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Adsorption of ciprofloxacin HCl from aqueous solution using activated kaolin

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ABSTRACT

This study involves the determination of the adsorption capacity of activated kaolin for the removal of ciprofloxacin hydrochloride from aqueous medium. The kaolin was activated through chemical (HCl and HNO_3) activation method, the adsorbent was characterize using Scanning electron microscopy (SEM) and Fourier transformed infrared spectroscopy (FTIR), the adsorption experiment was monitored using Ultra-violet visible spectrophotometer at maximum wavelength of 438 nm. The effect of concentration, pH, contact time and adsorbent dose were examined.

Keywords: Adsorption, Activated Kaolin, Ciprofloxacin, SEM, FTIR, UV-Spectrophotometer, Contact time, Adsorbent Dose

1. INTRODUCTION

Pharmaceutical industries from inception has been releasing large amount of water into water bodies in the form of wastewater. The wastewater in question is composed of water, API (active pharmaceutical ingredient), TSS (total suspended solid), TDS (total dissolved solid), etc. Water is an essential ingredient of pharmaceutical preparations and used primarily for manufacture of oral preparation, besides the washing of machineries and bottles, leading to a large volume of wastewater at the end of operations. Presence of toxic substances in such effluents resulted in lesser COD removal efficiencies (Chelliapan et al. 2006). Biological

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treatment of effluent although common and economical has proven to be insufficient for the removal of all potential poisons or contaminant present in wastewater (Kulik et al., 2008; Joss et al., 2005; Suman Raj and Anjaneyulu, 2005).

In early 2000s, membrane bioreactors (MBR) technology, advance oxidation and ozonation processes showed varying degree of efficiency for the treatment of pharmaceutical effluents (Andreozzi et al. 2006; Addamo et al. 2005). Fusing various biological and more advanced treatment methods for their additive potential may provide solution to the removal of potential hazardous substances in pharmaceutical effluents (Ikehata et al. 2006)
Adsorption of natural and synthetic organic contaminants using (activated carbon) ACs and (activated kaolin) AKs is one of number of other options that is being explored in the removal of APIs from effluents (Annesini et al. 1987).

2. AIM AND OBJECTIVES OF THE RESEARCH

The aim of the research is to determine the efficacy of activated kaolin for the removal of Ciprofloxacin HCl from aqueous solution.

- Activation of kaolin
- Characterization of Adsorbent type using UV-spectroscopy and Scanning electron microscopy (SEM)
- Studying the adsorption activity of prepared activated kaolin on the removal of ciprofloxacin HCl from aqueous solution.

3. MATERIALS AND METHODS

The reagents and chemicals used in this research includes Hydrochloric acid (HCl)-(purity 37%, density 1.18 kg/cm^3), nitric acid (HNO_3)-(purity 98%, 1.51 gcm^3), sodium hydroxide (NaOH) and required standard solution of the drug used were prepared which all were of analytical grade.

Ultra-violet spectrophometer, centrifuge, the thermostated shaker, pH meter provided in the department of Chemistry, Kwara state University, Malete, Nigeria .Characterization was done by Fourier Transform Infrared Spectroscopy (FTIR),Scanning electron microscopy (SEM).

Wattman filter paper, mortar and pestle, glass funnels, clay pots, crucible, dessicator and well standardized measuring flasks. Also a laboratory test sieve from the department of Geology, Kwara State University, Malete, Nigeria.

3. 1. Preparation of Activated Kaolin

The kaolin clay sample was grounded, washed with deionized water, dried and sieved into particle size of <90 μm. It was then impregnated in 1M HCl solution for 4 hours to eliminate impurities, washed severally with deionized water and oven-dried. 100g of the clay sample was then activated with 400 mL of 1M HNO_3 and stirred at 500 rpm for 1hour 30 mins at a temperature of 90 ºC. The sample was then filtered, washed to neutral pH with deionized water and oven dried at 105 ºC to obtain activated kaolinite clay (AKC) samples.

3. 2. Ciprofloxacin Standardization And Wavelength

Ciprofloxacin (CIP) used as adsorbate, obtained from Sam Pharmaceutical limited, Nigeria. A stock solution of 1000 mg/L was prepared by dissolving appropriate amount of (CIP) in 1000 mL de-ionized water in volumetric flask, different concentrations were prepared by diluting the stock solution to the initial concentrations ranging from 20 to 100 mg/L. The maximum wavelength (λmax) was observed at 438 nm which was adopted for absorbance measurement. Measurements of the absorbance of each standard solution (and mg/L) in 1cm cuvette at 438 nm, using de-ionized water as a blank to verify Beer's – Lambert law were carried out.

3. 3. Effect of Process Parameters

Batch adsorption experiments for adsorption of CIP on AC Kaolin were conducted using aqueous solutions of CIP HCl. A stock solution of 1000 mg/L was prepared by dissolving appropriate weight of CIP from Sam Pharmaceutical limited, Nigeria. The stock solution was diluted as required to obtain different concentrations of antibiotic solutions. For each run, a definite amount of AC Kaolin was added to 20 mL of CIP solution taken in 100 ml Erlenmeyer flasks. All the adsorption experiments were carried out at constant temperature of 25 °C.

3. 4. Effect of pH

Effect of pH on antibiotic adsorption was monitored over a pH range of 2 to 12, using electronic pH - Meter (SP/DPM/03.). In this study, 20 mL of separate solutions 120 mg/L (CIP) was transferred into 100 mL conical flasks shaking well for 30 min with 0.2g AC Kaolin at 25 °C. The mixture was filtered and the filtrate analyzed for residual CIP using UV visible Spectrophotometer (Genesys 105 UV-VIS).

3. 5. Effect of Contact Time

In order to study the effect of contact time on the percent removal of (CIP) from aqueous solution, experiments were carried out at initial concentration of mg/L using (0.2g) AC Kaolin dose and different contact times from - to- minutes The mixtures were filtered and residual of (CIP) in filtrate analyzed spectrophotometrically.

3. 6. Effect of Adsorbent Dosage

To determine the optimum adsorbent dosage, experiments were carried out by adding different weights of AC Kaolin ranging from (0.025 to 0.2 g) to 20 mL of desired concentration of (CIP) in 50 mL conical flask at pH 4, temperature 25 °C and shaken for a time range of 5min to 24hrs. Aliquots concentration was analyzed to determine the extent of adsorption of (CIP) at equilibrium.

3. 7. Effect of Initial Drug Concentration

20 mL solutions of CIP drug with different initial concentrations (50-200 mg/L) were contacted with optimized adsorbent dosage 0.2 g and pH at 4. The mixtures were shaken well for 120min at 25 °C. The mixtures were filtered and filtrate analyzed for residual drug concentrations.

4. RESULTS and DISCUSSION

4. 1. Effect of Initial Ciprofloxacin Concentration

The initial concentration of CIP in the solution is an important parameter since its concentration change over abroad range in effluents applications. The batch adsorption experiments were carried out with different initial concentrations (Co) (and mg/L). The variation of percentage removal the drug with different initial concentration for the prepared AC Kaolin was clarified in Figure 1. The figure shows an excellent performance of the prepared activated kaolin at equilibrium state and clarifies the optimum drug initial concentration used at confined experimental conditions. It is also evidently observed that the percentage removal of the CIP drug is sufficiently high, (97.38%) at low concentration (40 mg/L) and no significant further increases the concentration increases.

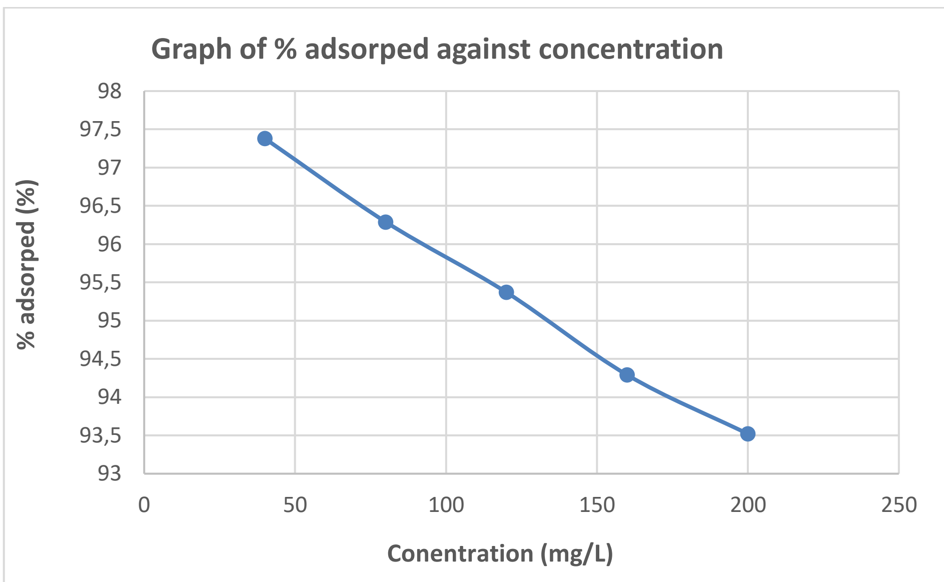

Figure 1. Graph of % adsorbed against concentration

4. 2. Effect of pH

Solution pH is one of the important process parameters that significantly influences the adsorption of CIP on adsorbent. The adsorption of CIP from 120 mg/L concentration on given AC Kaolin was studied at pH ranging (2-12). The result in Figure 2, shows that theadsorption of CIP increased from the initial pH to 4and then decrease over the pH rang of 6-12. Therefore, in this study we found that pH 4 as the optimum pH. At low pH region the surface of the adsorbent will be largely protonated. The positive ions (H^+) provide an electrostatic attraction between the AC Kaolin surface and the drug molecules leading to maximum adsorption.

On the other hand, at pH above 4 the degree of protonation of the surface of the AC Kaolin will be less, which result in the decrease in adsorption, thereby due to increase in electrostatic repulsion. Furthermore, lower adsorption of the Drug molecules in acidic medium can be attributed to the competition from excess hydrogen ions (H^+) with the drug molecules for the adsorption sites.

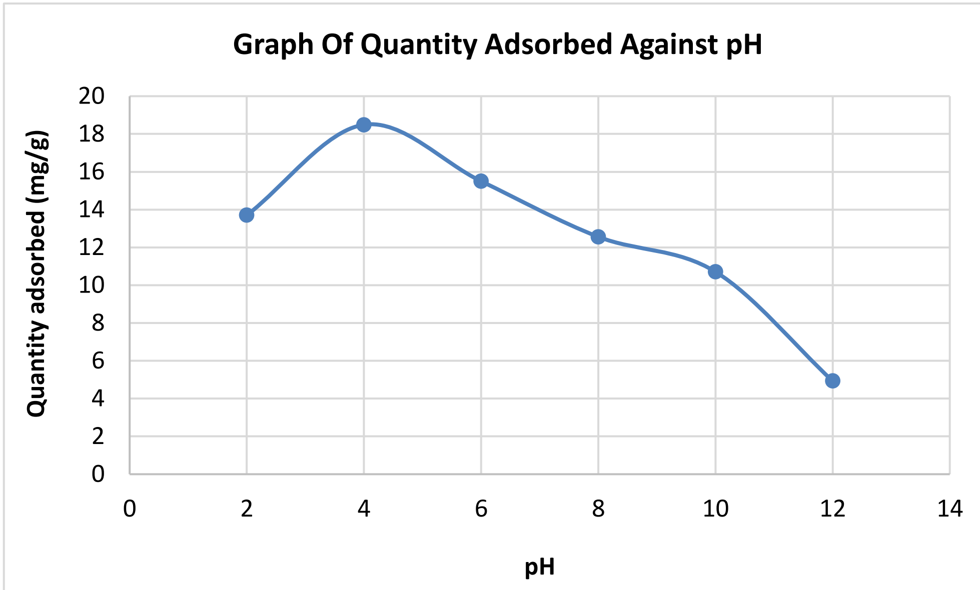

Figure 2. Graph of quantity adsorbed against pH

4. 3. Effect of Contact Time

The effect of contact time on the removal of CIP is shown in Figure 3. The amount of the adsorbed drug increases with increasing time until saturation is reached after 2 hours. A constant adsorption is indicative of equilibration due to saturation of adsorption sites. Rapid adsorption of CIP drug during the initial stages was due to the large initial concentration gradient between the adsorbate in solution and the number of available vacant sites on AC Kaolin adsorbent surface.

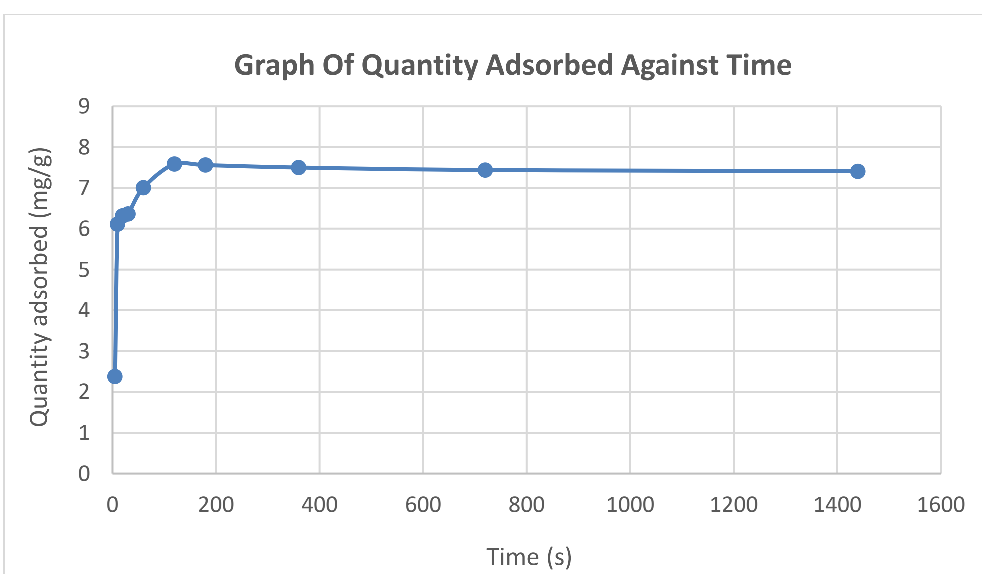

Figure 3. Graph of Quantity Adsorbed Against Time

4. 4. Effect of Adsorbent Dose

The effect of adsorbent dose on adsorption percentage of CIP using AC Kaolin was illustrated in Figure 4. Different doses of adsorbents ranging from 0.1 – 0.6 g were considered and other process parameters were maintained constant (pH – 4, CIP concentration – 120 mg/L, agitation speed – 200 rpm, contact time –min, and temperature –25 °C). An increase in adsorption capacity with increasing adsorbent dose up to a maximum of 0.2 g giving the corresponding optimum adsorption percentage of 37.97 %.

On the other hand, it was found that any further addition over the above mentioned weight (0.2 g) will not make any enhancement in the adsorption process, where almost negligible increase of removal efficiency over the specific adsorbent dose. The initial increase in adsorption capacity with increasing adsorbent mass is explained by the increasing the number of exchangeable sites for CIP adsorption, after which equilibration was attained.

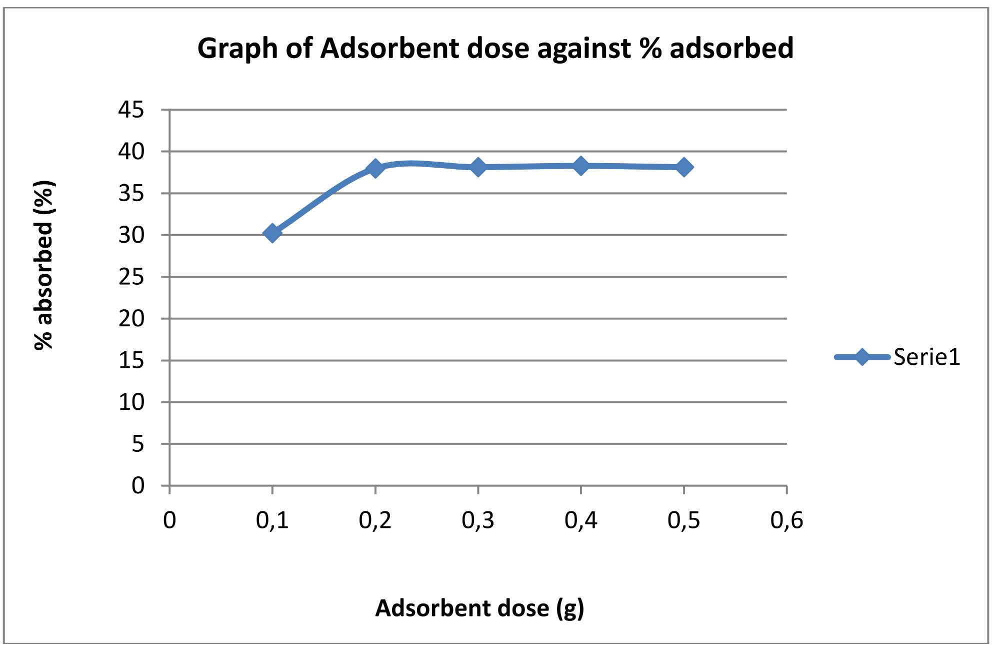

Figure 4. Graph of Adsorbent dose against % adsorbed

4. 5. Testing Results with Different Isotherm Model

4. 5. 1. Applying Langmuir adsorption isotherm

The linear forms of Langmuir equation and separation factor are given as follow:

$$\frac{c_e}{q_e} = \frac{1}{k_L q_{max}} + \frac{1}{q_{max}} c_e$$

$$R_L = \frac{1}{1 + K_{L\, c_o}}$$

q_e is the amount adsorbed per adsorbent mass (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), K_L is the Langmuir's constant and q_{max} is the maximal adsorption efficiency (mg/g). $0<R_L<1$the adsorption is feasible when R_L value falls between the range
Calculation:

$Y = 0.0556X - 0.017$

Slope = 0.0556 = 1 /q_{max}

q_{max} = 17.99 mg/g

$1/K_L qmax = 0.017$

$1/K_L x17.99 = 0.017$

$K_L = 3.3$

$R_L = 1/1+K_L C_o$

$R_L = 1/1+3.3(0.2)$

$R_L = 1/1+0.66$

$R_L = 1/1.66$

$R_L = 0.60$

The Langmuir plot in Figure 5 shows that the adsorption process conforms to the model with R^2 value of 0.999. This implies that the adsorption process is well described through the Langmuir proposed mechanism.

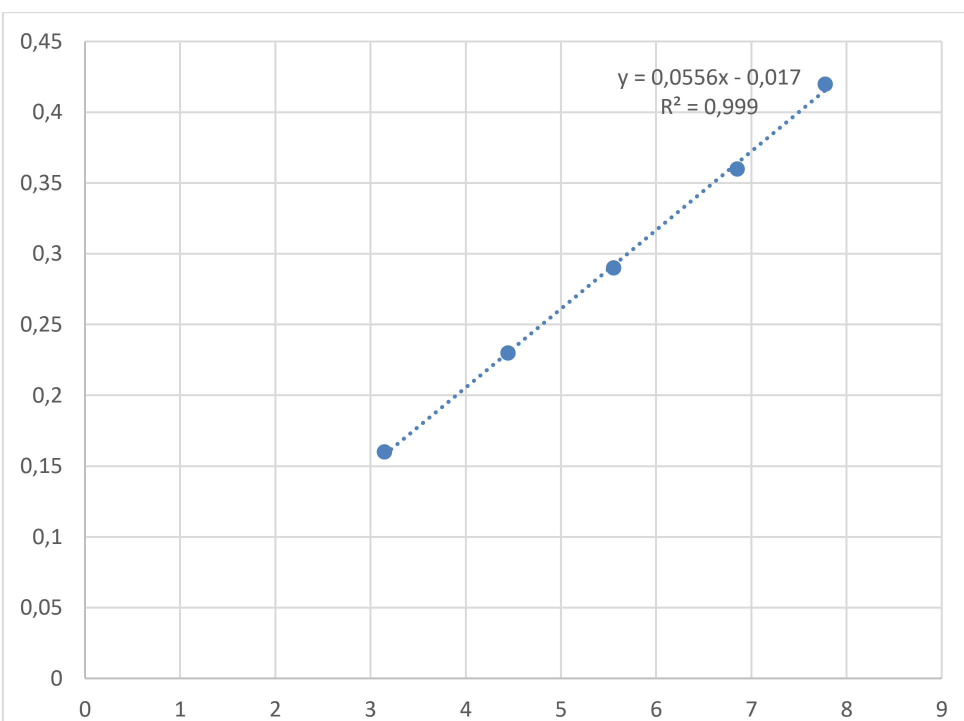

Figure 5. A Plot of Ce against Ce/qe

4. 5. 2. Applying Freundlich Isotherm

The linear form of the Freundlich equation is given by q_e is the quantity adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), 1/n is the heterogeneity factor, K_f is Freundlich's constant (mg/g) (Ramalakshmi *et al*. 2012).

$$logq_e = \log K_f + \frac{1}{n} \log C_e$$

Calculation:

Y = -17.057x + 51.881

Slope = 17.057

logKf = 51.881

Slope = 17.057

17.057 = 1/n

N = 1/17.057

n = 0.059

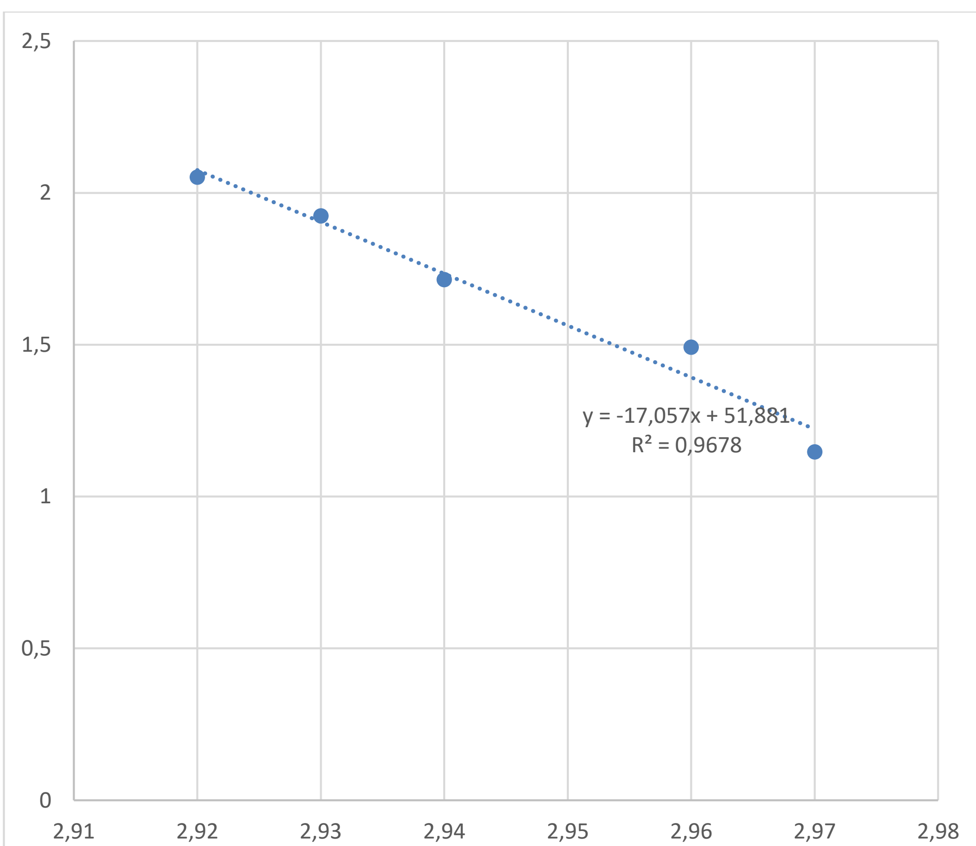

Figure 6. A plot of ln q_e versus ln C_e

5. CONCLUSIONS

The adsorption of Ciprofloxacin hydrochloride (CIP) onto Activated kaolin derived from clay has been studied. The adsorption experiments were tested with various parameters such as effect of concentration, pH, contact time, and adsorbent dosage. The equilibrium data were analyzed using Freundlich and Langmuir isotherm models and the results fitted into these models with better conformity with Langmuir isotherm. The optimum condition obtained in the adsorption experiment in aqueous phase are 40 mg/l for initial CIP concentration, pH 4 (solution acidity), 2 hours for contact time and 0.2g for adsorbent dosage. The adsorbent was characterized using SEM and FTIR, the image of surface morphology of the adsorbent revealed a good adsorption features. The FTIR adsorption signals of the adsorbent before contacting with the adsorbate (CIP) shows good surface characteristics for adsorption.

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