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

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ABSTRACT

Ciprofloxacin (CIP) is a second generation fluoroquinolone antibiotic of high use. It has a high aqueous solubility and a long environmental half-life. 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, kinetic, thermodynamic and equilibrium. Under the established experimental conditions the adsorption reached equilibrium in about 60 mins and the optimum adsorption capacity attained was 16 $x10^{-6}$ mol/g between pH of 5and 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 was 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

1.0 INTRODUCTION

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. [1] and Méndez-Díaz et al. [2] studied the batch adsorption on activated carbon of imidazoles and sulphonamides with trimethoprim, respectively. In these two studies about 90% removal was achieved. A similar study was developed by Kim et al. [3], but they investigated whether batch or continuous adsorption of trimethoprim, obtaining also removals above 90%. Chen and Huang [5] 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. 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 many types of adsorbents. The results on kaolin were limited. Hence, the research on adsorption of ciprofloxacin on kaolinite. Nanoparticles of different adsorbent have been confirmed as good adsorbents for the removal antibiotics in aqueous medium but report on adsorption of ciprofloxacin on hematite nanoparticles is limited. Hence the adsorption of ciprofloxacin needs to be investigated. 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 aqueous media

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2.0 Experimental

2.1 Synthesis Of Hematite Nanoparticles

The hematite was prepared by transformation of ferrihydrite method [6]. Ferrihydrite was precipitated by adding 300ml 1 M KOH that had been preheated to 90^0C to 40g of Fe $(NO_3)_3{\cdot}9H_2O$ in 500ml deionized water preheated to 90^0C, then 50ml of 1M $NaHCO_3$, preheated to 90^0C was added to the precipitate in a closed flask and held at 90^0C 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 90µm, 112µm, 120µm and 250µm 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

TechConnect Briefs 2015, TechConnect.org, ISBN 978-1-4987-4727-1

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 [7].

Characterization of the Adsorbents

The particles were characterized using infrared spectroscopy (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.

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 mechanical shaker for different time. After shaking, the solution was then filtered and analysed using UV/visible spectrophotometer. The amount of Ciprofloxacin adsorbed, qe (mol/g) was calculated using the equation below:

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

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 [170].

3. Results and Discussion

The X-ray diffraction spectrograph of the 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 [8]. The position of all maxima coincided with peaks characteristic of hematite phase. There was no other diffraction line corresponding to other phases, indicating a high purity of the sample, which is in line with reported studies on hematite. The XRD pattern of hematite-kaolin composite material shows the presence of both hematite and kaolin. The SEM micrograph revealed the morphology of the adsorbent.

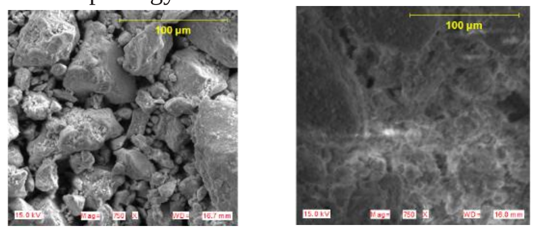

Fig1: SEM of nHematite and Hematite-kaolin

Results of Adsorption Studies

The adsorption of Ciprofloxacin from aqueous solution by kaolin, hematite and hematite-composite at different temperature showed that 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 [8].

CONCLUSION

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.

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