



Removal of p-Nitrophenol from Aqueous Solution Using Synthesized Silica-Magnetite Composite

Adekola*F.A., Orimolade**B.O. and Adebayo G.B.

Department of Industrial Chemistry, University of Ilorin, Ilorin, Nigeria.

*Author for correspondence; e-mail: fadekola@unilorin.edu.ng; **orimoladeben@yahoo.com

Received: 16 October 2015

Accepted: 24 January 2016

ABSTRACT

Silica-magnetite composite was synthesized as model adsorbent for the removal of p-nitrophenol (p-NP), a problematic toxicant present in effluents from pharmaceutical and allied industries. The adsorption behavior was studied by batch method. Prepared adsorbent was fully characterized using Fourier Transform Infra-red spectroscopy (FTIR), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and X-Ray Fluorescence. The optimum conditions of adsorption were determined by investigating the effect of initial p-NP concentration, contact time, adsorbent dose, pH value of aqueous solution and temperature. Adsorption equilibrium time was found to be 60 min. The optimum initial concentration of p-NP was 70 mg/L while the optimum temperature and pH were 30 °C and 2 respectively. The equilibrium adsorption experimental data were fitted best the Langmuir isotherm. The pseudo-second order kinetic model described the adsorption kinetics more effectively. The thermodynamic studies revealed that the adsorption process is spontaneous and feasible. The experimental results have revealed the potential of synthesized material for the removal of p-nitrophenol from aqueous solution.

Keywords: silica, magnetite, p-nitrophenol, adsorption

1. INTRODUCTION

P-nitrophenol (p-NP) is a toxic phenolic compound which can be derived from phenol by substitution of hydrogen atom by nitro group ($-\text{NO}_2$) in para position. Paranitrophenol may be introduced into the environment via various anthropogenic activities as well as some natural sources. Nitrophenols, particularly 2-nitrophenol and 4-nitrophenol, are formed in the reaction of phenol with nitrite ions in water. The reactions proceed under the influence of UV irradiation (sunlight) and in the wide range of pH values. The reactions of phenol, nitrite ions and hydroxyl radical leads to the formation of 2 nitrophenol and other nitrated compounds [1].

p-nitrophenol (p-NP) was chosen as the representative member of this pollutant group because of its environmental importance. It is one of the 114 organic compounds listed by EPA as hazardous. Since it has a significant water solubility, 1.6 g/100 ml, it is often present in wastewater generated from pharmaceutical, agrochemicals and petrochemical industries. It may also be found in ground water wells and surface waters where it has to be removed in order to achieve drinking water quality [2].

p-nitrophenol is carcinogenic and toxic in nature and it poses great danger to living organisms in the biosphere and hence it has been included in the both of USA and EU

Environmental Protection Agency (EPA) list of priority pollutants [3]. It is compulsory to remove this compound from wastewaters generated from industries such as the pharmaceutical and petrochemical industries before safe disposal into the surface waters. Various treatment technologies have been used to remove these contaminants from wastewaters. Among these, adsorption is found to be the best technique that is widely employed for the treatment of wastewater. Powdered and granulated activated carbons are the most widely used adsorbents due to their favorable surface physical and chemical adsorptive properties [4]. Hamdaouia et al. [5] studied and modeled the adsorption equilibrium isotherms of five phenolic compounds from aqueous solutions onto GAC. They observed that the uptake of phenols correlated well with respective increase in molecular weight of the phenolic compounds, cross-sectional area, and hydrophobicity and decrease in solubility and pKa. Chen et al. [6] studied the adsorption of phenol and 4-nitrophenol on Mg Al-mixed oxide derived from Mg Al-layered double hydroxide. They noted that the adsorption capacity for 4-nitrophenol can be as high as 367.8 mg/g while that of phenol is 25.5 mg/g at room temperature. The Langmuir model fits the equilibrium data for 4-nitrophenol well while the Freundlich model fits that of phenol.

Unfortunately, there are some disadvantages that may be associated with these adsorbents when used to remove phenols, such as the high regeneration cost and the generation of fine carbon. Due to recent advancement in nanotechnology, nano materials such as metal oxides are now being used as adsorbents for the removal of contaminants from water due to their relatively large surface area. Oxide nanoparticles can exhibit unique physical and chemical properties due to their small size and a high density of corner or edge surface sites. Coating of metal oxides improves their stability and adsorption capacity [7]. No research work

has earlier been reported on the use of silica-magnetite composite to remove p-nitrophenol from solution.

The overall aim of this research work is to carry out the adsorption studies on the removal of p-nitrophenol using synthesized silica-coated magnetite composite material. The effect of some physicochemical parameters such as pH, adsorbent dose, temperature, the effect of initial concentration of p-nitrophenol and the effect of contact time on the sorption capacity were investigated. The kinetics and thermodynamic studies of the adsorption process were also carried out.

2. MATERIALS AND METHOD

2.1 Collection of Rice Husk Waste Material

Rice-husk which is an agro-residue waste material was collected from a processing center at a local market in Ilorin, North-Central Nigeria.

2.2 Preparation of Silica from Rice Husk

The rice husk was milled and washed with distilled water to remove all impurities. The material was then oven dried at 105 °C for 5 hours. It was thereafter sieved and the fraction with particle size $300 < \phi < 250$ μm was selected for further pretreatment. The rice-rusk was purified in 500 ml of 3.0M HNO_3 over night and mechanically stirred at moderate speed. It was then washed thoroughly with large quantity of deionised water to neutrality and subsequently air dried at 105 °C for 24 hours, the material was then ashed at 550 °C in the muffle furnace [8].

2.3 Synthesis of Magnetite

The co-precipitation method described by Hamid et al. [9] was employed for the synthesis of the magnetite nano-particles. The iron salts solution was prepared by dissolving 3.24 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.99 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 20 mL de-ionized water at 25 °C for 20 minutes. 8 mol/L of alkaline solution was prepared

by adding 4.58 g of NaOH to 14 mL of de-ionized water and stirred for 30 minutes at 25 °C. Magnetite particles were then precipitated by adding the iron salts solution drop-wisely into the NaOH solution at 80 °C while stirring. The co-precipitated samples were washed with deionised water and acetone to remove the NaCl.

2.4 Preparation of Silica Coated Fe₃O₄ Composite

Rice husk ash and magnetite in the ratio of 1:1 were dispersed in 0.5M HCl to form slurry. The slurry was stirred and evaporated to dryness in an oven. The composite material was washed with deionised water, filtered and further dried in an oven at 100 °C for 12 hours [10]. By acidifying the magnetite, the active sites on the magnetite surface were formed facilitating the interaction between the magnetite surface and the silica which resulted to formation of covalent bonds, Fe-O-Si, on the magnetite surface as shown in Figure 1 [11].

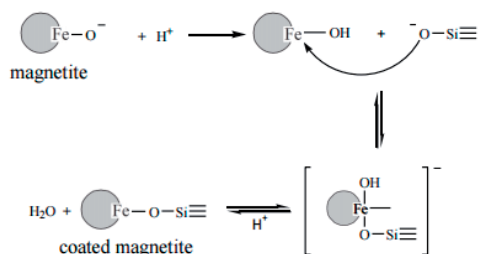


Figure 1. Formation of Fe-O-Si on magnetite surface.

2.5 Characterization of Materials

Phase composition of the samples (magnetite and composite) was analyzed using X-ray diffractometer. The mean crystallite size of the samples was calculated by XRD line broadening technique using Scherrer formula. SEM was used to determine the morphology of the samples and Fourier Transform Infrared was used to determine the functional groups present.

2.6 Sorption Experiment

Batch experiments were used for the adsorption studies. This was done by contacting 0.1 g of the composite sample (adsorbent) with the 25 mL of p-NP solutions and then agitated at a specific time and temperature. The solution was then filtered and the absorbance taken using the UV-Visible spectrophotometer and corrected to concentration values using the calibration curve. The quantity of p-NP adsorbed (q_e) was calculated by using equation (1).

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of p-NP respectively. V is the volume of p-NP used while W is the mass of composite sample taken.

Similarly, the %Adsorbed was calculated using equation (2).

$$\% \text{Adsorbed} = \frac{C_0 - C_f}{C_0} \times 100 \quad (2)$$

Where C_0 and C_f represent the initial and final concentrations p-NP

2.7 Adsorption Isotherms Studies

The experimental data were fitted using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms. The Langmuir isotherm represents the equilibrium distribution of substrate ions between the solid and liquid phases [12]. The Langmuir isotherm equation is written as:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \quad (3)$$

C_e is the equilibrium concentration of adsorbate (mg/L) and q_e is the amount of p-NP adsorbed per gram of the adsorbent at equilibrium (mg/g). Q_0 (mg/g) and K_L (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of Q_0 and K_L were calculated from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$.

Freundlich adsorption isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface [13]. These data often fit the empirical equation proposed by Freundlich:

$$Q_e = K_f \times C_e^{1/n} \quad (4)$$

K_f is Freundlich isotherm constant (mg/g), n is adsorption intensity, C_e is the equilibrium concentration of adsorbate (mg/L) and Q_e is the amount of p-NP adsorbed per gram of the adsorbent at equilibrium (mg/g). The linearized form of Freundlich adsorption isotherm is given as:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process [14]. If $n = 1$ then the partition between the two phases are independent of the concentration. If value of $1/n$ is below one it indicates a normal adsorption. On the other hand, $1/n$ being above one indicates competitive adsorption [15].

The Temkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbent–adsorbate interactions. The Temkin isotherm equation is applied for isotherm analysis in the following form [16]:

$$q_e = B \ln A_T + B \ln C_e \quad (6)$$

Where C_e is the equilibrium concentration of adsorbate (mg/L) and q_e is the amount of p-NP adsorbed per gram of the adsorbent at equilibrium (mg/g). According to Temkin isotherm, the linear form can be expressed by equation (7)

$$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b} \right) \ln C_e \quad (7)$$

Where $RT/b = B$ (J/mol), which is the Temkin constant related to heat of sorption, whereas A_T (1/g) represents the equilibrium binding

energy, R (8.314 J/mol/K) is the universal gas constant at T (K) which is the absolute solution temperature.

2.8 Adsorption Kinetics Studies

The kinetics of the adsorption process were studied by analyzing the experimental data using Pseudo first order, pseudo second order, Elovich and Intra-particle diffusion models.

The pseudo-first order model is expressed using equation 8 [17]

$$\log (q_e - q_t) = \log q_e - \frac{K_{ad} t}{2.303} \quad (8)$$

where q_e (mg/g) is the mass of p-NP adsorbed at any time t and k_{ad} (min^{-1}) is the equilibrium rate constant of pseudo first order adsorption. The values of k_{ad} and q_e are determined from the slope and intercept of the plot of $\log (q_e - q_t)$ versus t , respectively.

The pseudo-second order model is based on assumption that sorption follows a second order mechanism. The rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. The equation can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{K_{ad} q_e^2} + \frac{t}{q_e} \quad (9)$$

where k_{ad} is the pseudo-second order rate constant (g/mgmin). The value of q_e is determined from the slope of the plot of t/q_t versus t .

One of the most useful models for describing ‘activated’ chemisorption is the Elovich equation. The Elovich equation can be written as [5]:

$$q_t = \frac{1}{\alpha} \ln(\alpha \beta) + \frac{1}{\alpha} \ln t \quad (10)$$

here q_t is the quantity adsorbed (mg g^{-1}), α is the initial adsorption rate, β is the desorption constant during each experiment at time t .

2.9 Thermodynamic Study

The thermodynamic parameters were obtained by varying the temperature conditions between 30 °C and 70 °C while keeping other

variables constant including metal concentration, pH, adsorbent dose and contact time. The values of the thermodynamic parameters such as ΔG° , ΔH° , and ΔS° , were calculated using the expression described in equations 11 – 13. [18]. Equation 13 is the Gibb's relation.

$$\Delta G = -RT \ln K_d \quad (11)$$

$$\ln K_d = \Delta S/R - \Delta H/RT \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

where ΔG° is the standard Gibb's free energy change for the adsorption (J/mol), R is the universal gas constant (8.314 J/mol/K) while T is the temperature (K). K_d is the distribution coefficient of the adsorbate and it is equal to q_e/C_e (L/g). The plot of $\ln K_d$ versus $1/T$ gives a straight line with the slope and the intercept giving values of ΔH° and ΔS° respectively. ΔG was then calculated using the equation 13 at temperatures of 303–343 K.

3. RESULTS AND DISCUSSION

3.1 Characterization of Adsorbents

3.1.1 XRF elemental analysis

The X-Ray fluorescence analysis data show the concentrations of important elements present in the synthesized materials. The results of XRF analysis of the rice husk ash, synthesized magnetite and the synthesized composite material are shown in Table 1.

The data obtained from the analysis of rice husk ash reveal that silica (SiO_2) is the major constituent of the ash with a percentage composition of 92% (Table 1. Previous researchers have reported similar results for the XRF analysis of rice husk ash [8, 19]. Table 1 also shows that iron oxide with 95% is the major compound present in the synthesized magnetite. The percentage of the iron oxide and silica present in the composite material are 38% and 56% respectively.

3.1.2 Scanning electron microscopy

The SEM images of the synthesized magnetite and the silica-coated magnetite composite before adsorption are shown in Figures 2a and 2b respectively. The SEM image of the magnetite shows that the particles are in aggregated form rather than existing as separate particles which could have been caused by the large surface area and magnetic dipole-dipole interactions of the individual particles [20]. The SEM image of the composite material as shown in Figure 1b revealed that the iron particles are surrounded by the silica particles which indicate that the nano particles of the magnetite are well coated with the silica. The surface of the composite material appeared to be rough and coarse with cracks which indicate that it will be a good adsorbent.

The SEM image of the adsorbent after the adsorption processes is shown in Figure 2c. By comparing the image with the SEM image of the adsorbent before adsorption, it can be observed that the roughness, coarseness

Table 1. X-Ray fluorescence of rice husk ash, magnetite and composite material.

Compds	Conc (%) RHA	magnetite	Composite
SiO_2	92.64	2.8	55.6
TiO_2	0.031	-	-
Fe_2O_3	0.27	-	-
Al_2O_3	0.269	0.99	-
MnO	0.072	0.30	0.091
CaO	1.60	0.12	0.231
MgO	0.828	-	-
Na_2O	0.73	-	-
Ag_2O	2.06	-	1.63
K_2O	0.75	0.042	0.314
P_2O_5	0.19	0.20	3.07
Eu_2O_3	0.43	0.54	0.28
Re_2O_7	0.12	0.10	0.06
V_2O_5	-	0.036	0.019
Cr_2O_3	-	0.056	0.030
Fe_3O_4	-	94.51	38.48
CuO	-	0.050	0.032
ZnO	-	0.061	0.02
In_2O_3	-	0.13	-
La_2O_3	-	0.10	0.099

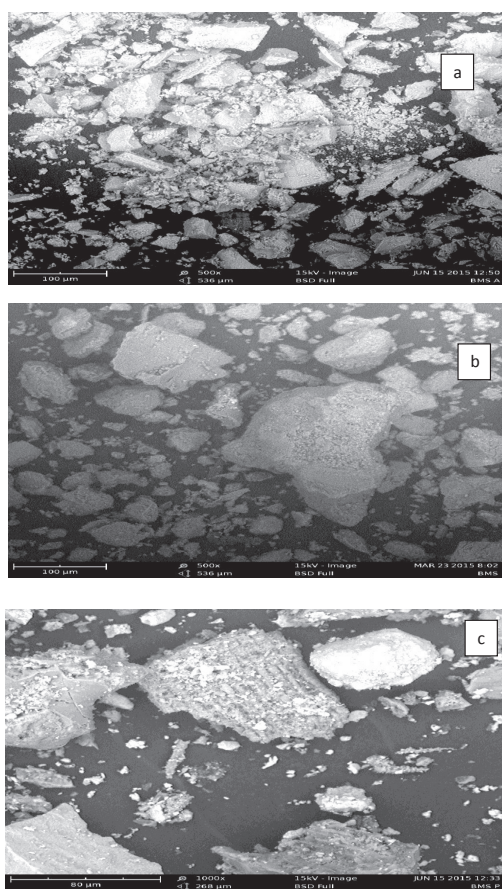


Figure 2. SEM images of magnetite(a), SiO₂-nFe₃O₄ composite before adsorption(b) and SiO₂-Fe₃O₄ composite after adsorption(c).

and presence of cracks in the adsorbent surfaces facilitated the sorption of p-NP from aqueous solution. The cracks present on the surfaces of the adsorbent appeared to have been partially filled which shows that the adsorbates have successfully percolated on to the surface of the adsorbent as seen in Figure 2c.

3.1.3 X-ray Diffraction

Figure 3a illustrates the XRD patterns of the synthesized magnetite particles.

The position and relative intensity of all diffraction peaks match well with those of the magnetite (JCPDS 19-629) and broad peaks indicates nano-crystalline nature of the

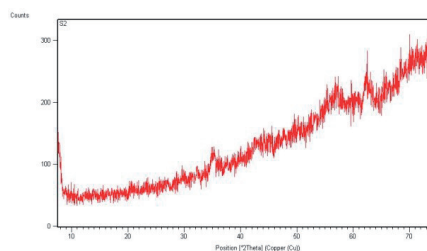


Figure 3a. XRD of synthesized magnetite.

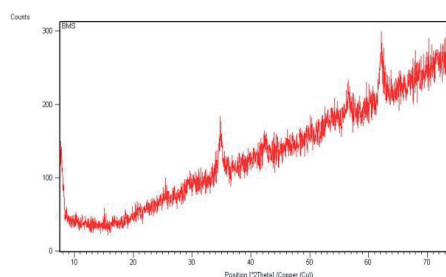


Figure 3b. XRD of SiO₂-Fe₃O₄.

particles. Figure 3b shows XRD pattern of silica coated Fe₃O₄ composite, the broad peak is due to amorphous silica. Thus XRD pattern indicates the presence of amorphous silica coating on magnetite particles surface. The broadened peak at 10-20 degree corresponds to SiO₂ and the rest of peaks are as those in XRD patterns of Fe₃O₄. It can be seen from Figure 2b that coating process of magnetite does not change the peak position corresponding to magnetite between 30 and 40 degree but rather the intensity of the peak.

3.1.4 Infra red spectroscopy

The IR spectra of the synthesized magnetite and the silica-magnetite composite are presented in Figure 4. The band at 565.14 cm⁻¹ has been assigned to Fe-O bond and attributed to formation of ferrite phase. Different from magnetite, FT-IR spectra of silica coated magnetite, shows pronounce changes, particularly at region of 1300–700 cm⁻¹, indicating the presence of silica coating. The presence of silica coating on the magnetite is shown with characteristic

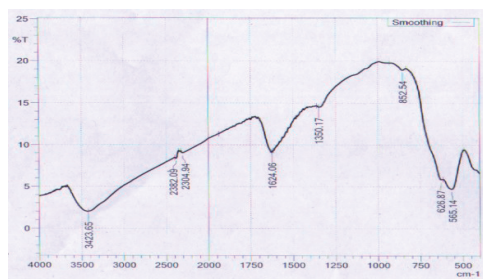


Figure 4a. FTIR spectra of magnetite.

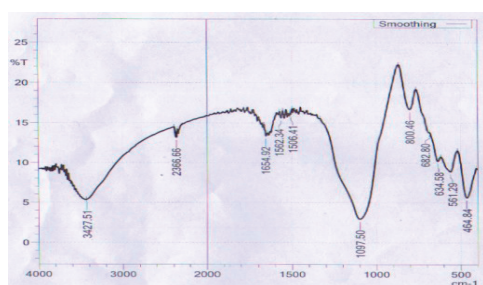


Figure 4b. FTIR spectra of $\text{SiO}_2\text{-Fe}_3\text{O}_4$ composite.

band at 464.84 cm^{-1} from bending vibration of Si-O-Si. FTIR band of 1099.43 cm^{-1} has been assigned to asymmetric bending vibration corresponding to Si-O-Si bond. FTIR bands in coated magnetite FT-IR spectra around 1654.92 cm^{-1} and 3427 cm^{-1} come from bending and stretching vibration, respectively, of -OH groups from both Fe-OH and Si-OH. The band at 561 cm^{-1} is an indication of the presence of Si-O-Fe bond. Stretching vibration of Si-O-H bonding results in an absorbance band at 800.46 cm^{-1} . In FTIR spectra of magnetite coated only with silica, absence of Si-OH vibration band was due to overlap with broad band of stretching vibration from Si-O-Si.

3.2 Adsorption Studies

3.2.1 Effect of initial concentration of p-nitrophenol

The initial concentration provides a significant driving force to overcome all mass transfer

resistances of solutes between the aqueous and solid phases. In this study, the influence of initial concentration on the removal of p-NP by silica-coated magnetite composite material was studied at initial concentrations of 5-100 mg/L and the results are shown in Figure 5.

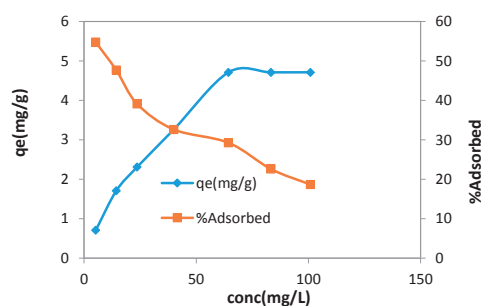


Figure 5. Effect of concentration on the sorption of p-NP on $\text{SiO}_2\text{-Fe}_3\text{O}_4$ (weight= 0.1 g, pH 7.45, Temperature= $30 \pm 2^\circ\text{C}$ for 240 min).

The result shows that the adsorption capacity of p-NP on the composite material increases with increase in concentrations. Therefore the adsorption of p-NP onto the adsorbent is greatly influenced by the initial concentration of p-NP. The adsorption capacity increased from 0.71-4.71 mg/g as the concentration of p-NP increased from 5-100 mg/L. It reached saturation at about 70 mg/L. The increase in sorption capacity with increasing concentration of p-NP could be due to higher probability of collision between p-NP molecules and the adsorbent surface. Similar trends were observed in the adsorption of 2, 4- DCP on palm pith carbon, and the adsorption of 2, 4, 6-TCP onto activated clay [21, 22].

3.2.2 Effect of initial pH

The pH of the solution affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate species, which may lead to change in kinetics and equilibrium characteristics of the adsorption process. In this study, the effect of pH on p-NP adsorption

capacity onto the adsorbent was conducted between pH 2 to 10 with 75 mg/L fixed initial p-NP concentration and adsorbent dose of 0.1 g for 120 min.

Figure 6 shows that the adsorption capacity was maximum at lower pH (pH 2) and it decreases very slightly with increase in pH. The pKa value of p-NP is 7.15 [23] and being a weak acid will dissociate at $\text{pH} > \text{pKa}$. At lower pH, p-NP is present in the unionized form and there is nearly no electrostatic repulsion between the adsorbent and the adsorbate and hence the amount adsorbed is at the maximum at pH 2. The lowest adsorption capacity is observed at pH 10 due to ionization of p-NP molecules. Similar result was reported by Liu and Pinto [24] for granule and spherical activated carbon.

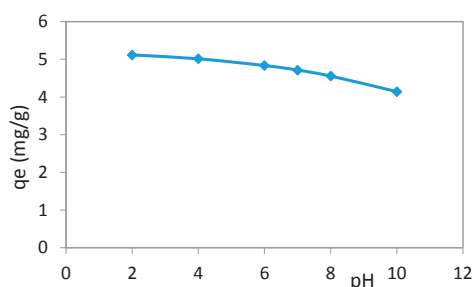


Figure 6. Effect of pH on the sorption of p-NP on silica-magnetite composite ($C_0=75$ mg/L, weight = 0.1 g, Temperature = 30 ± 2 °C for 120 min).

3.2.3 Effect of contact time

The graph of the adsorption capacity of p-NP against contact time is presented in Figure 7. It shows that the adsorption process was rapid initially but became slower near the equilibrium time of 60 min. The maximum quantity adsorbed was 4.71 mg/g at equilibrium time of 60 min. Thereafter, there was no significant change in the quantity of p-NP adsorbed. The saturation curve rises sharply in the initial stages (i.e the uptake was rapid), this is indicative of the fact that there are several

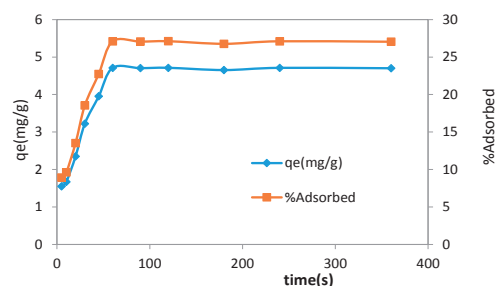


Figure 7. Effect of contact time on the sorption of p-NP on Silica-magnetite composite ($C_0=69.52$ mg/L, weight= 0.1 g, Temperature= 30 ± 2 °C).

available sites to be occupied at the beginning of adsorption process and after a lapse of time, remaining vacant surface sites were difficult to be occupied due to repulsive force between solute molecules on the solid and bulk phases [21]. The adsorbent became saturated at the plateau region. The high adsorption rate at the beginning of adsorption may also be due to the adsorption of p-NP by exterior surface of the adsorbent. When saturation was reached at the exterior surface, the p-NP molecules would then enter the pores of adsorbent and were adsorbed by the interior surface of the particles [22].

3.2.4 Effect of adsorbent dosage

The graph of percentage of p-NP adsorbed with varying dosage of silica-magnetite composite reveal that the percentage adsorbed increases with increasing dose of the adsorbent as shown in Figure 8. The percentage increased from 8% with 0.01 g dose of adsorbent to 27% with 0.1 g adsorbent dose. This can be attributed to the increase in the surface area which leads to an increase in number of active sites for adsorption [25, 26]. The adsorption capacity on the other hand decreased with increase in dosage from 0.01 g up to 0.05 g and there seem to be no practical influence of adsorbent dose from 0.05 g upward. This could indicate that the doses above 0.05 g are in excess.

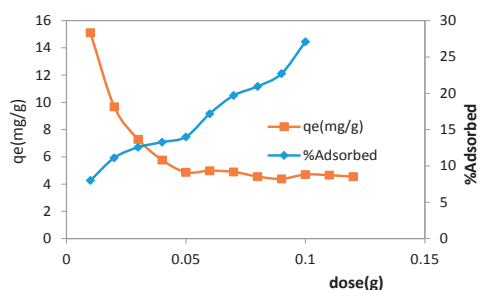


Figure 8. Effect of adsorbent dose on the sorption of p-NP onto $\text{SiO}_2\text{-Fe}_3\text{O}_4$ ($C_0 = 69.52$ mg/L, Temperature = 30 ± 2 °C for 120 min).

3.2.5 Effect of temperature

The result of the effect of temperature on the adsorption process is shown in Figure 9. It can be seen from this figure that the amount of p-NP adsorbed decreases with increase of adsorption temperature indicating the apparent exothermic nature of the entire process. The optimum temperature was found to be 30 °C. In the liquid phase, an increase in temperature commonly increases the solubility of the molecules in the solution [27] and hence less molecules of the adsorbate would be available for adsorption on the surface. Similar influence has also been reported by other researchers [27, 28].

3.2.6 Adsorption isotherms

The equilibrium adsorption data were analysed using adsorption isotherm models. The

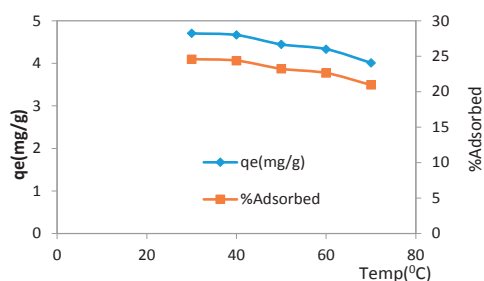


Figure 9. Effect of temperature on the adsorption of p-NP onto silica-magnetite composite.

closer the value of the regression coefficient (R^2) to unity (1), the better is the agreement of the experimental data with the model isotherm. The following experimental conditions were used to analyse the adsorption data with the isotherms: $w = 0.1$ g, $\text{pH} = 7$ at 30 ± 2 °C for 120 min

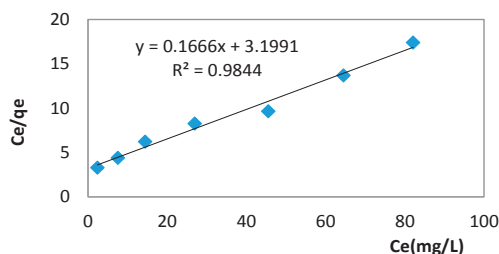


Figure 10. Langmuir isotherm.

The adsorption data fits best the isotherms in this order: Langmuir > Freundlich > Temkin. The adsorption parameters for the adsorption isotherm are shown in Table 2. The data can best be explained using the Langmuir isotherm which has the regression value of 0.99. The Langmuir model is based on the supposition of a homogeneous adsorbent surface with identical adsorption sites [29]. The Langmuir constant R_L (0.16) indicates that the adsorption is favourable since it is less than 1 as shown in Table 2.

Table 2. Isotherm parameters for sorption of p-NP onto $\text{SiO}_2\text{-Fe}_3\text{O}_4$.

Isotherm	Parameters	Values
Langmuir	Q_m (mg/g)	6.02
	K_L	0.05
	R_L	0.16
	R^2	0.99
Freundlich	K_f	0.51
	n	1.84
	R^2	0.96
Temkin	b_T	2008.89
	A_T	0.60
	R^2	0.95

3.2.7 Kinetic studies

The adsorption kinetics of p-NP on silica-magnetite composite was studied using affixed initial concentration of p-NP at 30 ± 2 °C. The Pseudo first order, Pseudo second order, Elovich and Intra-particle diffusion kinetics models were used to analyse the adsorption process.

The linear plots of all the kinetics models used are shown in Figures 11 and the adsorption kinetic parameters were calculated from the slopes and intercepts of the plots. The results revealed that the experimental data did not fit well into the Pseudo-first order and Elovich models since the regression values were low.

The experimental data show a good agreement with Pseudo second order kinetic model with a regression value of (0.996). The slope and intercept plot of t/q_t against t were obtained to calculate the Pseudo second order rate constants k_2 and q_e and the values are summarized in Table 3. The experimental quantity adsorbed (4.710 mg/g) and the calculated quantity adsorbed (4.950 mg/g) from pseudo second-order were in close agreement. Since the Pseudo second order mechanism is predominant, the overall rate of the adsorption process of p-NP can be said to be controlled by chemical process.

The intra-particle diffusion constant K_{diff} and C values were evaluated from Figure 11b and presented in Table 3. The larger intercept values suggest that intra-particle diffusion has a lesser role to play compared with surface diffusion. The multi-linearity observed is an indication that two steps occur in the adsorption process. The sharply rising part is the external surface adsorption stage while the second linear part is the gradual adsorption stage corresponding to intra-particle or pore diffusion. The high regression value of the sharply rising part are suggestive that external surface adsorption is dominant and hence rate-limiting step. The deviation of the lines from the origin and the low regression value of the gradual adsorption

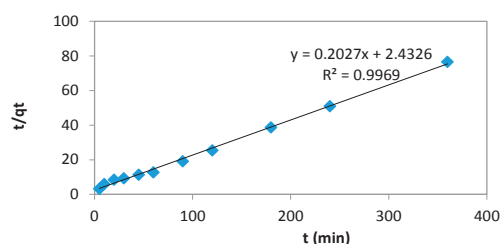


Figure 11a. Pseudo-second order kinetics.

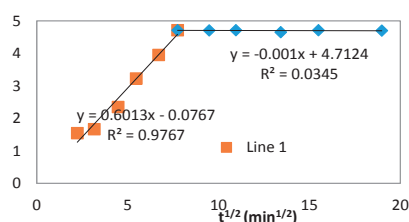


Figure 11b. Intra-particle diffusion model.

Table 3. Kinetics parameter for the sorption of p-NP.

Kinetics model	Parameters	Values
Pseudo-second order	q_e	4.95
	k_2	0.02
	R^2	0.99
Elovich	α	1.12
	β	1.06
	R^2	0.85
Intra-particle diffusion		
Line 1	k_1	0.60
	C	-0.08
	R^2	0.97
Line 2	k_1	-0.00
	C	4.71
	R^2	0.03

stage suggest that intra-particle diffusion is not the sole rate limiting step.

3.2.8 Thermodynamics studies

Figure 12 shows the Van't Hoff plot which is a straight line. The values of enthalpy change (ΔH) and entropy change (ΔS) are calculated from the slope and intercept values respectively. The change in enthalpy and entropy

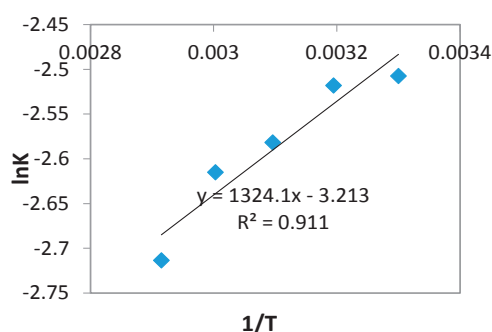


Figure 12. Van't Hoff plot for the sorption of p-NP onto SiO₂-Fe₃O₄.

are negative. This implies that the reaction was exothermic; being unfavourable at higher temperatures [30]. Decrease in adsorption with increase in temperature has been attributed to a weakening of adsorptive forces between the active sites of the adsorbents and adsorbate species and also between adjacent molecules on the adsorbed phase [30]. The values of the adsorption entropy changes are negative which is indicative of the fact that the mobility of adsorbate on the surface of adsorbents is being more restricted as compared with that of those in solution. The negative values of the adsorption free energy (ΔG) in Table 4 demonstrate that the adsorption process is spontaneous and feasible. The thermodynamic results obtained in this study are in agreement with the results of previous researchers [31].

Table 4. Thermodynamic parameters for the Sorption of p-NP onto SiO₂-nFe₃O₄.

Temp(K)	$\Delta G(\text{Jmol}^{-1})$	$\Delta H(\text{Jmol}^{-1})$	$\Delta S(\text{Jmol}^{-1})$
303	-2914.59	-11008.60	-26.71
313	-2647.46		
323	-2380.33		
333	-2113.20		
343	-1846.08		

CONCLUSIONS

From this study, it can be concluded that the silica-coated magnetite composite is an effective adsorbent for the removal of p-nitrophenol from aqueous solutions. The quantities of p-nitrophenol adsorbed were found to depend on the amount of the adsorbent, the initial concentrations of the adsorbates, the pH, contact time of adsorption and temperature. The optimum initial concentration of p-NP was 70 mg/L while the equilibrium adsorption time was 60 min. The kinetics of the adsorption process studied was found to be well described by Pseudo second order kinetics. From the isotherm modeling of the adsorption data, Langmuir isotherm described the adsorption processes better than all other isotherm models that were used and the values Freundlich parameter n obtained indicated that all the adsorption process is favourable. The values of the Gibbs free energy obtained from the thermodynamic studies further revealed that the adsorption process is feasible and spontaneous.

REFERENCES

- [1] Harrison M., Bara S., Borghesi D., Vio D., Arse C. and Ol-Ariu R., *Atmospher. Environ.*, 2005; **39**: 231. DOI 10.1016/j.atmosenv.2004.09.044.
- [2] San N., Hatipoglu A., Koçtürk G. and Çınar, Z., *J. Photochem. Photobiol. C.*, 2002; **146**: 189-197. DOI 10.1016/S1010-6030(01)00620-7.
- [3] Kumar A., Kumar S., Kumar S. and Gupta D., *J. Hazard. Mater.*, 2007; **147**: 155-166. DOI 10.1016/j.jhazmat.2006.12.062.
- [4] Ku Y. and Lee K.C., *J. Hazard. Mater.*, 2000; **80**: 59. DOI:10.1016/S0304-3894(00)00275-2.
- [5] Hamdaoui O. and Naffrechoux E., *J. Hazard. Mater.*, 2007; **147**: 381-394. DOI 10.1016/j.jhazmat.2007.01.023.

- [6] Chen S., Xu, Z. P., Zhang Q., Maxhu G. Q., Hao Z. P. and Liu S., *Sep. Purif. Technol.*, 2009; **67**: 194-200. DOI 10.1016/j.seppur.2009.03.016.
- [7] Gleiter H., *Nanostruct. Mater.*, 1995; **6**(1-4): 3-14.
- [8] Adekola F.A., Hodonou D.S.S. and Adegoke H.I., *J. Appl. Water Sci.*, 2014; **1**: 1-12. DOI 10.1007/s13201-014-0227-1.
- [9] Hamid K., Abolghasem A. and Fereshteh R., *Int. J. Mod. Phys. Conf.*, 2012; **5**: 160-167. DOI 10.1142/S2010194512001973.
- [10] Ayanda O S., Fatoki S.O, Adekola F.A and Ximba B.J., *J. Chem. Technol. Biotechnol.*, 2013; **88**(12): 2201-2208. DOI 10.1002/jctb.4088.
- [11] Durdureanu-Angheluta A., Ardeleanu R., Pinteala M., Harabagiu V., Chiriac H. and Simionescu B.C., *Digest J. Nanomat. Biostruct.*, 2008; **3**: 33-40.
- [12] Vermeulan T.H., Vermeulan K.R. and Hall L.C., *Ind. Eng. Chem.*, 1966; **5**: 212-223. DOI 10.1021/i160018a700.
- [13] Hutson N.D. and Yang R.T., *J. Colloid Interf. Sci.*, 2000; **1**: 189
- [14] Voudrias E., Fytianos F. and Bozani E., *Global Nest, Int.J.*, 2002; **4**(1): 75-83.
- [15] Mohan S. and Karthikeyan J., *Environ. Pollut.*, 1997; **97**: 183-187. DOI 10.1016/S0269-7491(97)00025-0.
- [16] Temkin M. and Pyzhev JAV., *Acta Physiochem.*, 1940; **12**: 217-222.
- [17] Ho Y.S., Wase D.A. and Forster C.F., *Environ. Technol.*, 1996; **17**: 71-77. DOI 10.1080/09593331708616362.
- [18] Khan A.R., Tahir H., Uddin F. and Hammed U., *J. Appl. Sci. Environ. Manag.*, 2005; **9**(2): 29-35.
- [19] Nik A.N. and Alias M.Y., *Malays. J. Anal. Sci.*, 2007; **11**(1): 76-83.
- [20] Li A., Wu H., Zhang Q., Zhang G., Long C., Fei Z., Liu F. and Chen J., *Chin. J. Polym. Sci.*, 2004; **22**(3): 259-267. DOI 10.1016/S0045-6535(01)00222-3.
- [21] Ahmed A.A., Hameed B.H. and Aziz N., *J. Hazard. Mater.*, 2007; **141**: 70-76. DOI 10.1016/j.jhazmat.2006.06.094.
- [22] Sathishkumar M., Binupriyu A.R., Kavitha D. and Yun S.E., *Bioresour. Technol.*, 2007; **98**: 866-873. DOI 10.1016/j.biortech.2006.03.002.
- [23] Suresh S., Srivastava V. C. and Mishra I. M., *Chem. Ind. Chem. Eng. Q.*, 2013; **19**(2): 195-212. DOI 10.2298/CICEQ111225054S.
- [24] Liu X. and Pinto N.G., *Carbon*, 1997; **35**: 1387-1397.
- [25] Lakshminarayanan K.C., Rao K. and Krishna A., *Indian J. Chem. Technol.*, 1994; **1**: 13-19. DOI 10.1016/S0960-8524(99)00123-6.
- [26] Mckay G. and Ho Y.S., *Biochemistry*, 1999; **34**: 451-465. DOI 10.1016/S0032-9592(98)00112-5.
- [27] Cotoruelo L.M., Marqués M.D., Díaz F.J., Rodríguez-Mirasol J., Rodríguez J.J. and Cordero T., *Chem. Eng. J.*, 2012; **184**: 176. DOI 10.1021/ie061415h.
- [28] Tang D., Zheng Z., Lin K., Luan J. and Zhang J., *J. Hazard. Mater.*, 2007; **143**: 49-56. DOI 10.1016/j.jhazmat.2006.08.066.
- [29] Al-Aoh H.M., Maah M.J., Yahya R. and Radzi bin Abas M., *Asian J. Chem.*, 2013; **25**(17): 9573-9581. DOI 10.14233/ajchem.2013.15082.
- [30] Kadirvelu K., Kavipriya M., Karthika C., Radhika M., Vennilamani N. and Pattabi S., *Bioresour. Technol.*, **87**: 129-132. DOI 10.1016/S0960-8524(02)00201-8.
- [31] Pan S.C., Lin C.C. and Tseng D.H., *Resour. Conserv. Recy.*, 2003; **39**: 79-90. DOI 10.1016/S0921-3449(02)00122-2.