ADSORPTION OF CIPROFLOXACIN USING COMPOSITE MICROPLASTICS

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Abstract

Antibiotic residue concentrations rise in the environment and are found in practically all water bodies, including lakes and rivers, as a result of inadequate management of residential and medical wastes. Contrarily, there is a substantial chance of medication toxicity and resistance. On their surfaces, plastic particles in water often carry organic molecules like medications. Plastics can therefore be utilized as an adsorbing medium to remove antibiotic residues from water. This study investigated the use of microplastics produced from composite plastic wastes from the landfill site in the removal of ciprofloxacin in water. The coefficient of determination was used to measure the goodness of fit of the adsorption results to the Freundlich and Langmuir models. The R^2 values were 0.09 and 8.55 for Langmuir and Freundlich respectively. This means the Freundlich model was shown to be more accurate than the Langmuir model when adsorption findings were applied to them.

Keywords: *Microplastics, Antibiotics, Adsorption, Ciprofloxacin, Water*

1.0 INTRODUCTION

Antibiotics are widely used all around the globe, pseudo-persistent, and of major health concern because of their resistance development (Koch et al., 2021). In many developing countries such as Ghana, antibiotics can be easily purchased as an over-the-counter drug (Agyenim & Gupta, 2012). Leftover drugs, and expired drugs disposed into landfills or sewage systems by individuals, pharmacies, or the industry's pharmaceuticals are sources of antibiotics contamination in the environment in addition to metabolic excretion, which is the main source of antibiotics in the environment (Hullmam, 2009). Antibiotics are one of the significant medications having ecotoxicological effects, according to BIO Intelligence Service research from 2013. Antibiotics in soils can hinder germination, reduce biomass allocation, and change the species makeup of plants (Minden et al., 2017). By absorbing them, plants may experience interference with physiological processes like photosynthesis, which is influenced by chloroplast gene expression and cell growth, and mitochondrial function, which is influenced by the oxidative stress response (Wang et al., 2015).

The manifestation of the pharmaceutical in the raw and treated wastewater has been well documented with the concentration being an average ranging from fewer than 10ug/L in finished wastewater to more than 100ug/L in the raw wastewater (Hullmam, 2009).

The manufacture of plastics histrionically increased in the past decades, from 0.5 million tons/year to 280 million tons in 2012 (European Parliament, 2021). According to (Barnes et al., 2009) 10% of global annual production finds its way into the oceans and it has a global environmental effect on the marine system, as well as abyssal regions and polar areas. In recent years, the attention of science has focused on microplastics, with fragments; grin smaller than 5mm, products for their use in cosmetics, industrial or medical applications, or from the debris of the microplastic due to physical, chemical, and biological degradation (Barnes et al., 2009). Microplastic is already known as an emergency pollutant that can transport the pollutant and spread it. Microplastic adsorption behavior is currently one of the research hot spots (Fu et al., 2021). MPs can be adsorbed by the animal and provoke intestinal or liver damage or death (Wang et al., 2020). They can also harm human health through animals (Zhang et al., 2020). The removal of pharmaceutical compounds from wastewater is effective with adsorption methods like activated carbon adsorption and graphene (Darmey et al., 2023; Al-Khateeb et al., 2014; Teixeira et al., 2012). However, these materials are not inexpensive to produce, so despite their good efficiency and applicability for adsorbing a wide variety of materials, their use may occasionally be restricted due to economic considerations (Gupta et al., 2009). Microplastics is known to have a high adsorption affinity with organic pollutant which is two to six times greater than seawater and sediment respectively (Teuten et al., 2007) and readily available as waste with an increasing generation rate in Ghana (Tulashie et al., 2020). While absorption takes place under the partition effect, microplastics can adsorb the organic contaminant onto their surface through hydrophobic, electrostatic, and non-covalent interactions (Guo & Wang, 2019). This makes MPs a good low-cost adsorbent due to their availability and their affinity with antibiotic pollutants. This suggests that MPs can be produced locally in laboratories or on an industrial scale and in shredders in mills for use as adsorbent. This will function as both a water treatment approach to remove pharmaceutical residue from water bodies and a recycling method to lessen the quantity of plastic trash released into the environment. The present work was undertaken to explore the feasibility of the discovery of low-cost effective adsorption, of microplastics for the removal of antibiotic pollutants in water. The correct comprehension and unambiguous interpretation of the pollutant's sorption in aqueous solutions is required for inexpensive adsorbent. The objective of this work was to investigate the adsorption ciprofloxacin on the microplastics (PET and HDPE) collected and produced from the landfill side, by determining equilibrium period, and determining which adsorption isotherm models will fit linear, Freundlich, and Langmuir sorption study.

2.0 MATERIALS AND METHOD

2.1 Preparation of Microplastics

High-density polyethylene (HDPE) water sachets and polyethylene terephthalate (PET bottles) were gathered from a trash recycling facility in Kumasi. The waste PET and HDPE

were shredded, composited, washed, and oven-dried overnight. The mill reduced the sample size to 70 m particles.

Figure 1 Schematic diagram of microplastic adsorbent preparation.

2.2 Reagents

The standard antibiotic solution (50 ppm) was made by weighing 0.5g of ciprofloxacin into a 100 ml volumetric flask, dissolving it in 10 ml of methanol, and then diluting the solution to 100 ml with distilled water. After that, 6ppm was made from the standard solution to ascertain the equilibrium time. From the stock solution, a series of dilutions of 2, 4, 6, 8, and 10 ppm were created. For the sorption studies, serial dilution solutions were employed. All glassware that was used for tests, dilution, and storage was washed with detergent solution, rinsed with distilled water, and then allowed to soak in 10% (v/v) HNO_3 for the night. Before usage, they were rinsed three times with distilled water, 0.5% (w/v) $KMnO_4$, and distilled water again.

2.3 Determination of Equilibrium Time for Sorption Studies

0.1 grams of adsorbent were precisely weighed in triplicate into a 3 ml centrifuge tube, along with 2 ml of a 6-ppm ciprofloxacin solution, to assess the amount of time needed to reach equilibrium. At various intervals (0 hr, 0.2 hr, 0.5 hr, 1 hr, 4 hours, and 8 hr), the suspension-containing tubes were shaken at a speed of 300 rpm. Following the requisite amount of shaking, tubes were taken out and centrifuged at a speed of 4000 rpm for 10 minutes. To analyze the supernatant, it was collected and put through a 0.32 m microfilter into an HPLC vial. The difference between the ciprofloxacin solution's initial concentration and equilibrium concentration was used to calculate the amount adsorbed.

2.4 Adsorption Study

With varying concentrations of ciprofloxacin (2, 4, 6, 8, 10 ppm) in a 1:20 (antibiotics as the adsorbent) solution, isotherm tests were carried out using the batch method. Adsorbent: antibiotic combination samples were shaken in triplicate for 45 minutes at 300 rpm. Samples were centrifuged and antibiotics were determined after the shaking period.

2.5 Ciprofloxacin Analysis Using HPLC

Ciprofloxacin concentration was determined using an Agilent 1200 Infinite Series HPLC (Cambridge, UK) fitted with a VWD Detector. Using an Agilent column (C18, 4.6 mm x 250 mm, 5 m, Agilent Technologies Inc, Palo Alto, CA, USA) at 30°C, the chromatographic separation was accomplished. 40:60 (v/v) methanol and 0.1% trifluoracetic acid were used in the mobile phase. The sample volume was fed into the HPLC at a flow rate of 1 ml/min. The detector's variable wavelength was set to 230 nm. Analysis was carried out three times.

2.6 Statistical Analysis Technique

Microsoft Excel was used for the statistical analysis of the data collected for this investigation. The quantitative description of the sorption of ciprofloxacin by microplastics was made using parameters from least square analysis with linear, Langmuir, and Freundlich isotherms.

To estimate the sorption parameters and choose the model that best fits the data from this investigation, Langmuir, and Freundlich models were applied. The link between the equilibrium ciprofloxacin concentration and the amount sorbed on the microplastics was demonstrated using a linear isotherm. The linear equation is described by:

$$C_s = K_d C_e \quad (1)$$

Where Cs is the amount sorbed per unit weight of soil (μg g^{-1}), Kd is the linear distribution coefficient (L kg^{-1}); and Ce is the equilibrium concentration (μg)

The linearized form of the Freundlich isotherm is as follows.

$$\ln Qe = \ln KF + \frac{1}{n} \ln Ce \quad (2)$$

Where KF is adsorption capacity (L/mg) and 1/n is adsorption intensity, it also indicates the relative distribution of the energy and the heterogeneity of adsorbent sites.

The Langmuir equation can be written in the following linear form:

$$\frac{Ce}{Qe} = \frac{1}{qmax\ \mathbf{kL}} + \frac{Ce}{qmax} \quad (3)$$

Where Ce is a concentration of adsorbate at equilibrium (mg).

Qe= the amount adsorbed (mg/g), k_L: Langmuir isotherm constant (L/mg), qmax: maximum monolayer coverage capacity (mg/g)

3.0 RESULTS AND DISCUSSION

3.1 Determination of equilibrium period

In the sorption investigation, it is crucial to measure the time of equilibrium to know when the adsorbent and adsorbate will reach a steady state. Figure 2 depicts the amount of ciprofloxacin sorbed against the time of shaking.

The initial sorption of antibiotics on microplastics occurred within 30 minutes, followed by a swift partial desorption and a steadily increasing steady state for the remaining time, as can be seen from the graph. After a delay in adsorption and desorption, a steady condition indicates that equilibrium has been reached. Some previous studies indicated the adsorption of antibiotics such as amoxicillin and tetracycline onto microplastics reaches their equilibrium period in 4 days (Li et al., 2018).

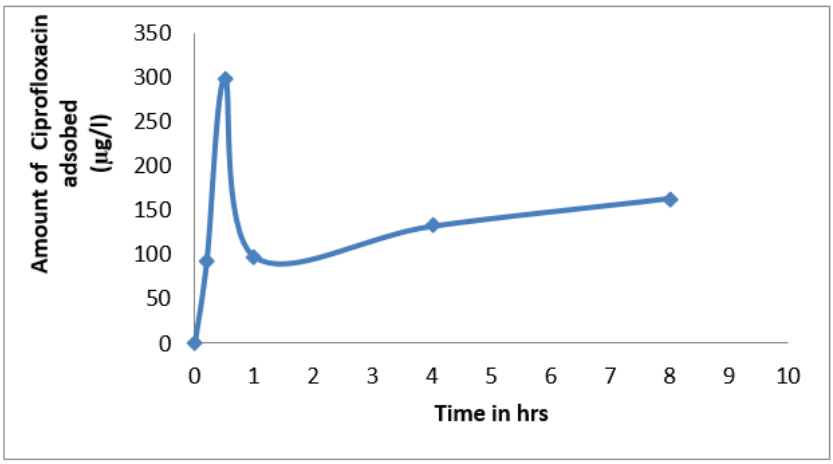

Figure 2. Rate of adsorption of ciprofloxacin onto microplastics.

However, this 30 mins. finding agrees with previous studies of paracetamol adsorption on MPs by Darmey *et al*., (2022).

In this study, microplastics most likely have the highest specific surface area, which is intriguingly correlated with their sorption affinities for antibiotics. The sorption capacity of a sorbent is significantly influenced by the surface area. Greater sorption of antibiotics may be facilitated by MPs' larger surface area. Previous studies showed that different types of microplastics have different physicochemical properties that affect how MPs and pollutants interact (Guo *et al*., 2018).

The absence of an adsorbent-specific area or a decrease in its availability for adsorption could be the cause of the decline in adsorption. The adsorption efficiencies of microplastics for antibiotics decreased because of the rapid adsorption site occupancies in the microplastics. According to Abdullah et al. (2009), the number of unoccupied sites is decreasing as the use of sites on MPs increases. A larger surface area can increase the availability of sorption sites, which may be the main factor in all antibiotics' high desorption efficiency.-

This study demonstrates that the antibiotic ciprofloxacin is absorbed by microplastics in the Batch method, showing that 30 minutes is sufficient to reach equilibrium.

Also, the rate of adsorption of antibiotics ciprofloxacin onto microplastics is 90 ug. g^{-1} .hr^{-1}.

3.2 Qualitative Description of Sorption Isotherms

The adsorption of organic contaminants on the MPs is widely studied using the adsorption isotherm models. To establish whether the adsorption process is linear monolayer coverage or multilayer adsorption, they are mostly used to compute the amount of adsorbate that may be adsorbed onto the adsorbent (Zhang et al., 2020). It is frequently possible to infer information about the sorption mechanism of organic contaminants (antibiotics) on MPs from morphology.

The performance of the sorption process is significantly impacted by the isotherm shape, for example, by fixing the bed (Inglezakis & Fyrillas, 2017)the vast majority of models employed are either phenomenological, based on chemical reaction kinetics, or limited to systems that obey simple equilibrium isotherms (favorable, unfavorable, linear, and

rectangular. According to the IUPAC classification, there are six (6) different sorts of shapes that can be assigned to the sorption isotherm (Sing, 1998).

According to classification by (Sing, 1998) and (Rouquerol et al., 2014), Figure 3 depicts the shape S isotherm formed by the adsorption of the antibiotic ciprofloxacin in water via microplastics. The sigmoid type 2 isotherm, also known as the so-called S-shape, is typically seen on the surface of the adsorbent, in this case, microplastics, and can be mono- or multilayer sorption.

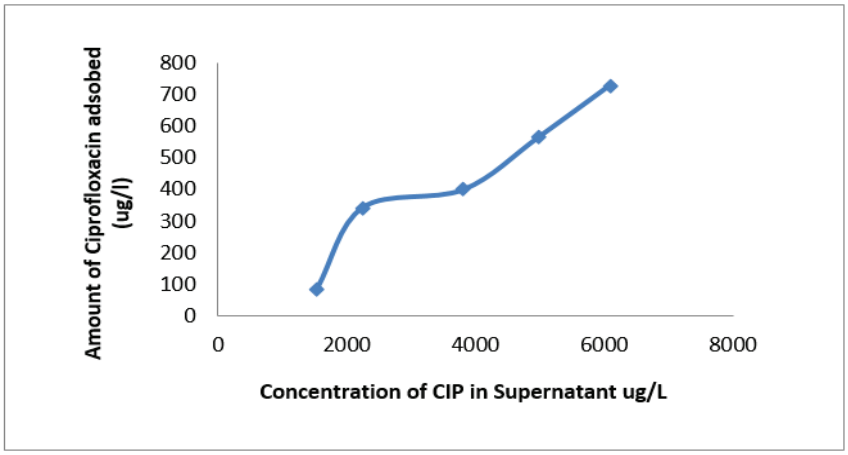

Figure 3. Amount sorbed against equilibrium concentration of CIP onto microplastics

According to (Aviara, 2020), the combined special effects (physical proprieties of the solution), capillary effects, and surface-water interaction can all be used to define the resulting curve. Poor concentrations of this type of isotherm on the surface have a poor affinity for adsorption, which intensifies at larger concentrations. A well-defined monolayer is often referred to as a "knee" in scientific terminology.

3.3 Quantitative Description of Sorption Isotherm

From Figure 4, it can be observed that Langmuir isotherm models poorly fit the sorption data with R^2=0.094, which indicates that the adsorption of CIP onto MPs does not occur in the homogeneous and mono-layer surface.

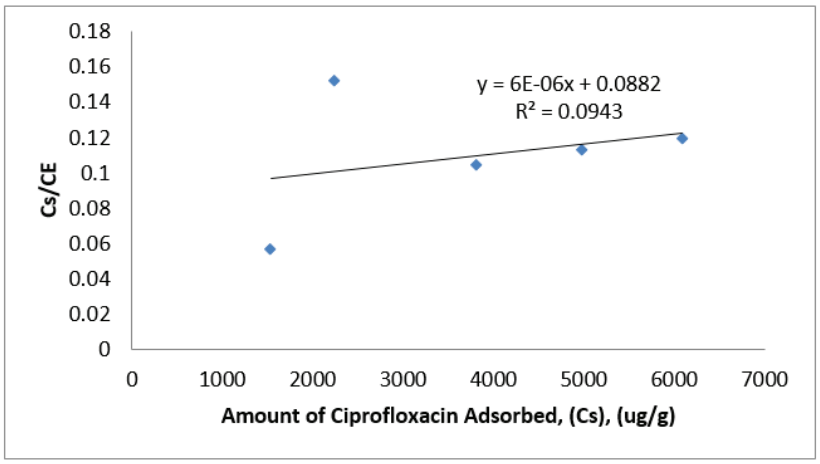

Figure 4. Langmuir Model for Adsorption of Ciprofloxacin onto Microplastic

Freundlich isotherm model gave an R^2 of 0.855, indicating a good fit of the sorption data of ciprofloxacin in water using the microplastics as shown in Figure 5. Therefore, the Freundlich model was the most appropriate model to describe the sorption of ciprofloxacin by microplastics. According to the postulate of the Freundlich model high energy sites are first occupied, followed by low-energy sites (Guo et al., 2020). Previous studies have confirmed the adsorption of CIP onto microplastics as non-uniform and multi-layer (Liu et al., 2019). This may be due to the physicochemical property of the organic pollutant CIP.

The highest value of R^2 of Freundlich models over the other model, as shown in Table 1, could be attributes of non-uniform surface energies and exponential supply of active site.

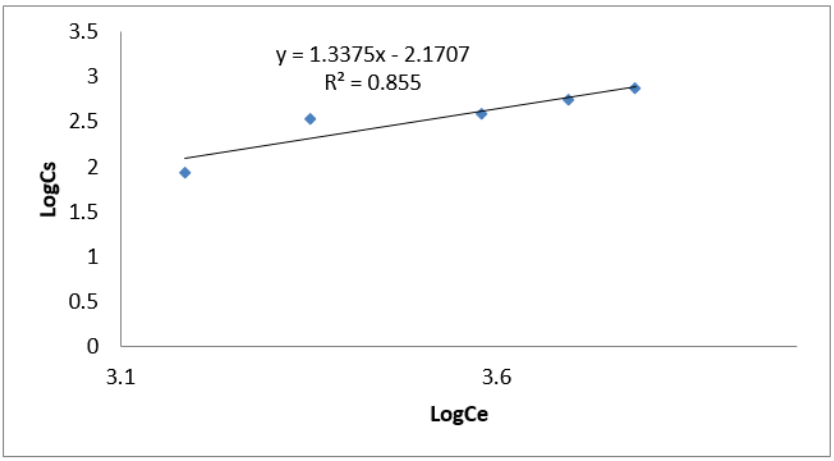

Figure 5. Freundlich Model for Adsorption of Ciprofloxacin onto Microplastic

Table 1: Parameters of the isotherms models of CIP adsorbed on Microplastics (PET and HDPE)

MODELs	EQUATION	R^2	Constant	Constant	Y=MX+B
Langmuir	Ce/Qe=1/ qmax*k+Ce/qmax	0.0943	Qmax=0.000354107	K=3201.6029	6E-06x+0.0882
Freundlich	lnQe=lnK+nlnCe	0.855	Kf=8.764416986	n=1.3375	1.3375x-2.1707

This indicates that MPs are an excellent, reasonably priced adsorbent for ciprofloxacin residues in water. This suggests that MPs can be produced locally in labs or on an industrial scale and that they can be used as an adsorbent in shredders in mills. MPs will serve as a recycling technique to reduce the amount of plastic waste released into the environment, as well as a water treatment method to remove pharmaceutical residue from water bodies.

4.0 CONCLUSION

Composite (waste HDPE and PET) microplastics were explored as adsorbents for the removal of antibiotics (ciprofloxacin) pollutants in water. Adsorption findings were applied to the Freundlich model and Langmuir model to ascertain the model that best describes the adsorption of ciprofloxacin by the composite microplastics under study. The composite microplastic used in this study was able to remove ciprofloxacin from water with a Langmuir maximum adsorption capacity of $3.54x\ 10^{-4}$. The r^2 values were 0.09 and 8.55 for Langmuir and Freundlich respectively. This means that the sorption of ciprofloxacin on microplastics can best be predicted by the Freundich model.

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