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Original Article

# A COMPARISON OF KINETIC STUDIES OF KAOLIN CLAY AND RICE HUSKS FOR CIPROFLOXACIN ADSORPTION

**HAYFAA JASIM SINBAH[1], MAJIDA HAMEED KHAZAAL[1], HUDA SABAH HASSEN[1], EKHLAS SABAH HASSAN[2*]**

**[1]Department of Chemistry, Faculty of Education for Girls, University of Kufa, Najaf, Iraq. [2]Department of Pharmacology and Therapeutics, Faculty of Medicine, University of Kufa, Najaf, Iraq**
**Email: ekhlass.khazaal@uokufa.edu.iq**

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**ABSTRACT**

**Objective**: to compare the absorption of this drug on two surfaces of Iraqi kaolin and rice husks, which are considered environmentally friendly natural products and available locally.

**Methods**: Ciprofloxacin adsorption from an aqueous solution was studied with respect to contact time, pH, and concentration. 30 min was determined to be the equilibrium time. Increasing the drug concentration on both adsorbents increased the adsorption rate, and the data fit well into a pseudo-second-order model. The solution concentration was analysed by UV-visible spectroscopy. Then the amount of adsorption was calculated, as well as the study of the reaction kinetics for both surfaces. The rice husk adsorbent showed faster removal with higher uptake than the Kaolin clay in both SGF and SIF solutions.

**Results**: The adsorption isotherms of type ($S_4$, $S_2$) were found on the surface of rice husks and kaolin clay type ($L_3$, $L_4$) in stomach and intestine fluids, respectively. On Iraqi kaolin clay, adsorption is well described by the pseudo-second-order model, and the Tempkin adsorption isotherm provides a good fit for the Stomach. Whereas adsorption on rice husk is well described by the Freundlich isotherm, which is a good fit for the intestine. the adsorption is predominantly physical. The best maximum adsorption capacities were calculated on both surfaces in the following order: stomach-kaolin>intestinal fluids-rice husks>stomach-rice husks>intestinal fluids-kaolin.

**Conclusion:** Both kaolin and rice husk are possible adsorbents that could be used to get antibiotics out of water.

**Keywords:** Ciprofloxacin, Rice husks, Iraqi kaolin clay, Freundlich, Langmuir and Temkin equations, Adsorption kinetics


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## INTRODUCTION

Ciprofloxacin is a synthetic antibiotic that frequently used to treat bacterial infections in both humans and animals [1]. It is a derivative of carboxylic acid belonging to the fluoroquinolone group, an antimicrobial agent. It inhibits bacterial DNA gyrase (a type-II topoisomerase) so preventing DNA supercoiling and DNA synthesis [2]. Ciprofloxacin has a molecular weight of 367.82 g/mol and a molecular formula of $C_{17}H_{18}FN_3O_3$. HCl. It was prescribed to treat infections caused by airborne bacteria, such as clots, which are caused by respiratory inflammation, ear infections, sinuses, urinary tract, tuberculosis, and dermatitis [3]. If the dose occurs, it will cause kidney toxicity, articular pain, and muscle aches. This medicine is given orally, absorbed through the digestive system, and then distributed widely throughout the body. It can be discharged into water sources due to a lack of human metabolism or the effluents of pharmaceutical companies, especially in developing countries [4-6].

One of the most effective ways is to use natural agricultural products as an adsorbent surface in processes for purifying water and lowering drug levels. Because wastewater treatment facilities only partially remove antibiotics like ciprofloxacin, residual amounts of these drugs may find their way into surface or groundwater. Even modest quantities of ciprofloxacin in wastewater and surface water can cause bacteria in the environment to become resistant to antibiotics [7-9]. Ciprofloxacin has been found in water and wastewater at quantities of less than 1 mg/l, although greater concentrations have been found in hospital effluents [10].

There are many materials that possess high adsorption efficiency, and these materials are of natural origin such as some husks that have been activated and prepared to be ready for use. Several studies mentioned in the literature have shown the effectiveness and efficiency of this plant material and certain types of clay. Its a great effect in many methods of treatment. Bentonite and kaolin [11, 12], date palm leaflets [13, 14], for their availability, cheapness, and low side effects. More applications are possible with adsorption because of its low cost, good performance, and adaptability [15]. The adsorption of ciprofloxacin hydrochloride drug with various adsorbents, such as fly ash [16], graphene oxide [17], Argentinian montmorillonite [18], activated carbon [19], pumice, and zeolite [20] has been investigated in several publications. Most of these studies have ignored the influence of pH on drug solubility, which can have a major impact on adsorption capacity.

The purpose of this research was to expand upon previous studies on adsorption onto rice husks and Iraqi kaolin clay [21, 22] surfaces, which are readily available agricultural waste in the world and Iraq in particular. As part of the investigation of affordable adsorbents for the treatment of (ciprofloxacin) overdose and poisoning, the influence of reaction circumstances such as acid function, the initial concentration of the drug, and temperature were studied.

## MATERIALS AND METHODS

### Materials

The ciprofloxacin was obtained from Fluka Chemie GmbH. The kaolin clay is supplied by the general company for the Geological Survey and Mining in Dwaikhla, Baghdad, Iraq and the commercial rice husk was gained from the local market. The pH of the artificial gastric and intestinal fluid habitats (1.2 and 6.8) was prepared according to the pharmaceutical process shown in the United States Pharmacopoeia.

Hydrochloric acid (1.19 g/cm$^3$, Sigma Aldrich, 99% purity), Sodium chloride (2.16 g/cm$^3$, Sigma Aldrich, 97% purity), Sodium hydroxide (2.13 g/cm$^3$, Sigma Aldrich, 98% purity), Potassium dihydrogen phosphate (alfa aesar, 96% purity).

### Preparation of adsorbents

For the kaolinite clay sample (50 mm), additional distilled water was used to wash it. For the next 24 h, it was heated in an oven ranging from 50 to 100 degrees Celsius, with the final 7 h at 100 degrees

Celsius. After it's been ground, it goes through a 50-millimeter sieve. Further tests make use of particles with a diameter greater than 50 mm [23].

For the rice husk surface, it was washed with excess water three times and then dried for ten hours in a 70-degree Celsius oven and ground before sieving with 212 mesh to create an absorbent with a high surface area. Finally, the dried surface particles were kept in a desiccator for adsorption experiments [21, 24].

Preparation of simulated gastric fluid SGF and intestinal fluid SIF

In 1 L of distilled water, 2 g of sodium chloride and 7 ml of hydrochloric acid were combined to prepare gastric fluid (pH = 1.2). As for the intestinal fluid pH = 6.8, it was made by dissolving 0.89 g of sodium hydroxide in distilled water and 6.8 g of potassium salt ($KH_2PO_4$) in a certain amount of distilled water [25]. The remaining 1 L was then filled with the same type of water. It is possible to modify the acidity or alkalinity measurements of a solution using a digital pH metre (720 WTW, 82362) [25].

**Standard calibration curve drawing**

50 mg of the ciprofloxacin antibiotic was melted in 100 ml of both gastric and intestinal fluids and then prepared by dilution ppm (3.9, 7.8, 15.6, 31.25, 62.5). The wavelength is 264 nm and 315 nm for the stomach and intestines, respectively, and draws a calibration curve at pH (6.8, 1.2) solution [25]. The Shimadzu Uv-Vis 1700 digital double-beam recording spectrophotometer was used for all spectrum and absorbance measurements, and 1 cm glass cells were used. As shown below, calibration curves for the simulated gastric and intestine fluids were plotted against the amounts of drug in both fluids [26].

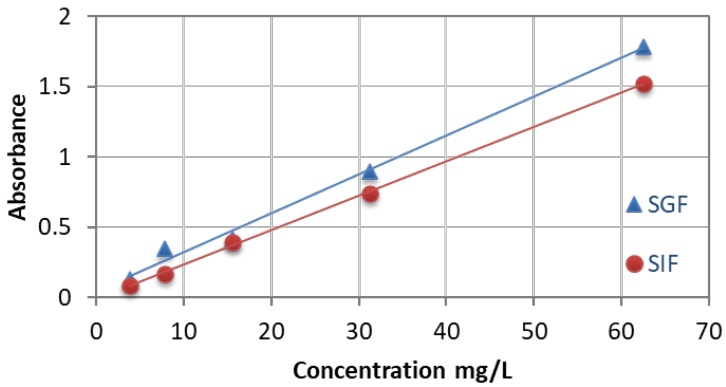


**Fig. 1: Standard calibration curve of ciprofloxacin at SIF and SGI**

**Determination of the equilibrium time of adsorption systems**

For the purpose of determining the equilibrium time between the adsorbed surface and the adsorbent, all conditions, such as acidity and temperature are stabilized with the change of one factor. 30 ml is taken from the prepared drug solution at a concentration of 62.5 ppm and placed in a volumetric flask of 50 ml after adding 0.1 gm of the adsorbed surfaces used in this study. Ten volumetric flasks were placed in the shaking device and sampled at different time intervals. The change in absorbance versus time at the drug's maximum wavelength at the 310K temperature and PH (6.8, 1.2) of the adsorption surfaces utilized in this study is shown in fig. 2. After 30 min, ciprofloxacin on the surfaces of rice husks and kaolin clay in the stomach solution and the intestine solution reach a state of equilibrium. This is because all the active sites on the solid surface are filled by this material [25, 27].

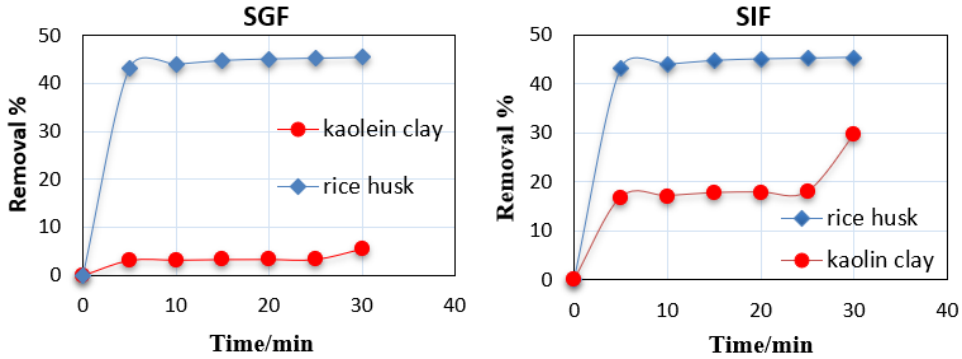


**Fig. 2: Ciprofloxacin absorbtion by rice husks and kaolin clay in SGF or SIF solutions after a certain amount of time**

**Investigations of adsorption**

In both SGF and SIF, a powder corresponding to 12.5 mg of ciprofloxacin powder was dissolved in 100 ml of distilled water. Various amounts of kaolin and rice husk samples ranging from 10 mg to 200 mg were weighed and then added to the interaction environment at 37 °C in a water bath shaker for 30 min. After reaching the specified time, the solution was filtered through Whatman filter paper. Then, for each solution, the filtrate was looked at with an UV spectrophotometer to find the best weight of surface that gives the best adsorption. If an adsorbate is physically or chemically bound to the adsorbent surface, this approach can be used to determine the kind of adsorption. UV spectroscopy was used to fig. out how well the drug ciprofloxacin stuck to the solid surface.

**Adsorption Isotherms at equilibrium**

To find adsorption isotherms for each compound by preparing five different concentrations of adsorbent within the range of (3.9-62.5 ppm) in a volumetric flask with a capacity of 100 ml and taking 30 ml from

each concentration, then placing them in contact with 0.1 g of adsorbent of each Kaolin clay and rice husks in a conical flask with a capacity of 50 ml. Then these flasks are placed in a water bath-controlled temperature up to 315 K equipped with a vibrator and after shaking for a period time up to 30 min, the solutions are filtered through filter paper to get rid of the surface. The concentration of the solution was analysed by UV-visible spectroscopy. The following equations can be used to fig. out the equilibrium concentration (Ce mg/l) of the calibration curve, the amount of adsorbent (Qe mg/g), and the percentage of removal [28]:

$$Q_e = \frac{(C_0 - C_e)V_L}{M} \ldots\ldots\ldots\ldots (1)$$

$$\% \text{ Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \ldots\ldots\ldots (2)$$

Where Ce (mg/l) is the concentration existing in the solution, Co (mg/l) is the premier concentration, V (L) is the volume of solution, and M (g) is the kaolin and rice husk samples mass.

The experimental data were calculated to describe adsorption equilibrium isotherms by using three main theories, Freundlich, Langmuir, and Tempkin models [29]. The main assumption of these adsorption model is that the surface of the adsorbent is covered with a monolayer of adsorbed molecules. Langmuir isotherms which represented by the linear equation:

**Table 1: Correlation coefficients of the various adsorption models for ciprofloxacin adsorption on both rice husks and Kaolin clay in each SGF and SIF solutions**

| Adsorption models | linear equations | $R^2$ for SGF | | $R^2$ for SIF | |
|---|---|---|---|---|---|
| | | Kaolin clay | Rice husks | Kaolin clay | Rice husks |
| Freundlich | $Log\ Q_e = Log\ K_f + \frac{1}{n} Log\ C_e$ | 0.897 | 0.806 | 0.886 | 0.951 |
| Langmuir | $\frac{C_e}{q_e} = \frac{1}{aK_l} + \frac{1}{a} C_e$ | 0.036 | 0.553 | 0.527 | 0.612 |
| Tempkin | $Q_e = \frac{RT}{b} ln\ ln\ K_T\ C_e$ | 0.905 | 0.649 | 0.841 | 0.949 |

### Adsorption kinetics calculations

Ciprofloxacin adsorption was studied to see if time had an influence on the interaction between the adsorb and the solid surfaces. A constant temperature of 310 K was used throughout the trials, which were carried out during time periods ranging from 5 to 30 min. The resulting suspension solutions in six distinct flasks were then picked out from the vibrator apparatus and filtered after each adsorption time. Measurements were made using spectroscopy to determine how much medication remained after adsorption. About both surfaces as well as in both gastric and intestinal solutions, the records data obtained have been analysed using pseudo-first-order as well as pseudo-second order equations.

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$$log\ log\ (q_e - q_t) = log q_e - \frac{K_1\, t}{2.303} \ldots\ldots\ldots (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} * t \ldots\ldots\ldots\ldots (4)$$

## RESULTS AND DISCUSSION

### Adsorption isotherm

Fig. 3 demonstrates the sum of drugs adsorbed (Qe) versus the equilibrium concentration (Ce) for every drug solution. The findings reveal that the concentration of every drug adsorbed rises as the preliminary drug concentration is increased, implying that such an adsorption mechanism is reliant on the preliminary concentration. As per the Gilles classification [31], the basic sense of isotherm adsorption of ciprofloxacin on the surface of rice husks is of type $S_4$-Shape for SIF solution and $S_2$-Shape for SGF solution. On the surface of Kaolin clay in the SIF of type L3, along with adsorption on the same surface in the SGI of type $L_4$. Langmuir, Freundlich, and Tempkin are by far the most commonly used models to define the equilibrium adsorption isotherm for ciprofloxacin adsorption.

The Freundlich, Langmuir, and Temkin isotherm plots acquired from the adsorption studies are shown in fig. (4–6). The $R^2$ values for the different forms of isotherms for these drugs are shown in Tables 2 and 3, which relies on the fundamentals of Freundlich adsorption and implies that the object's surface is not homogeneous. It is evident from the isotherms that the Freundlich equation for adsorption is more suitable on the surface of the Kaolin clay than on the surface of rice husks in stomach fluids. As for drug adsorption in intestinal fluids, the Freundlich equation becomes more suitable for rice husks than for Kaolin clay. The Timken equation corresponds to the surface of the kaolin clay more than rice husks in stomach fluids. The Timken equation equates to the surface of kaolin clay in stomach fluids more so than rice husks. The Langmuir equation doesn't match how the drug is absorbed on both surfaces and in both the stomach and intestines.

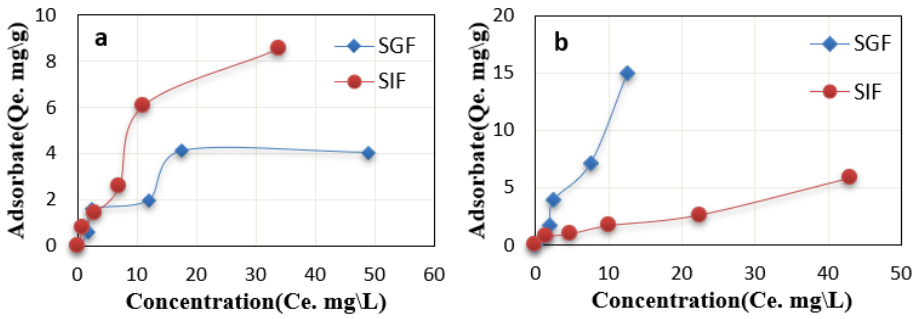


**Fig. 3: Adsorption isotherm of ciprofloxacin on: (A) Iraqi kaolin clay, and (B) rice husks at 310 k**

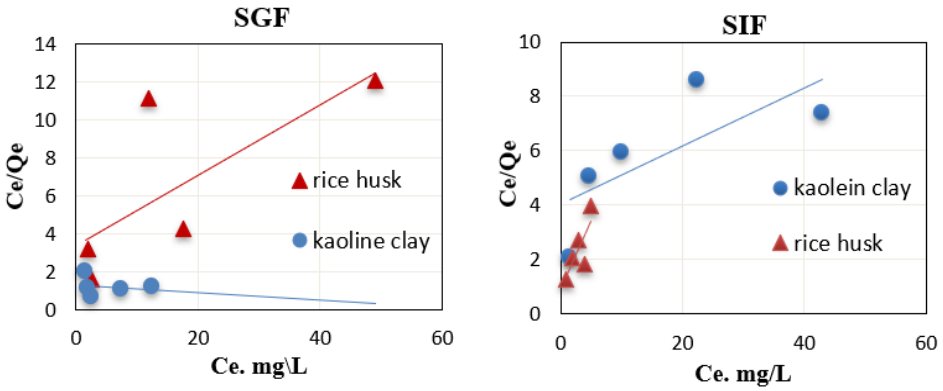


**Fig. 4: Linear langmuir adsorption isotherm on rice husk and Iraqi kaolin clay in simulated SGF and SIF fluids**

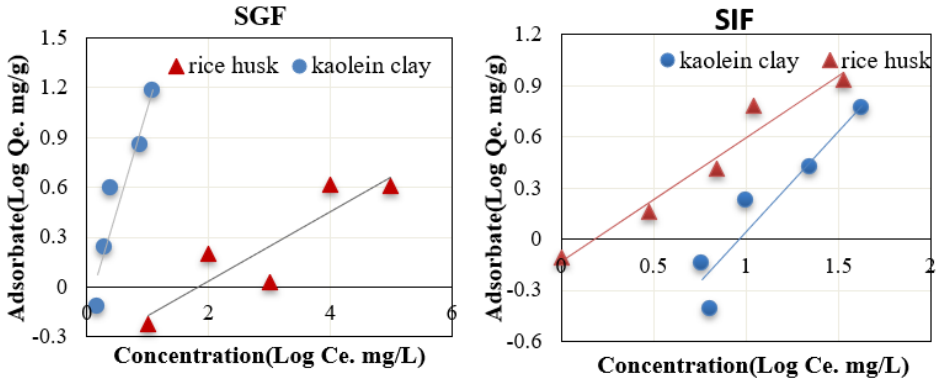


**Fig. 5: Linear freundlich adsorption isotherm on rice husk and Iraqi kaolin clay in simulated SGF and SIF fluids**

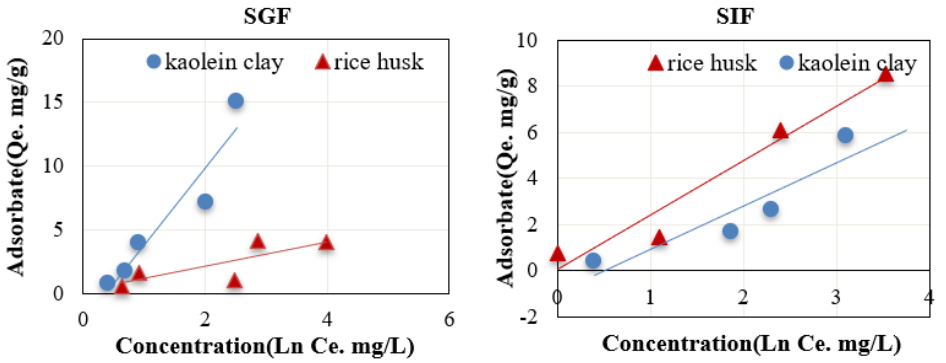


**Fig. 6: Linear tempkin adsorption isotherm on n rice husk and Iraqi kaolin clay in simulated SGF and SIF fluids**

The adsorption equilibrium between liquid and solid heterogeneous surfaces is mathematically expressed by the term "isotherms." The assumption by langmuir was that a surface with only a small number of adsorption sites could only support monolayer uptake. According to a theory that has been put forth, as the number of binding sites increases, the site occupation by adsorbents decreases [32]. Langmuir plots had lower $R^2$ values than SGF and SIF Freundlich, Langmuir, and Temkin plots, which meant that the model didn't fit the experimental data well.

**Table 2: Experimental constants and R2 of freundlich, langmuir and tempkin isotherms on Iraqi kaolin clay**

| Solution | Freundlich | | | Langmuir | | | Tempkin | | |
|---|---|---|---|---|---|---|---|---|---|
| | $K_f$ | n | $R^2$ | $K_L$ | $q_m$ | $R^2$ | B | A | $R^2$ |
| Stomach | 0.721 | 0.824 | 0.897 | -0.015 | -50 | 0.03 | 5.989 | 0.118 | 0.905 |
| Intestine | 0.075 | 0.854 | 0.886 | 0.263 | 33.529 | 0.528 | 1.409 | 0.909 | 0.679 |

**Table 3: Experimental constants and R2 of freundlich, langmuir and tempkin isotherms on rice husk**

| Solution | Freundlich | | | Langmuir | | | Tempkin | | |
|---|---|---|---|---|---|---|---|---|---|
| | $K_f$ | n | $R^2$ | $K_L$ | $q_m$ | $R^2$ | B | A | $R^2$ |
| Stomach | 0.424 | 4.830 | 0.806 | 0.297 | 18.132 | 0.552 | 0.971 | 1.193 | 0.649 |
| Intestine | 0.743 | 1.380 | 0.951 | 0.624 | 23.296 | 0.784 | 2.369 | 1.055 | 0.949 |

### Adsorption kinetics

An equilibrium study of adsorption must be conducted to evaluate a sorbent's ability to adsorb. But an excellent sorbent for drug control must not only have a high sorption capacity but also a quick sorption rate. Therefore, the kinetic study was conducted on ciprofloxacin adsorption onto the surfaces of kaolin clay and rice husks by a batch method and at an initial concentration equal to (62.5, 31.25) for the stomach and intestines, respectively, at a temperature of 310 K. On both surfaces and in both gastric and intestinal solutions, equation models (pseudo-first order, false second order, and pseudo-second order) were applied on both surfaces. The results are shown in fig. 7 and 8, and by observing the values of the constants and correlation coefficient for the Pseudo-first order and Pseudo-second order equations shown in table 4, it was found that the adsorption of ciprofloxacin on both surfaces and in both gastric and intestinal solutions matches the second pseudo-order equation because of the higher experimental value of correlation coefficient [33].

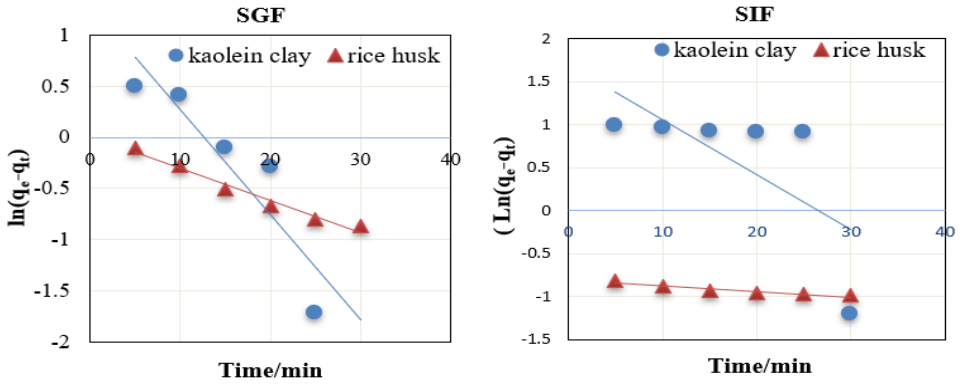


**Fig. 7: Pseudo first-order straight equation for adsorption of ciprofloxacin on rice husks and kaolin at SGF and SIF**

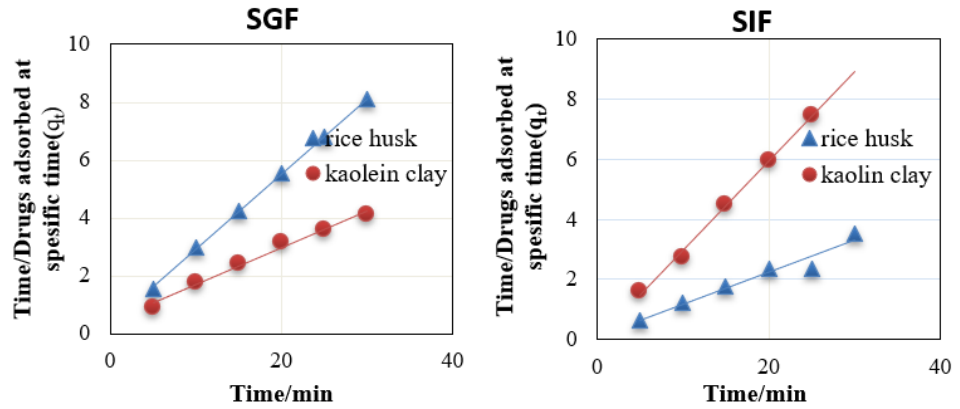


**Fig. 8: Straight line pseudo-second-order equation for adsorption of ciprofloxacin on rice husks and kaolin at SGF and SIF**

**Table 4: Values of adsorption kinetics equations of ciprofloxacin on the adsorbents of kaolin clay and rice husk in gastric and intestinal fluids**

| Solution | Kaolin clay | | | | | | Rice husk | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pseudo 1st order | | | Pseudo 2nd order | | | Pseudo 1st order | | | Pseudo 2nd order | | |
| | $Q_e$ | $K_{lp}$ | $R^2$ | $Q_e$ | $K_{lp}$ | $R^2$ | $Q_e$ | $K_{lp}$ | $R^2$ | $Q_e$ | $K_{lp}$ | $R^2$ |
| Stomach | 3.653 | 0.102 | 0.972 | 7.867 | 0.435 | 0.989 | 1.0139 | 0.0316 | 0.831 | 3.8431 | 0.2162 | 0.999 |
| Intestine | 5.465 | 0.063 | 0.463 | 3.346 | 0.425 | 0.997 | 0.444 | 0.006 | 0.881 | 9.433 | 0.092 | 0.954 |

### CONCLUSION

The surfaces of kaolin clay and rice husks have a high ability to remove the antibiotic ciprofloxacin. It was observed that all adsorption isotherms of ciprofloxacin are of type (S, L) according to Gilles classification on both surfaces. Therefore, it can be determined that the adsorption process is of the physical type. The percentage of removal (R %) in bowel fluids is lower than it is in stomach fluids in relation to the surface of kaolin. As for the surface of rice husks, the percentage of removal in bowel fluids is greater than it is in stomach fluids in relation to the surface of rice husks. The kinetic study indicated that the adsorption process of ciprofloxacin on both surfaces follows the pseudo-second-order kinetics model.

### FUNDING

Nil

### AUTHORS CONTRIBUTIONS

All authors have contributed equally.

### CONFLICT OF INTERESTS

The authors have no conflicts of interest regarding this investigation.

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