

Batch Sorption of Ciprofloxacin on Kaolinitic Clay and nHematite Composite: Equilibrium and Thermodynamics Studies

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Abstract

In this study nanoparticles of hematite and hematite-kaolin composite were prepared and characterized using X-ray diffraction, X-ray fluorescence (XRF), Scanning electron microscopy (SEM), Fourier transform infra-red spectroscopy (FTIR) and UV-visible spectroscopy analysis. The prepared materials were applied for the sorption of Ciprofloxacin (CIP) from aqueous solution. The effects of contact time, initial CIP concentration, pH and temperature were experimentally studied in batch mode to evaluate the adsorption capacity, kinetics, thermodynamics and equilibrium. Under the established experimental conditions the adsorption reached equilibrium in about 60 minutes and the optimum adsorption capacity attained was 16×10^{-6} mol/g between pH of 5 and 9 for hematite-kaolin composite. Ciprofloxacin uptake per unit mass was found to decrease with increase in adsorbent dosage. The adsorption process was found to be exothermic. The dynamic drug uptake data were applied to various kinetic models and their order of fitness was found to be Pseudo-second order > Elovich equation > Intra-particle diffusion > Pseudo-first order. It was found that the data fitted best with Temkin > Dubinin-Radushkevich > Freundlich > Langmuir, as indicated by their regression values.

Keywords: Adsorption kinetics and thermodynamics, Ciprofloxacin, Hematite nanoparticles, Composite materials, Scanning electron microscopy.

1. Introduction

Ciprofloxacin (CIP) is a synthetic antibiotic categorized as the second generation of fluoroquinolones (FQ) [1] 1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-quinoline-3-carboxylic acid having molecular formula $C_{17}H_{18}FN_3O_3$ and with molar mass 331.346g/mol. Ciprofloxacin hydrochloride (USP) is the monohydrochloride monohydrate salt of ciprofloxacin. It is a faintly yellowish to light yellow crystalline substance with a molecular

weight of 385.8 g/mol. Its empirical formula is $C_{17}H_{18}FN_3O_3HCl \cdot H_2O$ [2]. Ciprofloxacin is an agent of choice for the treatment of bacterial gastroenteritis [3]. It is widely useful for treatment of respiratory tract infections [4] particularly effective for controlling bronchitis and pneumonia [5,6]. It is particularly useful for the control of chronic infections characterized by renal tissue involvement. Ciprofloxacin is a broad spectrum antibiotic active against both gram positive and gram negative bacteria. The chemical structure of ciprofloxacin is illustrated below.

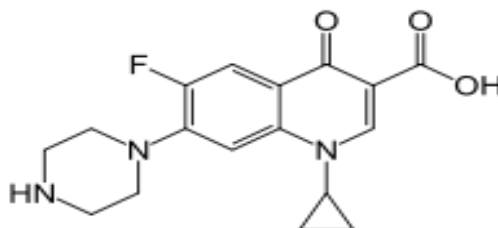


Fig 1.1: Chemical structure of ciprofloxacin

Its presence in drinking water may cause headaches, diarrhoea, nervousness, tremors, nausea, vomiting, etc. [7]. If this drug is present in relatively higher concentrations in drinking water, it may cause serious adverse effects including acute renal failure, elevation of liver enzymes, thrombocytopenia, eosinophilia and leucopenia[8].

Adsorption processes are widely used in industry to remove organic contaminants. The term adsorption is commonly used to describe the tendency of the molecules in fluid phase to adhere to a solid surface. Although adsorption is a well-known process, in the past ten years the study of this technology applied to antibiotics removal has not been much extended. Adams et al and Méndez-Díaz et al studied the batch adsorption on activated carbon of imidazoles and sulphonamides with trimethoprim, respectively. In these two studies about 90% removal was achieved [9,10]. A similar study was developed by Kim et al., but they investigated both batch and continuous adsorption of trimethoprim, obtaining removal above 90%[11]. Chen and Huang analysed the adsorption of three tetracyclines antibiotics on aluminium oxide. They concluded that these compounds were adsorbed (>50%) and besides that, they suffer structural transformations along the process[12]. These studies revealed that adsorption continues to be an effective method to remove antibiotics from aqueous effluents. Clay minerals are low-cost adsorbents, which are widely used to remove inorganic and organic pollutants from aqueous solution. Adsorption of ciprofloxacin has been carried out on adsorbents such as clay [13], kaolinite [14]. Zhaohui et al[15] also investigated the interaction between ciprofloxacin and kaolinite in aqueous solution by batch experiment. From their result, quantitative correlation between the exchangeable cations desorbed and ciprofloxacin adsorbed confirmed experimentally that cation exchange was the dominant mechanism for ciprofloxacin adsorption on kaolinite. Hence, the research on adsorption of ciprofloxacin on hematite and kaolinite. Nanoparticles of different adsorbent have been confirmed as good adsorbents for the removal of antibiotics in aqueous medium but report on adsorption of ciprofloxacin on hematite nanoparticles has been not reported. Hence the need for the study. Composite material gives more desired properties than individual material when used as an adsorbent, such as larger surface area and high adsorption capacity. The

main objective of this research is to evaluate the suitability of Kaolin, Hematite and their Composite as adsorbents for the removal of Ciprofloxacin in synthetic aqueous media

2. Experimental

2.1 *Synthesis of Hematite Nanoparticles*

The hematite was prepared by transformation of ferrihydrite method[16]. Ferrihydrite was precipitated by adding 300ml 1 M KOH that had been preheated to 90°C to 40g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 500ml deionized water preheated to 90°C, then 50ml of 1M NaHCO_3 , preheated to 90°C was added to the precipitate in a closed flask and held at 90°C for 48 hours. The precipitate was washed several times with deionized water by dialysis to remove nitrate ions, and then filtered by Millipore glass membrane vacuum filtration system. The precipitate was then oven dried at 40°C. Kaolin clay of Nigerian origin was grounded, washed with deionized water and sun dried. The sample was sieved with 90 μm , 112 μm , 120 μm and 250 μm Tyler screen standard sieves.

2.2 *Preparation of Hematite-Kaolin Composite*

The hematite-kaolin composite was prepared with hematite nanoparticles and kaolin in the ratio 1:4. A 5g of washed kaolin and 1.25g of synthesized hematite nanoparticles were weighed and then dispersed in 100ml 0.5M HCl to form slurry. The slurry was stirred to enable the kaolin particles enter the matrix of the synthesized hematite nanoparticles and then evaporated to dryness in an oven. The composite materials was washed with deionized water to pH 9, filtered with Millipore glass membrane vacuum filtration system and then further dried in an oven for 24 hours [17].

Characterization of the Adsorbents

The particles were characterized using physico-chemical methods such as pH, colour, point of zero charge (pzc) using the method of Kosmulski, and texture. The infrared spectra were obtained using (Shimadzu Spectrometer). The morphology of the particles were determined using NanoSEM 230 scanning electron Microscope. The elemental composition of the adsorbents determined by X-ray Fluorescence. The crystal structure of adsorbents were analyzed by x-ray diffraction (XRD) on a PW 3050/60 Goniometer X-ray powder diffractometer. The surface area, micropore volume and micropore area of the hematite nanoparticles were measured according to Brunauer- Emmett-Teller (BET) Micrometrics TRISTAR 3000 through Nitrogen adsorption at -196°C.

2.3 *Batch Adsorption Experiments*

2.3.1 *Adsorption capacity*

The removal of Ciprofloxacin (CIP) with kaolin, hematite and hematite-kaolin composite were carried out as batch experiments. The flasks used for contact experiments were wrapped with aluminum foils to prevent light induced decomposition. The experiments involved the preparation of 10mL of CIP solution with different initial concentrations obtained by serial dilution of the stock solution with deionized water. A known mass of the

adsorbents (0.5g kaolin, 0.05g hematite and 0.1g hematite-kaolin composite) were added to different flasks containing the CIP solution and then shaken on a mechanical shaker for different time. After shaking, the solution was then filtered and analysed using UV/visible spectrophotometer. The amount of Ciprofloxacin adsorbed, q_e (mol/g) was calculated using the equation below:

$$q_e = \frac{(C_o - C_f)V}{W}$$

Where C_o and C_f are the initial and final concentrations of Ciprofloxacin (M) respectively, V is the volume of the solution (L) and W is the amount of adsorbent used (g). The percentage adsorbed was calculated using:

$$\% = \frac{(C_o - C_f)}{C_o} \times 100$$

where C_o and C_f are the initial and final concentrations of Ciprofloxacin (M) respectively [15].

Optimization of some physico-chemical properties on sorption of Ciprofloxacin on the different adsorbents were also studied.

2.3.2. Effect of Initial Concentration of Ciprofloxacin

Different concentrations of ciprofloxacin 0.02×10^{-3} to 0.2×10^{-3} M were prepared by serial dilution of the stock solution. The stock solution of 0.01M Ciprofloxacin was prepared by weighing 3.3135g of anhydrous ciprofloxacin salt and then dissolved with deionized water and made up to the 1000mL mark of a standard flask. The initial concentrations were contacted with 0.5 g of kaolin, 0.05 g of hematite and 0.1 g of hematite kaolin composite at the natural pH 5 of the adsorbate with agitation speed of 150 rpm for 240 minutes.

2.3.3 Effect of Contact Time

The effects of contact time on the adsorption capacity of the adsorbents were studied in the range 5 – 1440minutes at the optimum concentration of 0.14×10^{-3} M for kaolin, 0.17×10^{-3} M for both Hematite and Hematite-kaolin to establish the equilibrium time. Equilibrium concentration of Ciprofloxacin for each adsorbent was prepared into different flasks and contacted with 0.5g, 0.05g and 0.1g of kaolin, hematite and hematite-kaolin composite respectively.

2.3.4 Effect of pH of the solution

The pH of solution has been identified as the most important variable affecting adsorption of adsorbate onto adsorbent. The pH of the adsorbate was adjusted to 3, 5, 7, 9 and 11 with 0.1 M HCl or 0.1 M NaOH and then contacted with kaolin (0.5g, 0.14×10^{-3} M, $30 \pm 2^\circ\text{C}$ for 120 minutes at 165rpm), Hematite (0.05g, 0.17×10^{-3} M, $30 \pm 2^\circ\text{C}$ for 60 minutes at 165rpm) and Hematite-kaolin composite (0.1g, 0.17×10^{-3} M, $30 \pm 2^\circ\text{C}$ for 60 mins at 165rpm).

2.3.5 Effect of Adsorbent dosage

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. Adsorbent dose was varied for kaolin (0.1-1.0g), Hematite (0.01-0.10g) and Hematite-kaolin composite (0.02-0.12g) then contacted with ciprofloxacin

0.14x 10⁻³M at pH 5 for kaolin and 0.17 x 10⁻³M at pH 5 and pH 9 for hematite and Hematite-kaolin composite respectively under optimal conditions obtained earlier.

2.3.5 Effect of Temperature

The effect of temperature was investigated at temperature range of 30-70°C. 0.14 x 10⁻³M Ciprofloxacin (pH 5) was contacted with 0.4 g of Kaolin for 120 minutes at 165rpm, 0.17 x 10⁻³M Ciprofloxacin (pH 5) was contacted with 0.05g of hematite for 60 minutes at 165rpm and 0.17 x 10⁻³M Ciprofloxacin (pH 9) was contacted with 0.08g of Hematite-kaolin composite for 60 minutes at 165rpm.

2.4 Adsorption Isotherm

Adsorption isotherms were obtained to assess ciprofloxacin distributions between solid and aqueous phases as a function of adsorbate concentration. The adsorption data were analysed using the linear forms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms.

2.5 Kinetics and Thermodynamic Model

The kinetics of adsorption was evaluated using pseudo-second order kinetics, Pseudo-first order model, Elovich rate equation and intra-particle diffusivity to test the data obtained for adsorption processes. The thermodynamic parameters of the sorption process were calculated using the following relationship:

$$\ln K_d = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (2.1)$$

Where K_d is the ratio of amount adsorbed to equilibrium concentration, ΔH is the change in enthalpy, ΔS is the change in entropy, R is gas constant, and T is the reaction temperature. The free energy change of sorption was obtained by

$$\Delta G = \Delta H - T\Delta S \quad (2.2)$$

3. Results and Discussion

3.1 Physicochemical Properties of the Adsorbents

The surface and physicochemical properties of the synthesized iron oxides nanoparticles are shown in Table 1.

Table 1: The physico-chemical properties of synthesized iron oxide nanoparticles

Iron oxides	Colour	pH	Bulk density (g/cm ³)	Pzc	Texture	% yield
Hematite	Reddish brown	9.06	1.417	9.35	Fine	81.3

3.1.1. X-Ray Diffraction (XRD)

X-ray diffraction gives the crystal phases of the samples. The XRD patterns of kaolin, hematite and hematite-kaolin composite are shown in Fig. 3.1a.

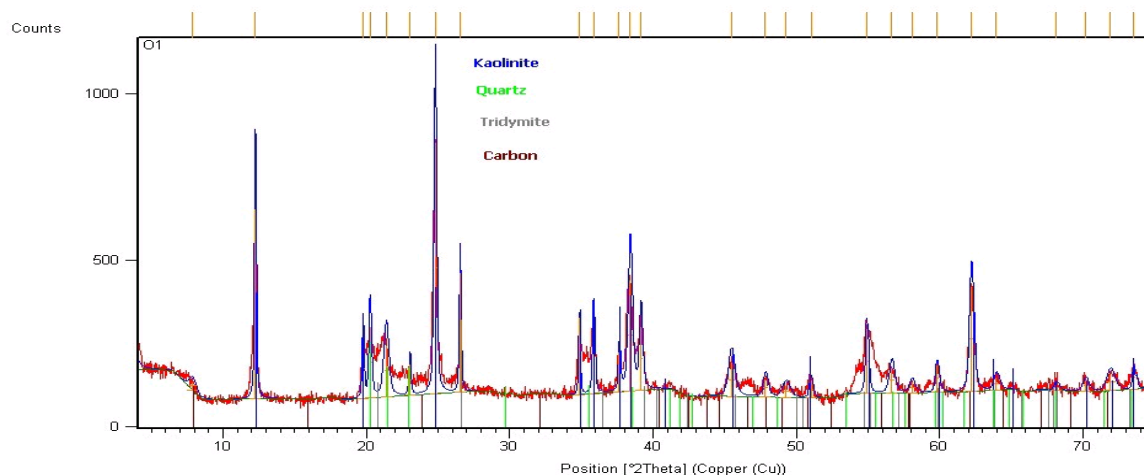


Fig. 3.1 XRD pattern of kaolin

The X-ray diffraction spectrograph of the kaolin clay is shown in **Fig. 3.1a**. Kaolin showed three intense diffraction peaks at 2θ value of 12.3° , 24.9° and 62.3° , less intense peaks at 2θ of 19.8° , 35.9° , 37.7° , and 38.4° which are all associated with kaolinite. Diffraction peaks of quartz could be found at 2θ values of 20.8° , 26.8° and 50.0° . Tridymite was also detected at $2\theta = 20.3^\circ$, 21.5° , 22.9° , 29.7° , 38.6° and 35.5° . Diffraction peaks of carbon was also found at 2θ values of 7.9° , 15.8° , 23.9° and 32° . This XRD result conforms with the existing literatures on kaolin[18, 19].

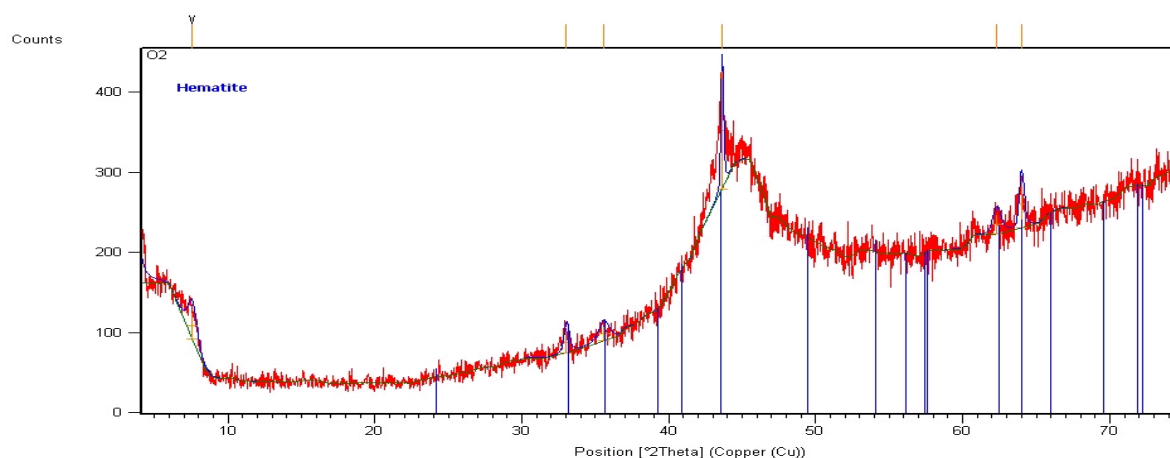


Fig. 3.1 b XRD pattern of Hematite

The X-ray diffraction spectrograph of the hematite is shown in **Fig. 3.1 b**. Hematite shows two intense diffraction peaks at 2θ value of 33.2° and 35.6° , less intense peaks at 2θ of 24.2° , 40.9° , 49.5° , 54.1° , 62.5° and 63.9° , which are all associated with hematite. The XRD result for hematite shows the presence of hematite with rhombohedra shape. The recorded indexed diffraction pattern shows sharp peaks expected for a highly

crystalline sample [20]. The position of all maxima coincided with peaks characteristic of hematite phase. There is no other diffraction line corresponding to other phases, indicating a high purity of the sample, which is in line with reported studies on hematite[20,21].

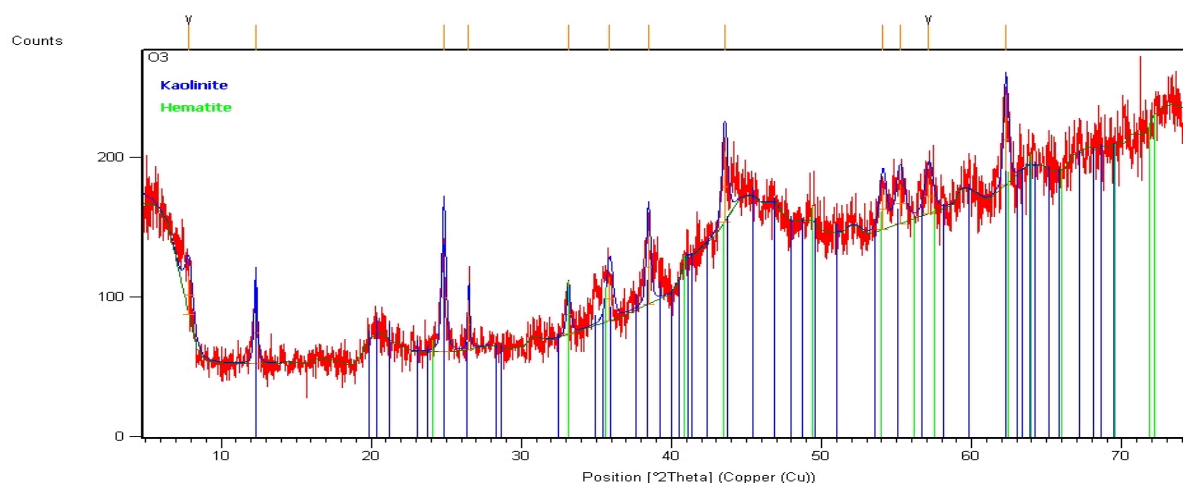


Fig. 3.1 c XRD spectra of hematite-kaolin composite

The XRD pattern of hematite-kaolin composite material showed the presence of both hematite and kaolin as shown in **Fig. 3.1c**. The spectrograph shows two intense diffraction peaks at 2θ value of 12.3° and 24.9° , less intense peaks at 2θ of 19.9° , 21.2° , 37.7° , and 38.4° which are all associated with kaolinite [22]. It also shows two intense diffraction peaks at 2θ value of 33.1° and 35.6° , less intense peaks at 2θ of 24.1° , 40.8° , 49.4° , 54° , 62.4° and 63.9° , which are all associated with hematite [20].

3.1.2 X-Ray Fluorescence (XRF)

The XRF analysis data of the three adsorbents revealed that the major constituents of the kaolin sample are silicon oxide and aluminium oxide (43.3% and 52.0 % respectively). This result is consistent with the XRD results reported by other researchers [23-25]. The results of XRF for hematite revealed hematite as the main constituent. The percentage Fe_2O_3 present in the sample is 97.02%, this complements the result obtained from XRD. This result agrees with those of other researchers [20]. The composition of hematite-kaolin composite provides evidence for the deposition of hematite on kaolin. The percentages of the major components present, Al_2O_3 , SiO_2 and Fe_2O_3 are 34.6%, 38.1% and 23.91% respectively.

3.1.3. Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) was used to check the morphology and average crystal size.

A. Kaolin

The SEM images of the kaolin before adsorption and after adsorption are shown in **Fig. 3.2 (a-d)**.

SEM micrograph of the kaolin clay sample suggests a very cohesive material, **Fig 3.2(a-d)**. The micrograph confirms that the material is forming micron-size agglomerates. A higher magnification micrograph of the same structure shows that the micro-size particles are composed of individual platelets, which conglomerate into larger size particles. The presence of pores on the surface of kaolin shown on SEM images **Fig.3.2(a-b)** before adsorption aids the adsorption of adsorbate on it. But after adsorption of ciprofloxacin on the kaolin, the SEM micrograph of kaolin shown in **Fig. 3.2 (c-d)** indicates that the pores were filled with the adsorbate, which shows that ciprofloxacin had been adsorbed by the kaolin.

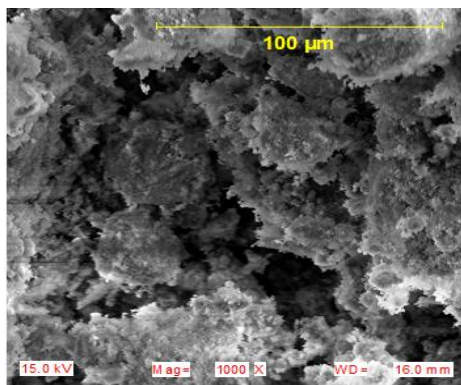


Figure 3.2a. Kaolin (Mag 1000x) before adsorption

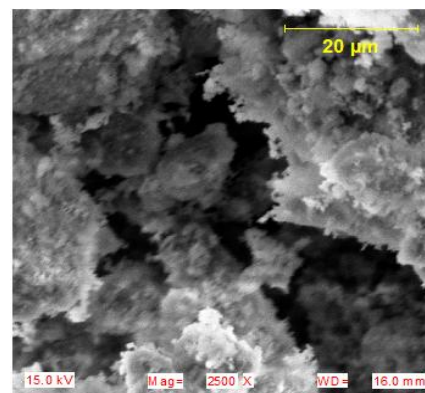


Figure 3.2b. Kaolin (Mag 2500x) before adsorption

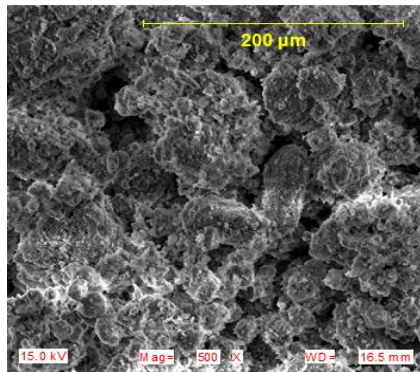


Figure 3.2c. Kaolin (mag 500x) after adsorption

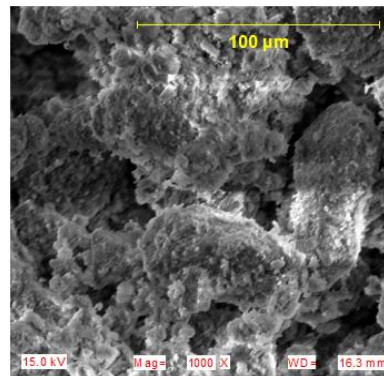


Figure 3.2d. kaolin (mag 1000x) after adsorption

B. Hematite

The SEM micrograph **Fig. 3.2 (e-f)** confirms that the synthesized hematite sample consists of particles of different morphological shapes such as triangular, plate-like, hexagonal and other irregular shapes. The micrographs show that hematite particles are aggregates of small particles. This sample also contains many pores showing its adsorption capability [20]. **Fig. 3.2 (g-h)** shows the micrograph of hematite after adsorption of ciprofloxacin, with most of its pores filled up.

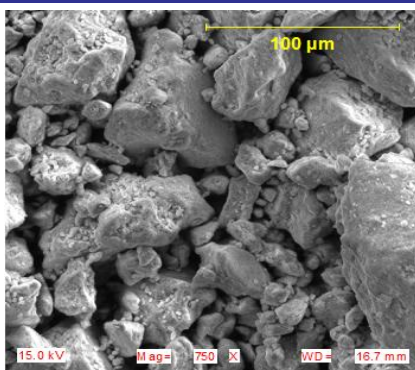


Figure 3.2e. Hematite (mag 750) before adsorption

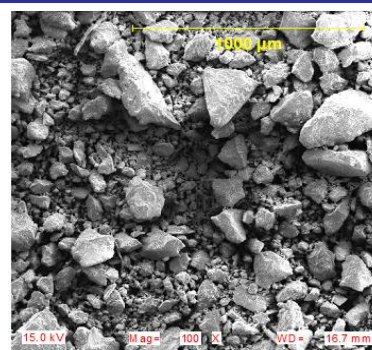


Figure 3.2f. Hematite (mag 100) before adsorption

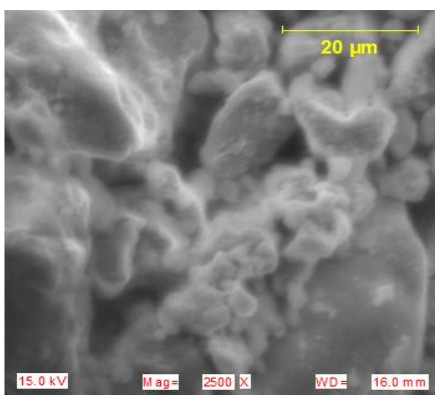


Figure 3.2g. Hematite (mag 2500) after adsorption

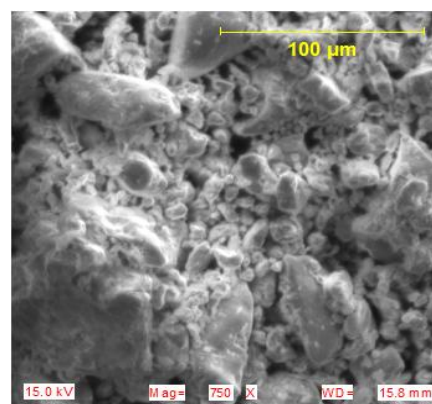


Figure 3.2h. Hematite (mag 750) after adsorption

C. kaolin-hematite composite

The SEM images in **Fig. 3.1(i-j)** show the composite before adsorption. It shows kaolin completely surrounded by nanoscale hematite. The pores on the surface of the kaolin have been filled with nanoscale hematite particles due to its small size. **Fig. 3.1(k-l)** shows the micrograph of the composite after adsorption of ciprofloxacin.

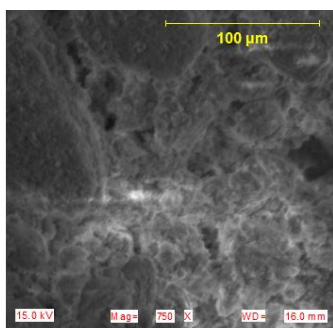


Fig 3.2i. Hematite-kaolin composite before adsorption

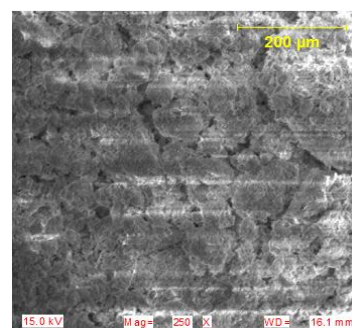


Fig 3.2j. Hematite-kaolin composite before adsorption

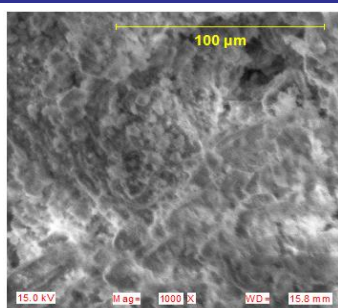


Fig 3.2k. Hematite-kaolin composite after adsorption

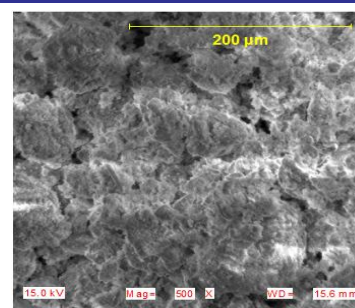


Fig 3.2l. Hematite-kaolin composite after adsorption

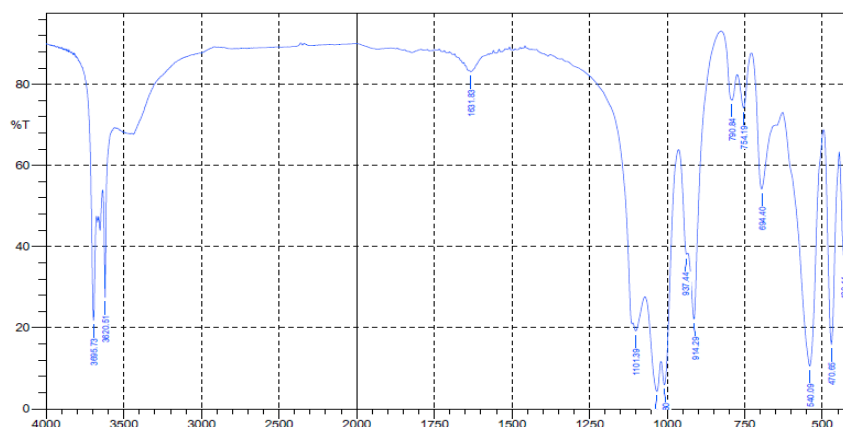
Fig. 3.2. (a-l) SEM images of the adsorbents with different magnifications

3.1.4. Fourier Transform Infrared (FTIR)

Infrared (IR) spectroscopy is a technique based on vibrations of atoms in a molecule. It is used for detection of functional groups present in a material. The FTIR spectra of the three adsorbents are presented in **Fig. 3.3-3.5**.

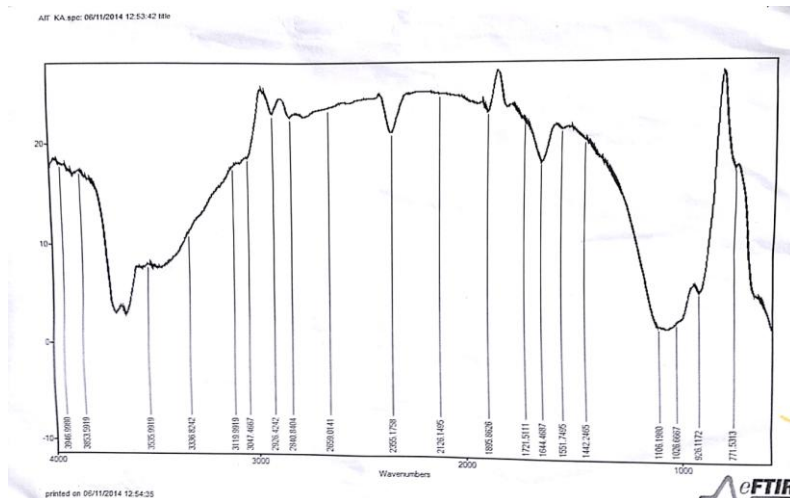
A. Kaolin

The FTIR Spectra of the kaolin, in the range of $400 - 4000 \text{ cm}^{-1}$ were measured to confirm the presence of functional groups that might be responsible for the adsorption process. They are presented in **Figures 3.3a-b**. Kaolin clay displays a number of peaks, reflecting the complex nature of the kaolin clay. The main bonds observed for kaolin before adsorption of ciprofloxacin were OH⁻ stretching, hydroxyl sheet at 3695.73 cm^{-1} and 3620.51 cm^{-1} . H₂O stretching was also found at 1631.83 cm^{-1} . Bands at 1101 cm^{-1} , 1033 cm^{-1} and 1008.8 cm^{-1} were assigned to Si-O bonds in the SiO₄ molecules [22,25]. The other bands at 937.44 cm^{-1} and 914 cm^{-1} were attributed to Al^{IV}-OH vibrations [22,26]. The bands at 790.84 cm^{-1} , 754.19 cm^{-1} and 694.40 cm^{-1} were Si-O symmetric stretching [27].



3.3a. FT-IR spectra of Kaolin before adsorption

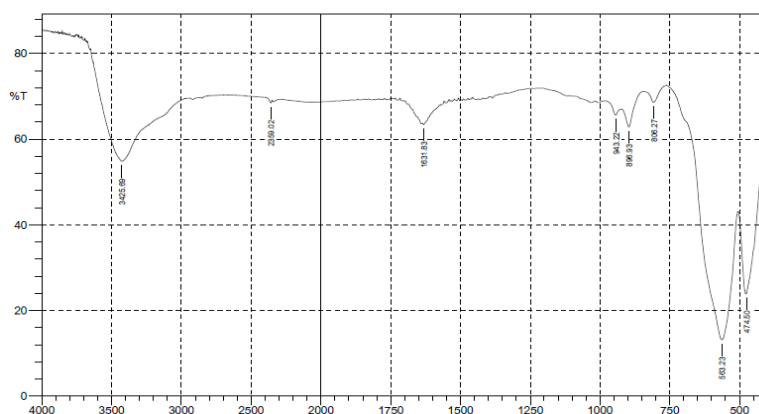
Absorption at 540.09 cm^{-1} was assigned to $\text{Si-O-Al}^{\text{VI}}$, where the Al is in octahedral coordination [26]. The interaction of Ciprofloxacin with kaolin is obvious from the spectra changes of some prominent peaks of the spectrum of the adsorbent before and after adsorption. **Fig. 3.3b** shows the new bonds observed for kaolin after adsorption of ciprofloxacin, these were C-F at 1442.2 cm^{-1} , N-H bending at 1551 cm^{-1} and the band 1721.5 cm^{-1} is attributed to C=O



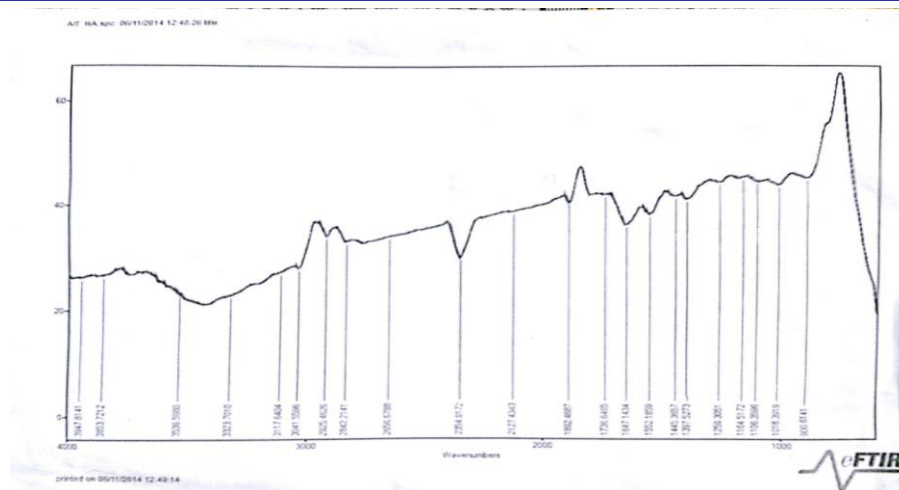
3.3b. FT-IR spectra of Kaolin after adsorption of CIP

B. Hematite

The FT-IR spectra of hematite before and after adsorption are shown in **Fig. 3.4a-b**. The spectra of the sample (**Fig. 3.3a**) before adsorption shows broad bands at 474.5 cm^{-1} and 563.23 cm^{-1} ; which can be attributed to Fe-OH bond vibration of Fe_2O_3 [20]. Band at 1631.83 cm^{-1} is assigned to the bending mode of water molecules. The band at 3425.69 cm^{-1} is assigned to O-H stretching vibration of adsorbed water. IR band at 943.22 cm^{-1} in the hematite spectrum is assigned to O-H deformation. The spectrum of hematite after adsorption (**Fig.3.4b**) shows the presence of different bands; C-F at peak 1445.3 cm^{-1} , C=O at peak 1736.6 cm^{-1} and alkenes stretch at peak 3041.6 . Bands 1552.2 cm^{-1} and $3117\text{-}3323.7\text{ cm}^{-1}$ are for N-H stretching and bending respectively.



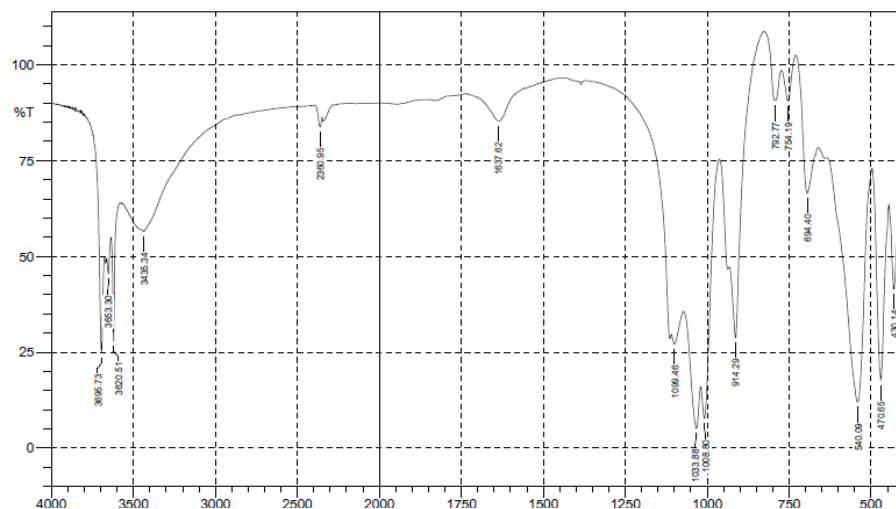
3.4a. FT-IR spectra of Hematite before adsorption



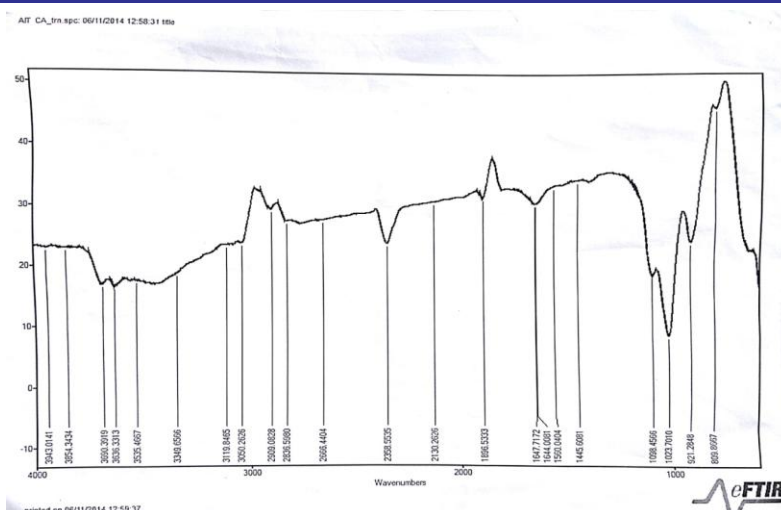
3.4b. FT-IR spectra of Hematite after adsorption

C. Hematite-Kaolin Composite

FT-IR spectra of nanoscale hematite-kaolin composite before and after adsorption are shown in **Fig. 3.5a-b**. Due to compositing of the nanoscale hematite with the kaolin, some prominent peaks from kaolin can be seen among the absorption bands of nanoscale hematite. The absorption bands in hematite-kaolin (**Fig. 3.5a**) are 3620.51, 3653.3 cm^{-1} and 3695.73 cm^{-1} attributed to O-H stretching. The interaction of Ciprofloxacin and hematite-kaolin composite can be seen from the spectra shown in **Fig. 3.3b**, C-F peak was observed at 1445.6 cm^{-1} and band 3349.65 cm^{-1} is for N-H stretching.



3.5a. FT-IR spectra of Hematite-Kaolin composite before adsorption



3.5b. FT-IR spectra of Hematite-Kaolin composite after adsorption

3.2 Results of Adsorption Studies

3.2.1 Effect of Concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of ciprofloxacin between the aqueous and the solid phase. The results are presented in **Figure 3.6**. The uptake of ciprofloxacin increases with the initial concentration of the adsorbate. This is true for the three adsorbents

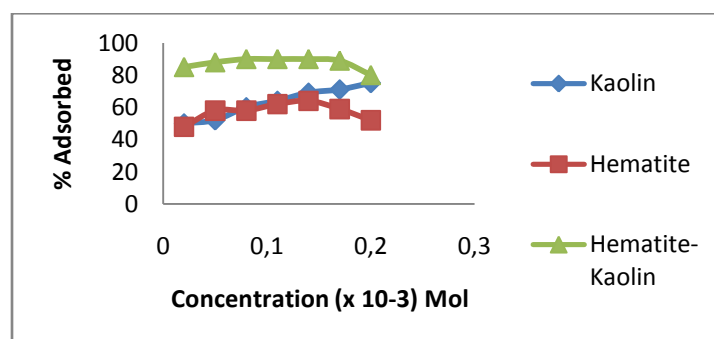


Fig. 3.6: Effect of conc (Kaolin, hematite and composite w= 0.5, 0.05 and 0.1g, pH 3, Temp= 30±2K for 240mins at 165rpm)

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 [28]. Variations of adsorption capacity of the three adsorbents for CIP with pH are shown in **Fig. 3.8**. From the graphs, the adsorption of CIP onto the three adsorbents is strongly dependent on the pH of the solution. CIP speciation diagram [15] indicates that the cationic form, CIP⁺, exists due to protonation of the amine group when solution pH is below 6. As the solution pH becomes greater than 8.7, the anionic form, CIP⁻ prevails, due to ionization of carboxylic groups. When solution pH is between 5 and 8 the neutral form, CIP, is

the dominant species, which results from the charge balance between the above two groups[15]. **Fig. 3.8** shows a rapid increase in CIP adsorption on kaolin from pH 3 to pH 5, which could be attributed to the net repulsion between the positively charged mineral surfaces and the CIP molecules. Thus, the slightly less CIP adsorption at pH 3 and 4 could be attributed to the pH-dependent surface charge of kaolinite, at which the surface was less negative. When pH was greater than 9 a drastic decrease in CIP adsorption was seen, which could be attributed to the net repulsion between the negatively charged mineral surfaces and the CIP molecules.

Maximum adsorption of CIP on hematite was observed at pH 5 shown in **Fig. 3.7** while the amount adsorbed decreased as the pH increased. The hematite surface might be highly protonated at pH 5, which favor the uptake of CIP in predominant cationic form (CIP^+) [15]. With the increase in pH from 5 to 11, the degree of hematite surface protonation reduced gradually, thereby resulting in decrease in adsorption capacity. The maximum adsorption of CIP on hematite-kaolin composite was achieved at pH 9. Low adsorption was observed at low pH due to increase in proton density on the surface sites and thus electrostatic repulsion occurred between the CIP ions and the composite. The percentages of CIP adsorbed at each optimum pH are 80%, 64% and 99% for kaolin, hematite and hematite-kaolin composite respectively.

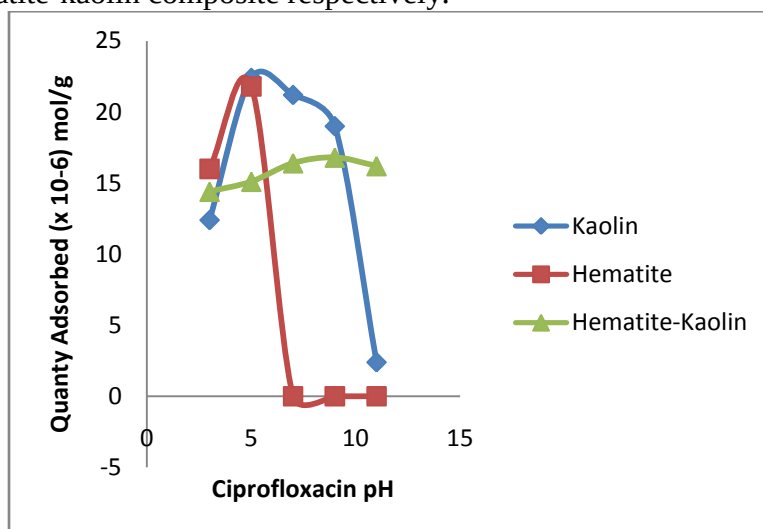


Fig 3.7: Effect of pH on Adsorption of Kaolin, Hematite and Hematite-Kaolin

3.2.3 Effect of Contact Time

Contact time is an important parameter to determine the equilibrium time of adsorption process [29]. The effect of contact time on the adsorption of CIP onto kaolin, hematite and hematite-kaolin composite are shown in **Fig 3.8**. It can be seen that the adsorption of CIP was rapid from the beginning of the experiment up to the first 120 minutes for kaolin, 60 minutes for hematite and hematite-kaolin composite where the maximum adsorption of CIP onto the adsorbents were observed; it can be said that beyond this there was almost no further increase in the adsorption. This was due to the decrease of adsorption sites on the adsorbents [19,20]. Therefore, 120 minutes for kaolin, 60 minutes for Hematite and hematite-kaolin composite were selected as the optimum contact time for subsequent experiments. On the basis of these results, it can be observed that kaolin, hematite

and hematite-kaolin composite can be used to remove this Ciprofloxacin. Similar results have been reported [19-20,22].

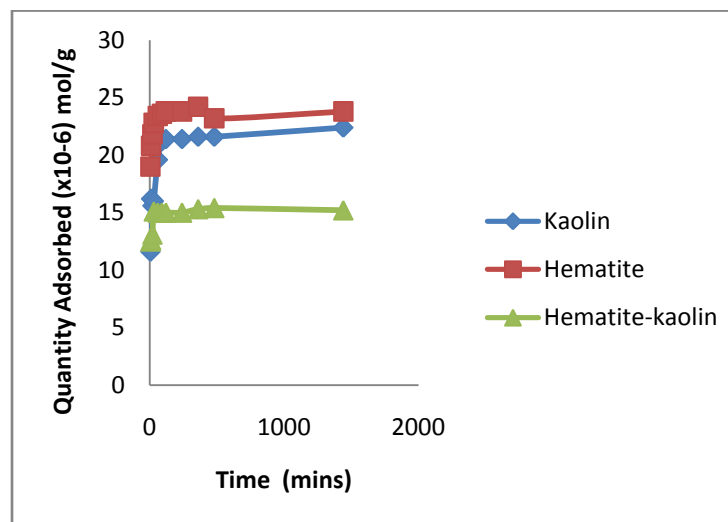


Fig.3.8: Effect of Time (Kaolin, Hematite and Hematite-kaolin composite, w= 0.5, 0.05, 0.1g, pH 5 and 9, $C_0 = 0.14 \times 10^{-3} \text{ M}$, $0.17 \times 10^{-3} \text{ M}$, $0.17 \times 10^{-3} \text{ M}$, temp= $30 \pm 2^\circ \text{C}$, 165rpm)

3.2.4 Effect of Adsorbent Dosage

This parameter determines the capacity of adsorbent for a given CIP concentration. **Fig. 3.9** shows the plots of the CIP uptake against the quantity of each adsorbent. The CIP uptake per unit mass decreased with increase in adsorbent dosage. The reason for this trend may be attributed to the fact that at high sorbent dosages, the available CIP molecules are not able to cover all the exchangeable sites on the adsorbent, resulting in low CIP uptake.

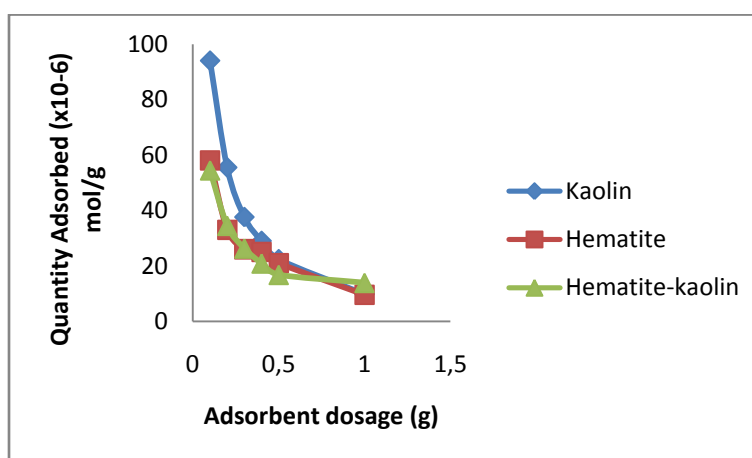


Fig.3.9: Effect of adsorbent dose (kaolin, hematite and hematite-kaolin pH 9, $C_0 = 0.14 \times 10^{-3} \text{ M}$, $0.17 \times 10^{-3} \text{ M}$, $0.17 \times 10^{-3} \text{ M}$ temp= $30 \pm 2^\circ \text{C}$, 60mins at 165rpm)

3.2.5 Effect of Temperature

The adsorption of Ciprofloxacin from aqueous solution by kaolin, hematite and hematite-composite at different temperature are shown in Fig. 3.10. The adsorption of CIP decreased with increase in temperature for all the adsorbents. This indicates the exothermic nature of the adsorption process. Similar phenomenon was reported by Adegoke et al [20].

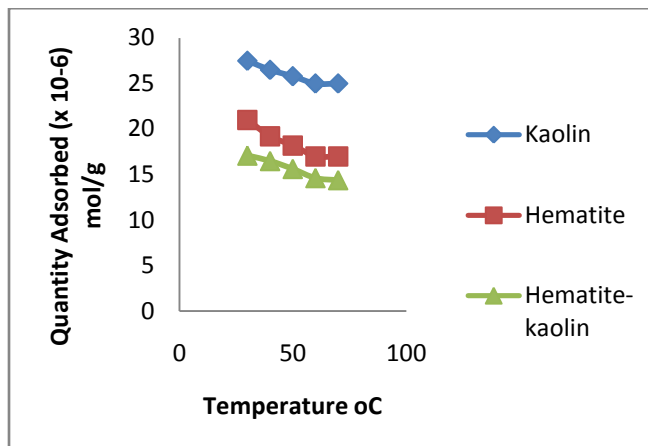


Fig. 3.10: Effect of Temp (kaolin, hematite and hematite-kaolin composite, w=0.08g, pH 9, $C_0=0.17 \times 10^{-3}M$, 60mins at 165rpm)

3.3. Adsorption Isotherms, Kinetics and Thermodynamic Models

3.3.1. Adsorption Isotherms

The adsorption isotherm provides a relationship between the concentration of CIP in solution and the amount of CIP adsorbed on the solid phase when both phases are at equilibrium at constant temperature. For this study, four important isotherm models used were the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models.

A. Kaolin

The graph of the isotherm that fitted the experimental data for adsorption on kaolin is presented in Fig. 3.11

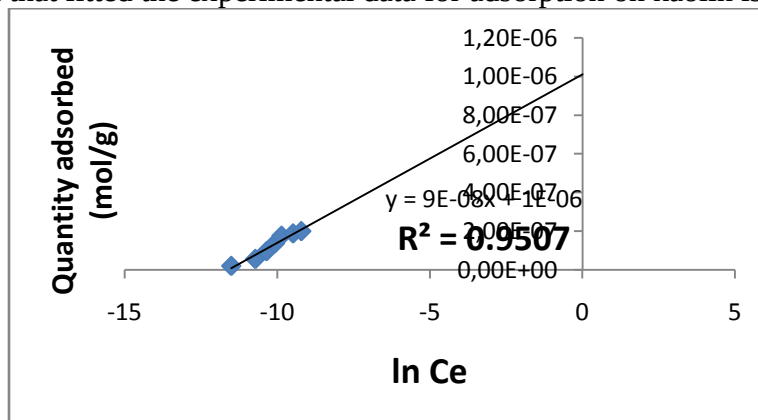


Fig. 3.11a: Temkin Isotherm (kaolin w=0.4g, pH 5, 120mins, temp=30°C at 165rpm)

The adsorption data fits best the isotherms in order of Temkin> Dubinin–Radushkevich> Langmuir>Freundlich. The characteristic sorption curve is related to the porous structure of the adsorbent as reported by Dubinin and Radushkevich. Temkin has a higher regression coefficient value of $R^2 = 0.9507$ compared to Freundlich ($R^2 = 0.8509$) and Dubinin-Radushkevich isotherm ($R^2 = 0.8410$) and Langmuir ($R^2 = 0.0323$) isotherms. The constant B_D in table 3.2a is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution, q_D is the monolayer adsorption capacity (mol/g) and E is the activity coefficient related to mean sorption energy (mol^2/J^2) which is the Polanyi potential. n is the Freundlich constant which indicates whether the nature of sorption is either favorable or unfavorable. In this study, $n < 1$ ($n = 0.426$) which indicates that the sorption intensity is not favorable over the entire range of concentrations studied. b_T constant in Temkin isotherm is 2.5×10^{10} J/mol which is an indication that heat of sorption corresponds to physical adsorption process.

Table 3.2a: Isotherm parameters for adsorption of CIP onto kaolin

ISOTHERM	PARAMETER	VALUES
Langmuir	$q_0(\text{mol/g})$	2.06E-6
	$K_L(\text{L/mol})$	7.57E-4
	R^2	0.0323
Freundlich	n	0.426
	$K_F(\text{mol/g})$	8541
	R^2	0.8509
Temkin	$B(\text{J/mol})$	9.0E-8
	A	6.02E-3
	$K_T(\text{L/g})$	6.69E4
	R^2	0.9507
Dubinin-Radushkevich	$E(\text{kJ/mol})$	5.000
	$B_D(\text{mol}^2/\text{kJ}^2)$	2E-8
	$q_D(\text{mol/g})$	0.051
	R^2	0.841

B. Hematite

The graph for the isotherm that fitted the experimental data of adsorption on kaolin is presented in **Fig. 3.12**. The adsorption data for hematite nanoparticles were better explained using the Temkin isotherm with good regression coefficient value ($R^2 = 0.9441$) with $B = 1\text{E-}05\text{J/mol}$ which is an indication that the heat of adsorption correspond to a physical adsorption process. These data are presented in Table 3.2b.

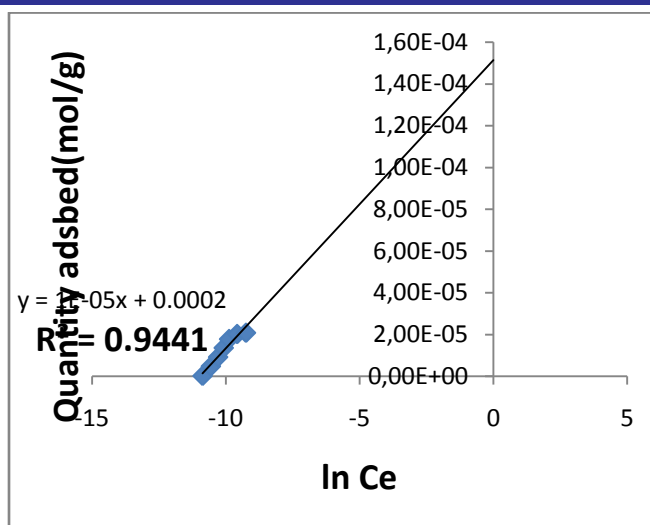


Fig. 3.12: Temkin Isotherm (hematite w=0.05g pH 5,60mins, temp=30°C at 165rpm)

Table 3.2b: Isotherm parameters for adsorption of CIP onto Hematite

ISOTHERM	PARAMETER	VALUES
Langmuir	$q_0(\text{mol/g})$	1.67E-7
	$K_L(\text{L/mol})$	7.78E-5
	R^2	0.2303
Freundlich	n	0.410
	$K_F(\text{mol/g})$	3.3E5
	R^2	0.674
Temkin	$B(\text{J/mol})$	1E-5
	A	0
	$K_T(\text{L/g})$	1
	R^2	0.9441
Dubinin-Radushkevich	$E(\text{kJ/mol})$	5.000
	$B_D(\text{mol}^2/\text{kJ}^2)$	2.0E-8
	$q_D(\text{mol/g})$	1.92
	R^2	0.6971

C. Hematite-Kaolin

The adsorption data were analysed with the isotherms, **Fig. 3.14a&b** shows the adsorption isotherms for adsorption of CIP on Hematite-kaolin composite. The adsorption data fits best the isotherms in this order Dubinin–Radushkevich > Temkin > Freundlich > Langmuir Isotherm. Temkin ($R^2 = 0.9305$) with $B=6.17\text{E}5\text{J/mol}$ indicates that heat of sorption is a physical process. Dubinin-Radushkevich ($R^2 = 0.9787$), the

constant B_D in table 3.3c, is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution.

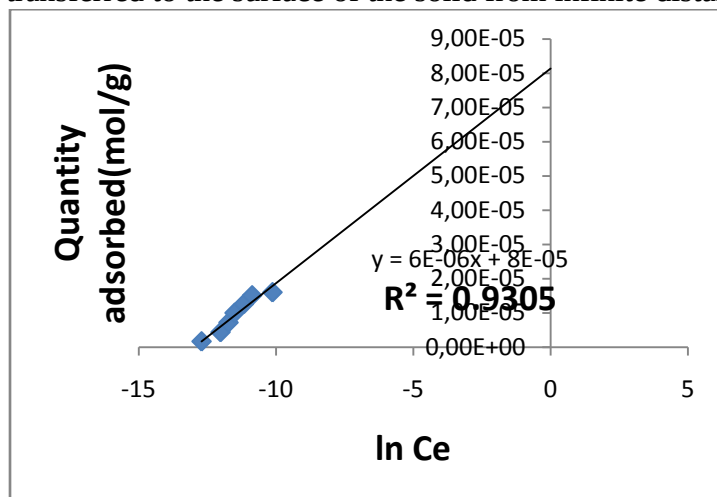


Fig. 3.13a: Temkin Isotherm (hematite-kaolin composite $w=0.1g$ pH 9,60mins, temp=30°C at 165rpm)

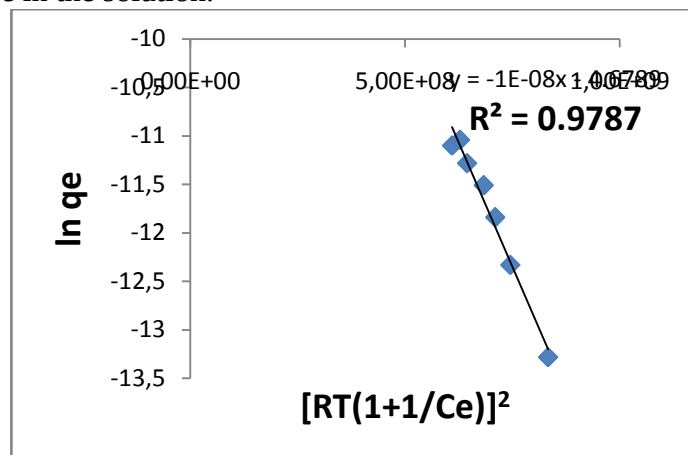


Fig. 3.13b: Dubinin–Radushkevich Isotherm (hematite-kaolin composite $w=0.1g$ pH 9,60mins, temp=30°C at 165rpm)

Table 3.2c: Isotherm parameters for adsorption of CIP onto Hematite-kaolin

ISOTHERM	PARAMETER	VALUES
Langmuir	$q_0(\text{mol/g})$	3.47E-5
	$K_L(\text{L/mol})$	3.63E-5
	R^2	0.4577
Freundlich	n	1.12
	$K_F(\text{mol/g})$	0.21
	R^2	0.8504
Temkin	$B(\text{J/mol})$	6.00E-6
	A	7.99E-5
	$K_T(\text{L/g})$	6.17E-5
	R^2	0.9305
Dubinin-Radushkevich	$E(\text{kJ/mol})$	7.071
	$B_D(\text{mol}^2/\text{kJ}^2)$	1.0E-8
	$q_D(\text{mol/g})$	9.28E-3
	R^2	0.9787

3.3.2. Kinetic Models

Four kinds of kinetic models were used to analyse the kinetic data of the adsorption. These are; Pseudo-first-order, Pseudo-second- order, Elovich and Intra-particle diffusion models.

A. KAOLIN

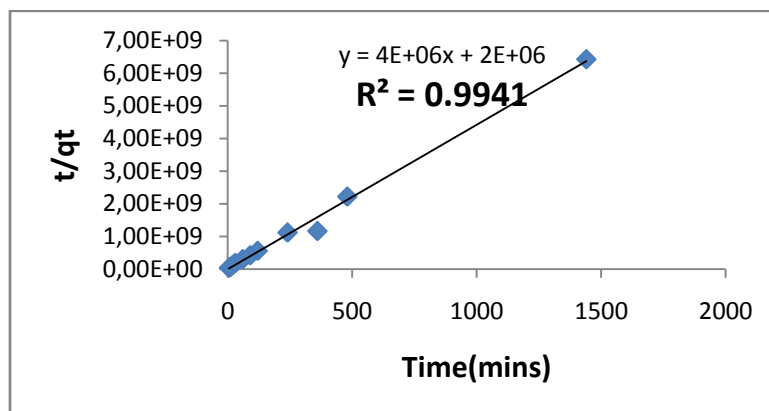


Fig. 3.14a Pseudo-second order (kaolin w=0.4g, pH 5, 0.14×10^{-3} , temp=30°C at 165rpm)

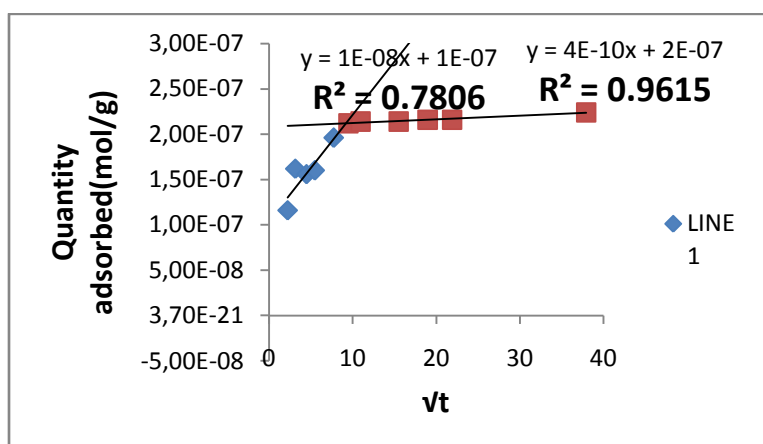


Fig. 3.14b: Intra-particle diffusion (kaolin w=0.4g, pH 5, 0.14×10^{-3} , temp=30°C at 165rpm)

Experimental data were best fitted with pseudo-second order with correlation coefficient of 0.9941 (**Fig 3.14a**), this show a good agreement between experimental and calculated q_e values presented in table 3.3a. A plot of q versus $t^{1/2}$ indicates that intra-particle diffusion is involved in the adsorption process and if the plot passes through the origin then intra-particle diffusion is the sole rate limiting step (Ozean et al.2007). The results, as shown in **Fig 3.14b** indicates a larger intercept values which suggest that intra-particle diffusion has a lesser role to play compare to the surface diffusion. The multi-linearity observed indicate that two steps occur in the adsorption process. The external surface adsorption stage is the sharply rising part and the second part is the gradual adsorption stage where intra-particle diffusion occurs. Since the lines deviate from the origin and the low values of the gradual adsorption stage suggest that intra-particle diffusion is not the sole rate limiting step. Elovich kinetic showed a better compliance with regression coefficient value of 0.8346 compared to that of pseudo-first order.

Table 3.3a: The values of parameters and correlation coefficients of kinetic models for kaolin
Initial concentration: $0.14 \times 10^{-3} \text{M}$

Kinetics models	Parameters	Values
Pseudo-first order	$K_1(\text{min}^{-1})$	$9.2\text{E-}4$
	$q_{e,\text{cal}}(\text{mol/g})$	$6.5\text{E-}8$
	R^2	0.4183
Pseudo-second order	$K_2(\text{g} \cdot \text{mol}^{-1} \cdot \text{min}^{-1})$	$8.0\text{E-}6$
	$q_{e,\text{cal}}(\text{mol/g})$	$2.5\text{E-}7$
	R^2	0.9941
Elovich	$\alpha(\text{mol}^{-1} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$	$3.3\text{E}6$
	$\beta(\text{g/mol})$	$5.0\text{E-}7$
	R^2	0.8346
Intra-particle diffusion		LINE 1 LINE 2
	$K(\text{mol/g} \cdot \text{min}^{-1/2})$	$1\text{E-}8$ $4\text{E-}10$
	C	$1\text{E-}7$ $2\text{E-}7$
	R^2	0.7806 0.9615

B. HEMATITE

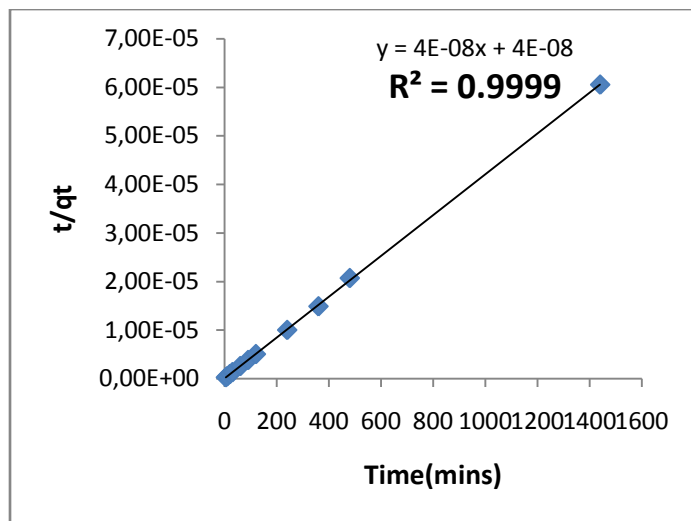


Fig. 3.15a: Pseudo-second order (hematite $w=0.05\text{g}$, pH 5, 0.17×10^{-3} , temp= 30°C at 165rpm)

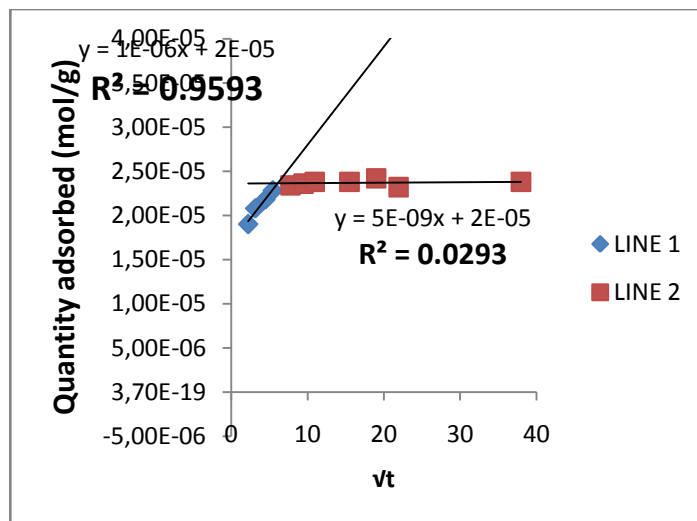


Fig. 3.15b: Intra-particle diffusion (hematite $w=0.05\text{g}$, pH 5, 0.17×10^{-3} , temp= 30°C at 165rpm)

It is evident from table 3.3b, that pseudo-second order kinetic model has the highest regression coefficient (0.9999) as shown in **Fig. 3.15a**. The deviation of straight lines from the origin (**Fig. 3.15b**) in the graph of

Intra-particle diffusion graph indicates that the pore diffusion is not the sole rate-controlling step. Elovich has a fairly good fitting on the data based on its regression coefficient ($R^2=0.7008$), while pseudo-first order kinetics with low regression coefficient $R^2=0.0108$ does not fit the data. This indicates that second-order kinetic model fits more to the adsorption data and can be applied to the removal of CIP using hematite nanoparticles as an adsorbent.

Table 3.3b: The values of parameters and correlation coefficients of kinetic models for hematite nanoparticles
Initial concentration: $0.17 \times 10^{-3} \text{M}$

Kinetics models	Parameters	Values	
Pseudo-first order	K ₁ (min ⁻¹)	0.00023	
	q _{e,cal} (mol/g)	1.19	
	R ²	0.0108	
Pseudo-second order	K ₂ (g.mol ⁻¹ min ⁻¹)	4.0E-8	
	q _{e,cal} (mol/g)	2.5E-7	
	R ²	0.9999	
Elovich	α (mol ⁻¹ g ⁻¹ min ⁻¹)	5.75E4	
	β (g/mol)	1.25E6	
	R ²	0.7008	
Intra-particle diffusion		LINE 1	LINE 2
	K (mol/g/min ^{-1/2})	1E-6	5E-9
	C	2E-5	2E-5
	R ²	0.9593	0.0293

C. HEMATITE-KAOLIN COMPOSITE

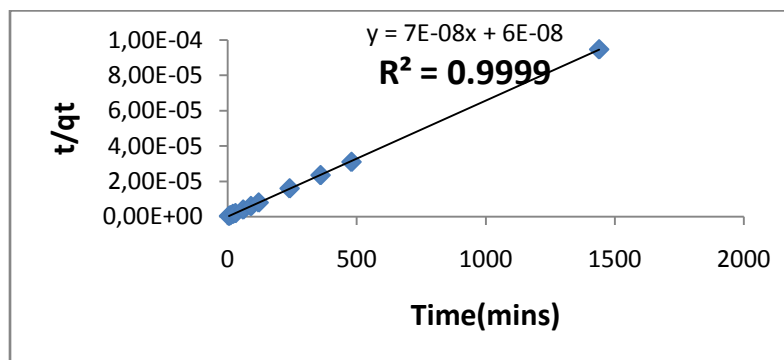


Fig. 3.16a: Pseudo-second order (hematite-kaolin composite $w=0.1\text{g}$, $\text{pH } 9$, 0.17×10^{-3} , $\text{temp}=30^\circ\text{C}$ at 165rpm)

The adsorption data fits more to the pseudo-second order model with regression coefficient value of 0.9999 as shown in **Fig. 3.16a**, than that of Elovich model (0.6897) on the adsorption of CIP on hematite-kaolin

composite. **Fig 3.16b** shows the deviation of the lines from the origin which indicates that diffusion through pores is not the sole rate-limiting step. The adsorption data was poorly fitted into Pseudo-first order kinetics. The kinetic constant parameters and correlation coefficients are presented in Table 3.3c.

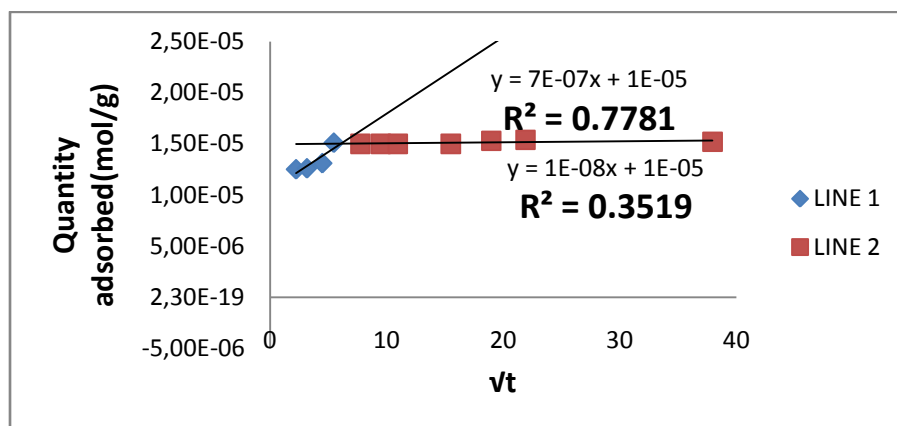


Fig. 3.16b: intra-particle diffusion (hematite-kaolin composite $w=0.1\text{g}$, $\text{pH } 9$, 0.17×10^{-3} , $\text{temp}=30^\circ\text{C}$ at 165rpm)

Table 3.3c: The values of parameters and correlation coefficients of kinetic models for hematite-kaolin composite Initial concentration: $0.17 \times 10^{-3}\text{M}$

Kinetics models	Parameters	Values
Pseudo-first order	$K_1(\text{min}^{-1})$	0.00014
	$q_{e,\text{cal}}(\text{mol/g})$	0.943
	R^2	0.1076
Pseudo-second order	$K_2(\text{g} \cdot \text{mol}^{-1} \cdot \text{min}^{-1})$	$8.16\text{E}-8$
	$q_{e,\text{cal}}(\text{mol/g})$	$1.43\text{E}-7$
	R^2	0.9999
Elovich	$\alpha(\text{mol}^{-1} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$	242
	$\beta(\text{g/mol})$	$2.0\text{E}6$
	R^2	0.6897
Intra-particle diffusion		LINE 1 LINE 2
	$K(\text{mol/g} \cdot \text{min}^{-1/2})$	$7\text{E}-7$ $1\text{E}-8$
	C	$1\text{E}-5$ $1\text{E}-8$
	R^2	0.7781 0.3519

3.3.3. Thermodynamics

The thermodynamics for the adsorption of ciprofloxacin on kaolin, hematite and hematite-kaolin composite was investigated in the range $303\text{--}343\text{K}$ and the influence of temperature on the adsorption under the optimized condition was studied. Thermodynamic parameter such as Gibbs free energy (ΔG), enthalpy (ΔH) and entropy

(ΔS) were determined. The graphs for the thermodynamic are presented in **Fig.3.17a-c**. Table 3.4 shows the thermodynamics adsorption parameters ΔG , ΔS and ΔH computed from the plots of $\ln K$ against $1/T$.

Negative values were obtained for ΔH of each adsorbent; -8.40kJ/mol for kaolin, -9.98kJ/mol for hematite and -14.80kJ/mol for hematite-kaolin composite which confirms the exothermic nature of adsorption of CIP. Negative values were obtained for ΔS of each adsorbent; -0.07kJ/mol/K, -0.04 kJ/mol/K and -0.05 kJ/mol/K for kaolin, hematite and hematite-kaolin composite respectively and this indicates that there is a decrease in the degree of randomness in solid/solution interface during the adsorption process[20].

The calculated free energy (ΔG) for the varied temperature for adsorption CIP on each adsorbent are shown in table 3.4.

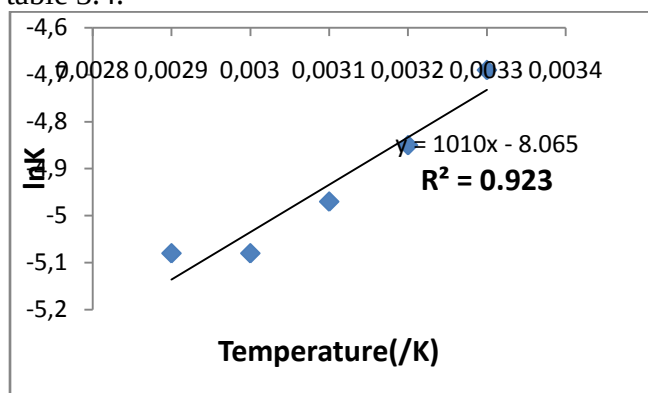


Fig. 3.17a: Kaolin (w=0.4g, pH 5, $C_0 = 0.14 \times 10^{-3}$ M, 120mins at 165rpm)

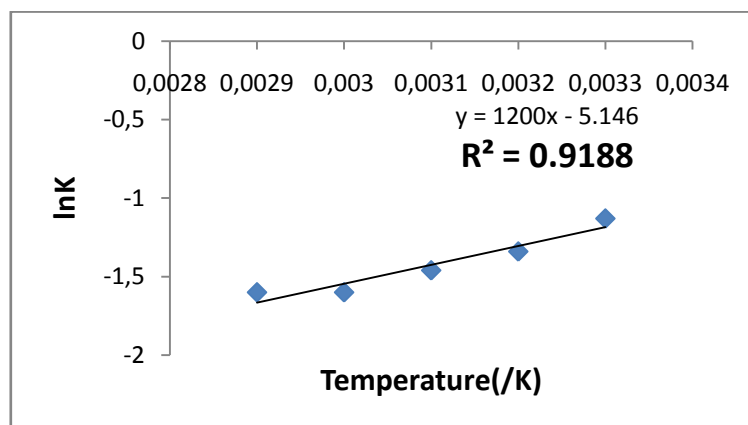


Fig. 3.17b: Hematite (w=0.05g, pH 5, $C_0 = 0.17 \times 10^{-3}$ M, 60mins at 165rpm)

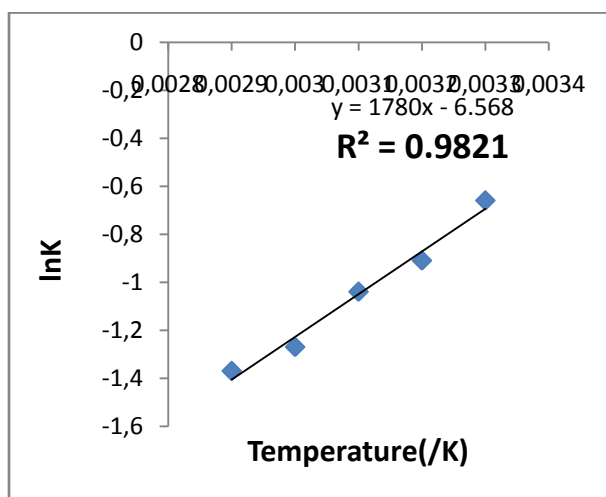


Fig. 3.17c: Hematite-kaolin composite (w=0.1g, pH 9, $C_0 = 0.17 \times 10^{-3}$ M, 60mins at 165rpm)

Table 3.4: Thermodynamic parameters for kaolin, hematite and hematite-kaolin

Adsorbents	Temperature(K)	$\Delta G(\text{kJ/mol})$	$\Delta S(\text{kJ/mol/k})$	$\Delta H(\text{kJ/mol})$
Kaolin	303	12.81	-0.07	-8.40
	313	13.50		
	323	14.21		
	333	14.70		
	343	14.61		
Hematite	303	3.05	-0.04	-9.98
	313	3.48		
	323	3.90		
	333	4.34		
	343	4.77		
Hematite-kaolin composite	303	0.35	-0.05	-14.80
	313	0.85		
	323	1.35		
	333	1.85		
	343	2.35		

Conclusion

The results of present investigation show that kaolin, hematite and their composite have suitable adsorption capacity with regard to the removal of ciprofloxacin from its aqueous solutions. The quantity and percentage adsorbed were found to be dependent on the initial concentration, pH, CIP-adsorbent contact time, adsorbent dosage and temperature. Experimental results were evaluated with Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The results of this study showed that Temkin and Dubinin-Radushkevich isotherm models are more suitable at describing the adsorption equilibrium of CIP onto all the three adsorbents used in this study. Pseudo-second order reaction kinetics has provided a realistic description for the removal of CIP with similar values $q_{\text{calculated}}$ and $q_{\text{experimental}}$, whereas in the first order kinetic the difference between these values is large. The correlation coefficient was also higher in pseudo-second order kinetics compare to others. The enthalpy change for the adsorption process was indicative of the exothermic nature of adsorption process. The results of this investigation showed that kaolin, hematite and their composite have suitable adsorption capacity with regard to the removal of ciprofloxacin from its aqueous solutions. The adsorption capacity of the prepared adsorbents is in the order: kaolin = hematite nanoparticles > composite.

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