as compared with the previous studies.

Adsorption is a surface phenomenon in which a solution containing the adsorbate gets adsorbed on the surface of an adsorbent. Adsorption phenomenon can be of two types; one is physico-sorption, in which the adsorbate binds to the adsorbent due to Vanda der Waals forces, and the other is chemisorption, which occurs due to chemical reaction between adsorbate and adsorbent. Physico-sorption is reversible, weak and usually endothermic, while chemisorption is irreversible, selective and exothermic Adsorption processes are extensively used in wastewater treatment for biological and physicochemical properties. Heavy metals are toxic elements having specific gravity greater than 5g/cm^3 e.g. Zn, Fe, Cu, Ni, Fe, Pb Cr, Hg, etc

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Because of the exponential development of industries, the tremendous amount of wastewater pollution into the atmosphere is one of the significant concerns that will seriously impact human health in the future. In particular, heavy metals are found in the majority of industrial wastewater as a group of toxic contaminants. This form of a pollutant can accumulate in living organisms and is not biodegradable (Pakdel Mojdehi et al., 2019).

It is essential to remove heavy metal ions from water sources because of their hazardous effect (García-Lestón Julia et al., 2010). Copper is one of the highly toxic heavy metals that can damage human organs, such as the liver and kidneys. Due to its adverse effect on the human being, copper ions are required to be removed from industries' wastewater before discharge (Pakdel Mojdehi et al., 2019).

Several methods have been developed to eliminate heavy metals, including copper ions, as a toxic metal ion (Ren et al., 2010). Lambert et al., (2014) reported 86% copper removal in leachate from mining residues using electrochemical technology via copper electrode and current intensity of 1.3 A during 80 min. So many studies have focused on the adsorptive elimination of Cu(II) by adsorbents or membranes (Jasiewicz & Pietrzak, 2013). Metal ions are highly toxic, non-biodegradable and may have a possible carcinogenic effect (Xiarchos et al., 2008). The EPA's list of priority pollutants includes heavy metals such as cadmium, copper, lead, arsenic, nickel and zinc (Kim et al., 2006; Xiarchos et al., 2008). High concentrations of heavy metals may accumulate in the human organs. If the ions mentioned above are discharged directly into the sewage system, the activity of biological treatment plants can be critically impaired (Xiarchos et al., 2008). According to the National Secondary Drinking Water Regulations of the EPA, the limit for zinc in drinking water is 5 mg L^{-1}. [(Dietrich & Burlingame, 2015). The wastewater standard is 2.61 mg L^{-1} for zinc according to the EPA (Yurlova et al., 2002).

Zinc is an essential heavy metal for biological functions; however, it becomes hazardous at specific concentrations, at high concentrations, causes gastrointestinal distress and diarrhoea (Corami et al., 2007). In 2004, the chemical industry accounted for 65 % of direct zinc discharges in Finland, according to the European Pollutant Pollution Register (EPER). Raw organic and inorganic chemicals are the sources of such wastewater (Scheumann & Kraume, 2009).

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According to the Iranian Department of Environment (IDE), 85% of direct zinc discharges in Iran is due to the electroplating industry in 2006. It is, therefore, essential to develop and apply effective treatment processes, and many methods have been used to regulate metal toxicants. Chemical precipitation, adsorption, ion exchange, chelating, evaporation, coagulation-flocculation, flotation, electro-deposition, liquid-liquid extraction, and so on are currently common techniques for the treatment of wastewater containing heavy metal ions. These methods, however, have their shortcomings, such as secondary deposition waste, inconvenient process, high cost, difficulty in recycling metal ions, etc.(Scheumann & Kraume, 2009)]. Treating wastewater effluent is crucial before releasing it into the environment. In light of this, wastewater effluent must be cleared of all biological and physico-chemical impurities before being released into the environment. The goal of this study is to compare the biological and physico-chemical characteristics of industrial wastewater effluent with the W.H.O. standard discharge limit.

Materials and Method

Sample Collection

A confined container was used to collect an industrial wastewater sample from the site. Standard Methods for the Examination of Water and Wastewater (APHA, 2005) were followed in the collection and preservation of the sample. The sample was taken right away to the lab and kept at 4 °C in a chiller. The Standard Method for the Examination of Water and Wastewater (APHA, 2005) was used to explore a few chosen parameters, including pH, COD, color, turbidity, TSS, TDS, Cu, Zn, Fe, and B.

Instruments and Chemicals Used:

Conical flask, cell holder, concentrated H_2SO_4 solution, deionized water, pipetted and burrate, UV-vis spectrophotometer (DR/4000u), System Milli-Q water (18 MO cm), and Boron ver 3 reagents. Cu ver 1 copper reagent powder pillow, Zinco Ver 5 Reagent powder pillow

Analytical Method

The continuous hybrid system study, investigated investigated based on the Standard Method for the Examination of Water and Wastewater (APHA,2005).

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These parameters were analyzed using the UV-spectrophotometer (HACH DR/400U) at an absorbance wavelength of 605, 560, 620 and 860 nm, respectively.

Magnetite (Fe_3O_4) Adsorption

In batch examinations, a standard zinc, copper, iron and boron solutions (1000 ppm) was prepared by dissolving 6.0 g of boric acid (H3BO3) in 1.0 L of deionized water. 100 milliliters of boric acid at different pH values (2–10), dosages (0.5–0.7g), and contact times (180–220 minutes) were added to a 250 milliliter conical stopper cork flask. The sample was put on an orbital shaker moving at 200 rpm and then removed at various intervals. A UV-vis spectrophotometer (Hach DR/4000u spectrophotometer) was used to measure the boron uptake. The adsorption capacity q_e (mg/g) and removal efficiency Re (%) of boron were calculated using equation () and (2) (Öztürk & Kavak, 2004).

$$q_e = \frac{(C_o - C_f)}{M} V \quad (1)$$

C_o *and* C_f are the initial and equilibrium concentration of boron in the sample (mg/L)

q_e Is the equilibrium boron concentration (mg/g),

M is the adsorbent mass (g), and V (L) is the volume of the boron from a stock solution

The percentage removal of boron was calculated using equation (9).

$$\text{Percentage Removal (\%)} = \frac{C_o - C_f}{C_o} \times 100 \quad (2)$$

C_o = the initial concentration in sample (mg/L) and C_f is the equilibrium concentration in sample (mg/L).

Copper Analysis

Bicinchoninate method 8506 was used to determine the copper concentration. Cu ver 1 copper reagent powder pillow was added to 10 ml of sample. The prepared sample is placed into the cell holder of UV-vis spectrophotometer (DR/4000u) at the wavelength of 560 nm, and then zeroing using the blank sample to ensure accuracy. Result in mg/L of copper is displayed. Afterwards, the concentrations of the samples were determined and recorded as either initial or final concentration using equation 1.

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Zinc Analysis

Hach program 3850 was selected on the UV-vis spectrophotometer at a wavelength of 620 nm. Zinco method 8009 was used to determine zinc concentration. 20 ml of sample was filled into a 25-mL graduated cylinder. Zinco Ver 5 Reagent powder pillow was added to the cylinder. The content inverted several times to dissolve the powder completely. 10 mL of the solution poured into the sample cell (blank). 0.5 mL of cyclohexanone was added into the remaining solution in the graduated mixing cylinder. After 30 minutes reaction, the solution was poured into the cell and then placed in the cell holder. Result in mg/L zinc displayed after the light shield closed.

Turbidity Analysis

The number of turbidity program was selected on the UV-vis spectrophotometer at a wavelength of 860 nm. The leachate and the blank samples were prepared in 10 mL vials tubes. The samples are placed into the cell holder, light shield closed. Result in mg/L of turbidity displayed. The percentage of turbidity removal was determined using Equation 1

Plastic Ball Sorbent (PBS) Re-usability Studies

The plastic ball sorbent (PBS) can regain its adsorptive capacity when it is subjected to a simple desorption treatment using hydrogen peroxide and ethanol solution (Tuzen et al., 2018). These reagents were chosen because of their availability and oxidizing capacity (Hager & Brolo, 2003). They also generate readily hydroxide radical, which is a very strong oxidant for desorption. For 30 minutes, the used PBS were dipped into a hydrogen peroxide solution and then moved to a 70% concentrated ethanol solution for 1h. To displace the adsorbate from the active sites, the PBS was placed under running tap water. The reusability studies of the treated PBS were repeated three times to confirm its adsorption recovery capacity. The percentage of Boron, copper, Zn and turbidity removal were used to the consistencies in the adsorption performance. Statistical analysis was carried out on the data obtained using ANOVA to check for significance in the variance at a confidence level of 95%.

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Result and Discussion

The wastewater sample's physical-chemical and biological characteristics. The physicochemical properties of the wastewater sample employed in this investigation are shown in Table 1. Table 1 showed that there was a considerable increase in boron, turbidity, zinc and copper content over the DOE standard. Consequently, it is essential that material be treated before to being released into the environment.

Table. 2: Characteristic of Wastewater Sample

Parameter	Average Value	DOE Standard A
pH	9.59 ± 0.05	5.5-9.0
TSS	426.67 ± 15.5	100
Turbidity	321.67 ± 8.5	NA
COD	2256.67 ± 100.5	200
Boron	8.2 ± 0.55	1.0
Zinc	1.06 ± 0.35	2.0
Color	229 ± 3.5	200
Copper	2.42± 0.12	1.0

(Department of Environment, 2010) *All units are in mg/L except pH

Plastic Ball Sorbent Reusability Analysis

Table **2** shows the % of the contaminant's removal at different cycle of filtrations. The result shows the as the time progresses the removal percentage increases with decrease in the filtrations cycles across all the contaminants. The first cycle shows higher ($p < 0.05$) of efficiency of the contaminant removal with the last cycle having the least. However, there was no significant ($p > 0.05$) different at time 50 minutes for Br and Cu. The filtrations cycle is sensitive in turbidity among all the varying time compare to Br, Cu and Zn. Consequently,

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as time and filtrations cycles increase, the removal efficacy decreases. This is attributed to deterioration in the availability of active pore sites. The results for all the contaminants seem to follow a definite trend. That is, as time advances, the improved efficiency and the efficacy of filtrations cycles reduce.

Table 2: % of contaminants removal at different cycle of filtrations

Parameters	Time (min)	Cycles			
		1	2	3	p value
Boron	50	62.2±0.70	62.2±0.70	60.98±0.70	0.4218
	100	65.85±0.70^{a}	63.01±0.41^{b}	62.20±0.70^{b}	0.0136
	150	68.29±70^{a}	64.63±1.86^{a}	64.63±0.70^{a}	0.125
	200	72.36±0.41	69.11±2.26	68.29±0.70	0.1715
	250	73.17±0.70^{a}	70.73±0.70^{b}	67.07±0.70^{c}	0.0025
Turbidity	50	62.31±0.18^{a}	61.01±0.18^{b}	59.19±0.18^{c}	<.0001
	100	66.98±0.18^{a}	62.31±0.18^{b}	60.75±0.18^{b}	<.0001
	150	69.47±0.18^{a}	63.55±0.18^{b}	61.99±0.18^{c}	<.0001
	200	71.65±0.18^{a}	64.59±0.27^{b}	63.44±0.10^{c}	<.0001
	250	71.34±0.18^{a}	64.38±0.27^{b}	63.86±0.18^{b}	<.0001
Copper	50	84.30a±0.24	83.06b±0.36	81.54c±0.24	0.0015
	100	85.68±0.36^{a}	84.30±0.24^{b}	82.64±0.24^{b}	0.0009
	150	86.78±0.24^{a}	84.57±0.36^{b}	83.88±0.24^{b}	0.0009
	200	88.43±0.24^{a}	85.95±0.24^{b}	85.95±0.24^{b}	0.0005
	250	88.43±0.23^{a}	85.67±0.28^{b}	86.78±0.24^{c}	0.0007
Zinc	50	85.85±0.54^{a}	83.02±0.54^{b}	80.19±0.54^{c}	0.001
	100	86.79±0.54^{a}	84.91±0.54^{b}	80.19±0.54^{b}	0.0004
	150	81.132±5.45^{a}	84.90±0.54^{a}	83.96±0.54^{a}	0.6978
	200	93.40±0.54^{a}	86.79±0.54^{b}	85.85±0.54^{b}	0.0001
	250	93.08±0.83^{a}	87.74±0.54^{b}	85.22±0.63^{c}	0.0005

a,b,c.. Means on the same raw carrying same superscripts are not significantly different. $P < 0.05$

Conclusion and Recommendation

The current study investigates re-usability efficiency on the adsorptive removal of some heavy metals from aqueous solution utilizing magnetite (Fe_3O_4) nanoparticles as a sorbent. Initially, at the adsorption section the wastewater was subjected to adsorption process for 250 minutes contact time, using nano-magnetite coated onto the plastic ball as a sorbent. The treated effluent was

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analyzed, and a substantial removal was achieved with 94.21%, 89.62%, 77.26%, and 74.39% at 250 minutes contact time, in the removal efficiencies of copper, zinc, turbidity and boron respectively. Base, on the high adsorption efficiencies recorded by Fe_3O_4 after three cycles of filtration. The Fe_3O_4 nanoparticle is highly recommended for the relation of heavy metals and other contaminants from wastewater.

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