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Removal of heavy metal ions from industrial waste water by nano-ZnO in presence of electrogenerated Fenton's reagent

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Abstract : In recent years, there has been increasing interest in finding innovative solutions for the efficient removal of contaminants from water, soil and air. The polluted wastewater using the Fenton's reagent with nano metal oxide has been systematically studied using experimental design technique. Experiments were conducted to examine the effects of pH, amounts of ferrous sulfate ($FeSO_4$), hydrogen peroxide (H_2O_2), temperature and the concentration of nano metal oxide on the removal of heavy metal ions. A second order kinetic model was adopted to represent the Fenton oxidation of wastewater. The relation between the reaction rate coefficient and Fenton was experimentally established.
Keywords: Fenton oxidation, hydrogen peroxide, kinetics and wastewater treatment.

1. Introduction

Water pollution is of great concern since water is the inevitable requisite for the survival of all living organisms. Water pollution has become a continuous increasing problem on the earth which is danger for living things. Among the various water pollutants, heavy metals require special attention because of their toxic effect on humans and the environment. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products[1]. The increased use of heavy metals by industries resulted in an increase amount of metallic substances in natural source water[2]. The sources of metal ion pollutants are wastewaters of mining industries, paints and pigment industries, fertilizer industries, metal plating industries, batteries and tannery industries[3]. A large number of elements fall into this category, but lead, copper and cadmium are those of relevance in the environmental context[4,5]. Removal of these heavy metals from industrial wastewater has become important because its toxicity in human leads to disruption of the biosynthesis hemoglobin, rise in blood pressure, kidney damage, miscarriages and abortions, brain damage and learning disabilities in children[6]. Commonly used methods for the removal of heavy metals from aqueous solutions are chemical precipitation, co-precipitation, adsorption, flocculation, reverse osmosis, ion exchange, electro deposition and filtration[7]. Most of these methods have several disadvantages such as chemical requirements, time consuming procedure, production of large amount of sludge, low efficiency and less cost effective[8]. However,adsorption method is considered to be more efficient, cost effective and free from sludge formation. Fenton with nano inorganic fillers is another advanced process for the mineralization of various pollutants. Nanomaterials have a wide range of applications, as in the technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine and water treatments[9,10]. The possibility of preparing Fenton's reagent in the form of nanoparticles has opened a new and exciting research field, with revolutionary applications not only in the electronic/modern technology but also in the field of environmental remediation. So, scientists are eager to resolve these issues to make the environment clean. In this work, we aimed to investigate the potential of zinc oxide in the presence of Fenton's reagent as adsorbent to remove heavy metals.

The synthesized nanoparticles were characterized using Fourier Transform Infra-Red spectroscopy (FT-IR) confirms the presence of corresponding functional moieties in the nanoparticles. Themorphology was studied using scanning electron microscopy (SEM). Thermal analysis (TGA) was carried out to investigate the thermal stability of the nanoparticles. The objective of this work was to investigate the potential of the synthesized nanoparticles as adsorbent to remove copper, cadmium and lead from simulated industrial wastewater. The removal efficiency and adsorption capacity of the synthesized nanoparticles in removing copper, cadmium and lead were compared. The influence of the factors such as pH has been investigated. Kinetic studies were also investigated.

2. Experimental methods

2.1 Procedure

The experiments were performed in glass reactors with magnetic stirrer. The prepared industrial waste water was put into reactors of 0.25 dm^3volume, and then acidified with H_2SO_4 to the selected values, as a Fenton reaction is effective in acidic pH range. After that, under vigorous stirring, the zinc oxide nanopowder and 30% H_2O_2 were added to the flasks. After 15 minutes the samples were alkalized with 0.1 N NaOH up to pH 9 in order to prevent further generation of hydroxyl radicals[11]. Then, the samples were centrifuged at3000 rpm (2.5 min) and analyzed using Atomic adsorption spectrometer.

2.2Characterisation

The synthesized Fenton's reagent with zinc oxide nanoparticles were characterized by various techniques. The formation of nanoparticles was confirmed by FT-IR spectroscopy. The microstructure and particle size of the nanoparticles were determined by SEM images. The Thermal stability was evaluated using TGA.

2.3 Preparation of simulated industrial wastewater

The 1000ppm standard solution of copper, cadmium and lead were prepared by dissolving appropriate quantities of their respective salts in distilled water. The simulated wastewater was prepared by using measured amount of standard solutions. The concentration of Cu, Cd and Pb were 20ppm, 10ppm and 5ppm respectively.

2.4 Adsorption experiment

Adsorption experiment was done by measuring 25mL of the wastewater sample and poured into a 100ml conical flask. 0.1g of the synthesized zinc oxide doped Fenton's reagent nanoparticles were added to different conical flask containing 25ml of wastewater. The conical flask containing the adsorbent and the wastewater was placed on a rotary shaker and shook at 120 rpm at a room temperature for a period of 150min to ensure equilibrium. The suspension was filtered using 0.5 micronfilter paper. Atomic adsorption spectro-photometer (AAS) was used to analyse the concentration of the different metal ions present in the filtrate[12-16]. The effect of pH on adsorption of metal ions in the pH range of 2-8 was studied under the specific condition (Temp = 30°C, agitation speed = 120rpm, adsorbent dose = 0.1 g and contact time = 150 min) using zinc oxide doped Fenton's reagent.

2.5 Effect of pH on adsorption

The effect of pH on adsorption of metal ions in the pH range of 2-8 was studied. For this investigation, 25 ml of simulated industrial wastewater was taken into different 100 ml conical flask and 0.1g of the zinc oxide doped Fenton's reagent was added and agitated at a speed of 120 rpm for 150min. The0.5 micronfilter paper was used to filter the mixture and the filtrate analyzed to determine the concentrations of metal ions using AAS[17-19].

3. Characterization Studies

In the Fenton reaction mechanism, the production of highly reactive perhydroxyl and hydroxyl radicals is responsible for the degradation of organic pollutants. Some authors, claim that Fe^{3+} species are responsible for the formation of various active intermediates to produce perhydroxyl and hydroxyl radicals. The reduced species Fe^{2+} again interact with H_2O_2 to produce hydroxyl radical.

$$Fe^{3+} + H_2O_2 \longrightarrow [Fe^{III}\,OOH]^{2+} + H^+$$

$$[Fe^{III}\,OOH]^{2+} \longrightarrow Fe^{2+} + OOH^{\cdot}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\cdot} + OH^-$$

The prepared ZnO might be retarding the recombination of photoinduced charge carriers to a great extent the efficiency of Fenton's reagent for the removal of pollutants from industrial waste water. The prepared product was analyzed by various characterization methods.

3.1 Fourier-Transform Infrared (FT-IR) spectroscopy

The FT-IR spectra recorded for the zinc oxide nanoparticles and shown in Figure1.The corresponding stretching vibrations of –OH groups obtained at 3368-3371 cm^{-1}. The peaks at 1598-1618 cm^{-1} indicates flexible vibrations of –OH groups caused by adsorbed water or humidity[20]. It is suggested that the surface of the samples contain active –OH groups. At low wave number, the peaks in the range of 828 to 764 cm^{-1}corresponds to metal-oxygen (Fe-O) stretching vibrations.

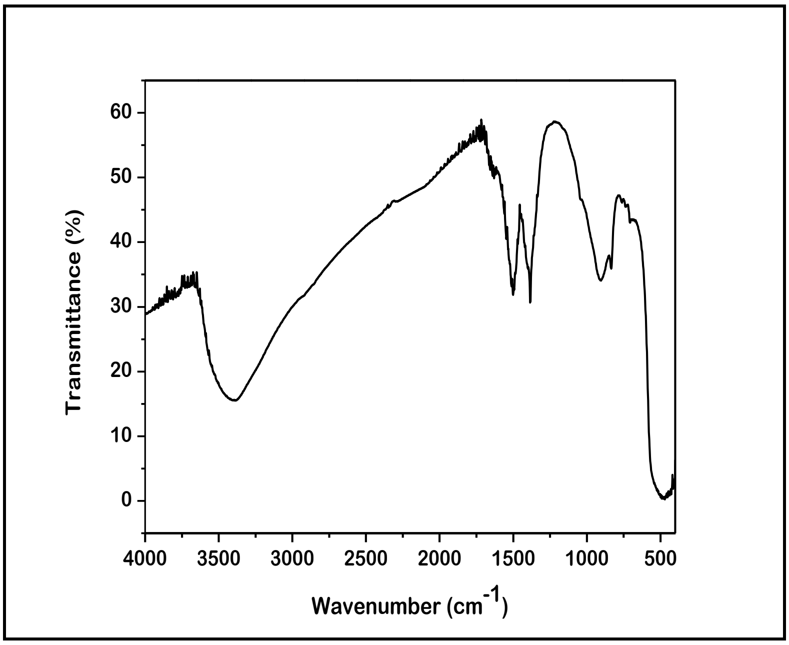

Figure 1: FTIR spectra of Zinc oxide nanoparticles

3.2Scanning Electron Microscopy (SEM)

The SEM images of zinc oxide nanoparticles are shown in Figure 2 and it reveals that sample exhibit a compact arrangement of homogeneous nanoparticles with spherical in shape. It has been observed that the particles are not aggregated having almost uniform size distribution and the average size of nano zinc oxide is 73 nm.

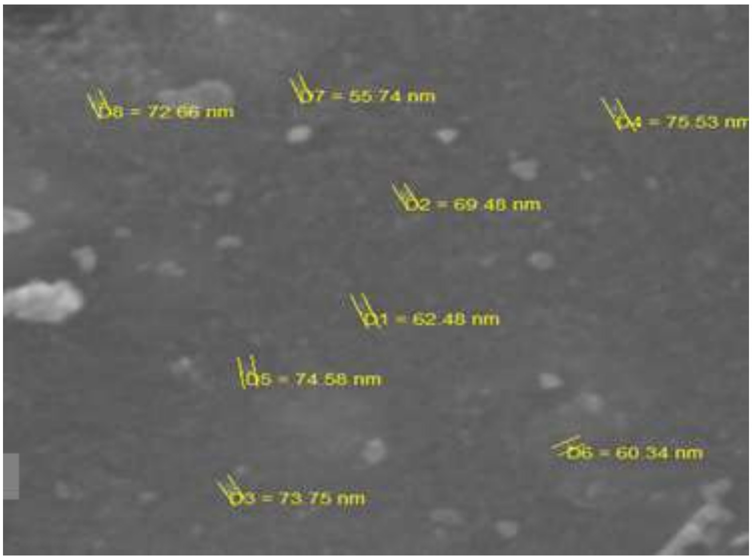

Figure 2: SEM image of nano zinc oxide

3.3Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis of synthesized zinc oxide doped Fenton's reagent nanoparticles are shown in Figure 3. The synthesized nanoparticles were heated from 100°C to 900°C under flowing N_2atmosphere and changes in weight losses are recorded. The weight loss in the temperature range of 200°C to 300°C which may due to evaporation of hydroxyl groups adsorbed on the surface of nanoparticles during synthesis. The last broadened exothermic peak at 780°C and 800°C with small weight loss could be considered as a solid reaction attributed to the gradual formation of nano zinc oxide. After 850°C, no further distinguishable weight loss was detected, indicating that all organic constituents were eliminated.

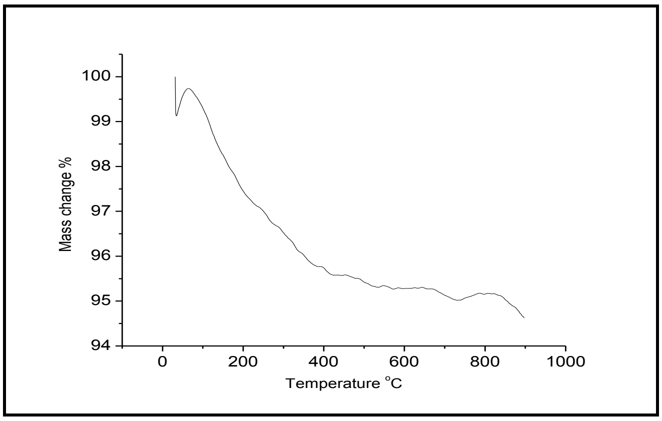

Figure 3: TGA analysis of zinc oxide doped Fenton's nanoparticles

3.4 Effect of pH on adsorption of heavy metals

The pH of the wastewater is one of the imperative factors governing the adsorption of the metal ions. The effect of pH was studied from a range of 2 to 8 under the precise conditions (Temp = 30℃, agitation speed = 120rpm, adsorbent dose = 0.1 g and contact time = 150 min). Effect of pH on adsorption of metal ions using zinc oxide doped Fenton's reagent were shown in Figure 4 (a), (b) and (c).

Table 1: Effect of pH on adsorption of heavy metal ions from simulated industrial wastewater using zinc oxide doped Fenton's reagent

pH	Removal efficiency (%) of Cu^{2+} using		Removal efficiency (%) of Pb^{2+} using		Removal efficiency (%) of Cd^{2+} using	
	Zinc oxide	Zinc oxide /Fenton's reagent	Zinc oxide	Zinc oxide /Fenton's reagent	Zinc oxide	Zinc oxide /Fenton's reagent
2	99.15	87.05	63.61	72.50	87.05	86.25
4	99.25	96.50	77.47	81.68	96.50	93.28
6	100	98.05	77.47	80.70	98.05	95.75
8	100	97.85	77.47	80.68	97.85	94.20

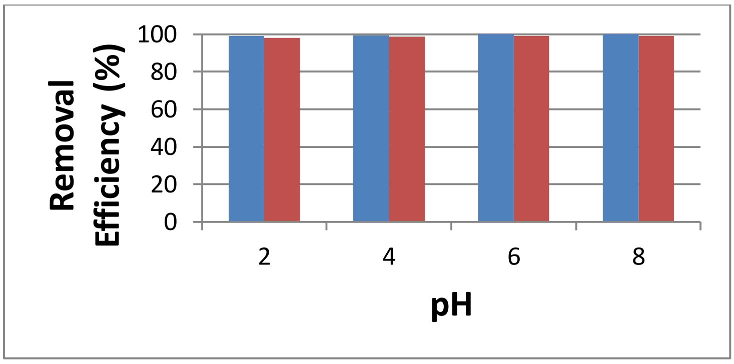

Figure 4:(a) Effect of pH on adsorption of Copper (Temp = 30°C, agitation speed = 120rpm, adsorbent dose = 0.1 g and contact time = 150 min)

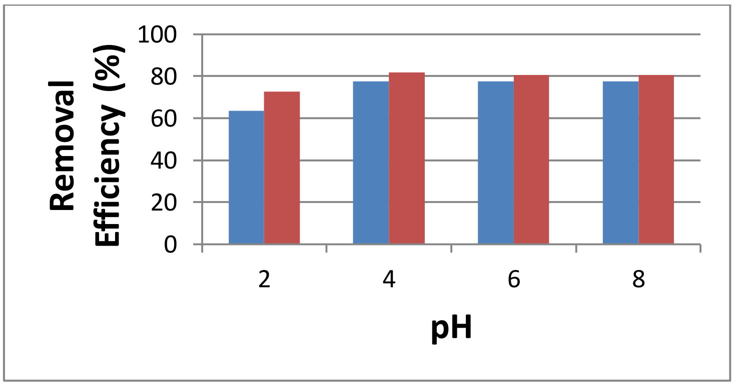

Figure 4: (b) Effect of pH on adsorption of Lead (Temp = 30°C, agitation speed = 120rpm, adsorbent dose = 0.1 g and contact time = 150 min)

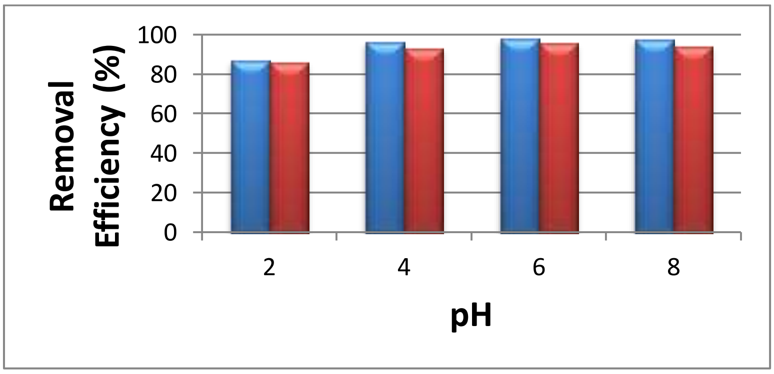

Figure 4: (c) Effect of pH on adsorption of Cadmium (Temp = 30°C, agitation speed = 120rpm, adsorbent dose = 0.1 g and contact time = 150 min)

Table 1 shows the removal efficiencies of heavy metal ions using zinc oxide and zinc oxide doped Fenton's reagent on the pH range of 2 to 8. It was observed that with increase in the pH from 2 to 6 of the simulated industrial waste water, the removal efficiencies of Cu^{2+} and Cd^{2+} increased upto 6 and maximum removal efficiency was obtained at pH 6 as shown in the Fig. 4 (a) and 4 (c) for both zinc oxide and zinc oxide doped Fenton's reagent. Above pH 6, there was no change in removal efficiency of Copper and the removal efficiency of Cadmium was gradually decreased. The maximum removal efficiency of Pb^{2+} was obtained at pH 4 and above pH 4as shown in the Fig. 4(b), there was no change in removal efficiency for zinc oxide nanoparticles. But, slight decrease in removal efficiency was observed for zinc oxide doped Fenton's reagent.

3.5 Pseudo-second order kinetic model

The pseudo-second order kinetic rate equation is expressed as shown in equation

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e}$$

The sorption capacities at equilibrium and at time t, are represented by $q_e$and q_t(mg.g^{-1}) respectively and $k_2$is the rate constant of the pseudo-second order sorption (g.mg^{-1}.min). The rate constant and adsorption capacity at equilibrium can be determined experimentally from slope and intercept of the plot[21].The plotted data for zinc oxide and zinc oxide doped Fenton's reagent of pseudo-second order reaction model are shown in Figure 5(a) and 5(b).

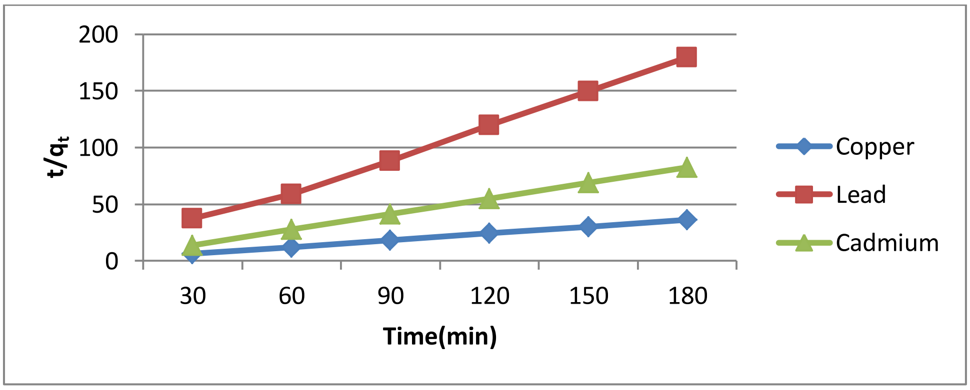

Figure 5: (a) Pseudo-second order reaction model for adsorption of heavy metals on zinc oxide nanoparticles

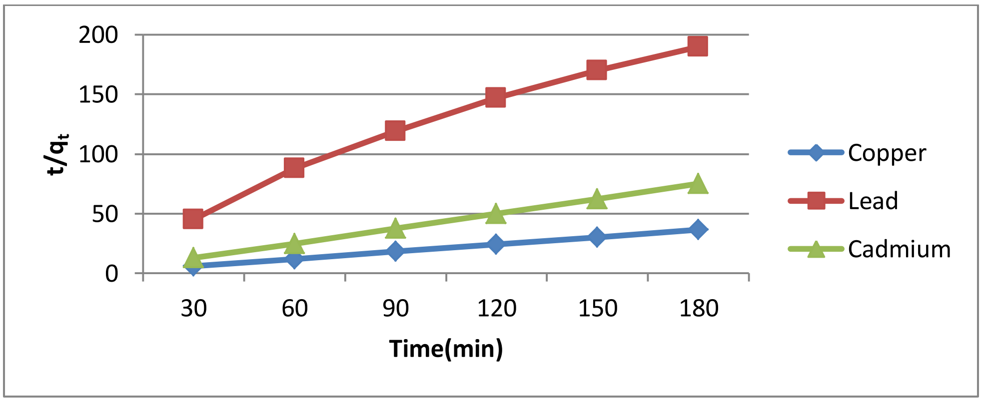

Figure 5: (b) Pseudo-second order reaction model for adsorption of heavy metals on zinc oxide doped Fenton's reagent nanoparticles

From the results of the plotted data, it is clear that pseudo-second order reaction model yield straight line, which was significantly scattered (nonlinear). These facts suggest that the adsorption of heavy metals by both zinc oxide and zinc oxide doped Fenton's reagent nanoparticles follows the pseudo-second order kinetic model. The equilibrium adsorption capacity (q_e) and the second order constants k_2(g.mg^{-1}.min)can be determined experimentally from the slope and intercept of plot t/q_t versus t shown Figure 5(a) and 5 (b). The k_2 and q_e determined from the pseudo-second order models of Zinc oxide nanoparticles and Zinc oxide doped Fenton's nanoparticles are presented in Table 2 along with the corresponding correlation coefficients. The values of the calculated and experimental q_e are represented in Table 2.

Table 2:Pseudo-second order kinetic model for adsorption of heavy metals on Zinc oxide nano particle and Zinc oxide dopedFenton's nanoparticles

Metal ions	Zinc oxide nanoparticles				Zinc oxide doped Fenton's reagent nanoparticles			
	$q_{e.cal}$ (mg/g)	$q_{e.exp}$ (mg/g)	K_2 (g/mg.min)	R^2	$q_{e.cal}$ (mg/g)	$q_{e.exp}$ (mg/g)	K_2 (g/mg.min)	R^2
Cu^{2+}	5.000	5.037	0.140	0.999	4.950	4.960	0.358	0.999
Pb^{2+}	1.001	1.033	0.231	0.998	0.960	1.050	0.033	0.990
Cd^{2+}	2.175	2.175	0.160	0.999	2.400	2.410	0.476	1.000s

From the Table 2, it is observed that there is a close agreement between q_e experimental and q_e calculated values for the pseudo-second order model for both zinc oxide and zinc oxide doped Fenton's reagent nanoparticles. For example, the calculated q_e value of Cu^{2+} ions using zinc oxidenanoparticles was 5 $mg.g^{-1}$ which is in close agreement with the experimental q_e value of 5.037 $mg.g^{-1}$ and the calculated q_e value of Cu^{2+} ions using zinc oxide doped Fenton's reagent nanoparticles was 4.95 $mg.g^{-1}$ which is in close agreement with the experimental q_e value of 4.960 $mg.g^{-1}$. Hence, the adsorption of heavy metals by both zinc oxide and zinc oxide doped Fenton'sreagent nanoparticles follows the pseudo-second order reaction model. The correlation coefficients, R^2 values suggest a strong relationship between the parameters and also explain that the process follows pseudo-second order kinetics.

Conclusion

The present investigation deals with the synthesis and characterisation of zinc oxide doped Fenton's reagent nanoparticles and the synthesized nanoparticles were characterized using FT-IR confirms the presence of corresponding functional moities in the nanoparticles. The morphology was studied by SEM. TGA was carried out to investigate the thermal stability of the nanoparticles. Thermal analysis showed that the synthesised nano particles have stable over wide range of temperature.

The adsorption experiment was conducted to examine the effects of pH on adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} ions from simulated industrial wastewater to obtain the optimum condition. The removal efficiency and adsorption capacity of synthesized nanoparticles in removing copper, cadmium and lead were compared.

From the result, it is evident that the adsorption of Cu^{2+},Cd^{2+} and Pb^{2+} ions are time dependent, adsorbent dosage dependent and pH dependent. Zinc oxide nanoparticles shows lower removal efficiency for Pb^{2+} with 63.61% and zinc oxide doped Fenton's reagent nanoparticles shows lower removal efficiency forPb^{2+} with 72.5%. Kinetic study revealed that the adsorption process of zinc oxide and zinc oxide doped Fenton's reagent nanoparticles was controlled by Pseudo-second order rate equation. The synthesized nanoparticles have greater potential for adsorption of heavy metal ions present in simulated industrial wastewater. These nanoparticles can be effectively used as adsorbents in the commercial scale to achieve the desired goal of clean environment.

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