Agitated tank biosorption of ibuprofen using corn cob.

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Biosorpción en tanque agitado de ibuprofeno utilizando mazorca de maiz

Biosorpció en tanc agitat d'ibuprofè utilitzant panotxa de blat de moro

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SUMMARY

The presence of emerging contaminants, especially drugs for human and veterinary use in natural waters, due to their high degree of persistence and the fact that the treatments used in wastewater treatment plants (WWTP) are not efficient at removing them, has been the subject of study by the scientific community.

In this work, the removal of ibuprofen from synthetic waters was studied working in an stirred tank using corn cob residues as a biosorbent. Aiming to achieve the highest drug removal rates, several parameters where studied such as: the concentration of biosorbent, the particle size of the biosorbent, the minimum contact time between both adsorbate and biosorbent to reach the equilibrium, the optimum pH and the temperature. The best conditions to remove ibuprofen (20 mg/L) from synthetic water were the use of 15 g/L of corn cobs with a particle size of 0.4191 mm stirring for one hour at pH 6.0. No matter the temperature, a removal rate of 50% was obtained after 10 minutes of contact, reaching an 89% at the equilibrium.

A kinetic study showed that the pseudo-second-order kinetic model was the one that best reproduced the experimental data with a determination coefficient (R^2) of 0.982, and for the equilibrium behavior, the Freundlich model was the best fit for the adsorption equilibrium data with a R^2 of 0.972.

Keywords: ibuprofen; corn cob; biosorption; kinetic studies.

RESUMEN

La presencia de contaminantes emergentes, especialmente fármacos de uso humano y veterinario en aguas naturales, debido a su alto grado de persistencia y a que los tratamientos utilizados en las plantas de tratamiento de aguas residuales (EDAR) no son eficientes para eliminarlos, ha sido objeto de atención. estudio por parte de la comunidad científica.

En este trabajo se estudió la eliminación de ibuprofeno de aguas sintéticas trabajando en un tanque agitado utilizando residuos de mazorcas de maíz como biosorbente. Con el objetivo de lograr las mayores tasas de eliminación de fármacos, se estudiaron varios parámetros como: la concentración del biosorbente, el tamaño de partícula del biosorbente, el tiempo mínimo de contacto entre el adsorbato y el biosorbente para alcanzar el equilibrio, el pH óptimo y la temperatura. Las mejores condiciones para eliminar el ibuprofeno (20 mg/L) del agua sintética fueron el uso de 15 g/L de mazorcas de maíz con un tamaño de partícula de 0,4191 mm agitando durante una hora a pH 6,0. Independientemente de la temperatura, se obtuvo una tasa de eliminación del 50% después de 10 minutos de contacto, alcanzando un 89% en el equilibrio.Un estudio cinético demostró que el modelo cinético de pseudo segundo orden fue el que mejor reproducía los datos experimentales con un coeficiente de determinación (R^2) de 0.982, y para el comportamiento de equilibrio, el modelo de Freundlich fue el que mejor se ajustaba a los datos de equilibrio de adsorción. con un R^2 de 0,972.

Palabras clave: ibuprofeno; elote; biosorción; estudios cinéticos

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RESUM

La presència de contaminants emergents, especialment fàrmacs d'ús humà i veterinari en aigües naturals, pel seu alt grau de persistència i pel fet que els tractaments utilitzats a les depuradores d'aigües residuals (EDAR) no són eficients per eliminar-los, ha estat objecte de estudi de la comunitat científica. En aquest treball, es va estudiar l'eliminació d'ibuprofè d'aigües sintètiques treballant en un dipòsit agitat utilitzant residus de panotxa de blat de moro com a biosorbent. Amb l'objectiu d'aconseguir les taxes d'eliminació de fàrmacs més altes, es van estudiar diversos paràmetres com: la concentració de biosorbent, la mida de partícula del biosorbent, el temps de contacte mínim entre adsorbat i biosorbent per arribar a l'equilibri, el pH òptim i la temperatura. Les millors condicions per eliminar l'ibuprofè (20 mg/L) de l'aigua sintètica van ser l'ús de 15 g/L de panotxes de blat de moro amb una mida de partícula de 0,4191 mm agitant durant una hora a pH 6,0. Independentment de la temperatura, es va obtenir una taxa d'eliminació del 50% després de 10 minuts de contacte, arribant a un 89% a l'equilibri.

Un estudi cinètic va demostrar que el model cinètic de pseudosegon ordre era el que millor reproduïa les dades experimentals amb un coeficient de determinació (R^2) de 0,982, i per al comportament d'equilibri, el model de Freundlich era el millor ajust per a les dades d'equilibri d'adsorció. amb un R^2 de 0,972.

Paraules clau: ibuprofè; panotxa de blat de moro; biosorció; estudis cinètics

INTRODUCTION

The release of different chemical products originated by industries has been a concern of the scientific community for several decades due to the fact that the various treatments used in wastewater management are deficient in the elimination of new emerging pollutants, which are finally discharged into water resources, causing eco-toxicological effects on animal species that live there[1].

Within this group of emerging contaminants are pharmaceutical products, which have reached the water compartment through effluents from industries, hospitals or excreted by humans. Such is the case of ibuprofen, which has been catalogued as the sixth most sold drug in the world, which favors its constant permanence in the environment[2,3]. Furthermore, there is the issue that the maximum permissible concentration limit of drugs in the environment is still unregulated, probably due to the lack of knowledge about long-term exposure to these compounds and their metabolites in the environment. Aguirre and collaborators have merged the results of the concentration of this pollutant at various emission points in the city of Cadiz, Spain, and found that the highest values are reported at the Wastewater Treatment Plants (WWTP), which receive discharges of all types[4].

Regarding the negative effects that ibuprofen can cause in water sources, it is reported that at a high concentration of 13.4 mg/L it affects the reproduction of *Daphnia magna*, an important indicator species of toxicological effects in water, while at low concentrations of 250 ng/L it causes damage to the membrane of the digestive gland of the mussel *M. galloprovincialis*, it also causes stimulation of abscisic acid production in the duckweed *Lemna minor*, which causes cessation of cell division and inhibits its growth. In the crab *Carcinus maenas*, the presence of ibuprofen plus other contaminants alters cell oxidation and causes oxidative stress, generating damage to deoxyribonucleic acid[4,5].

There has been increased attention by researchers on the removal of micropollutants from wastewater through various techniques. Methods such as adsorption, filtration, precipitation, flotation and flocculation were traditionally used for the removal of endocrine disruptors, pharmaceuticals, personal care products, pesticides, dyes and metals from water[6,7].

Biosorption, defined as the process of removing pollutants from aqueous solutions using biomass, has been presented in recent years as an innovative, economical process with low ecological impact and, above all, capable of retaining pollutants in low concentrations and handling waste from renewable natural materials. This work studies the removal of ibuprofen using corn cobs or corn stover, which is an abundant waste in Ecuador, since for every ton of corn harvested, 1.665 tons of waste are obtained, of which 0.613 tons are stalks, 0.309 tons of leaves, 0.277 tons of roots, and 0.186 tons of gourds.

A study of the main parameters affecting the process is carried out in addition to a kinetic and equilibrium study.

MATERIALS AND METHODS.

Preparation of biosorbent and solutions.

Synthetic solutions were prepared with a concentration of 20 mg/L of Sigma Aldrich analytical grade ibuprofen (purity > 98%), Merck brand methanol (purity 99.9%). A methanol/water (5:95) blank was used for the preparation of the serial solutions in order to solubilize the drug; this solution also served as a blank for the measurement of the different tests in the Ultraviolet–visible spectroscopy equipment.

The hydrochloric acid and sodium hydroxide used as pH regulators and neutralizing agents were Merck brand analytical grade reagents. All solutions were prepared with type II distilled water.

The biomass initially used was collected in the city of Cuenca, province of Azuay (Ecuador), and was washed, crushed, dried and sieved to a particle size of less than 0.4191 mm.

Adsorption study.

The adsorption study of ibuprofen in solution (20 mg/L) with corn stover was divided into six parts: (1) adsorbent dose study, (2) influence of particle size, (3) influence of pH, (4) influence of contact time, (5) kinetic study, (6) thermodynamic study under equilibrium conditions.

Stirred tank biosorption experiments.

The operating conditions consisted of 50 mL of 20 mg/L ibuprofen solution introduced in a 250 mL flask at 30°C, pH 6.0, one hour shaking at 1500 rpm with a Thermo Scientific Max Q4000 shaker, with a mass of biosorbent of 15 g/L.

When reaching the equilibrium, the solution was filtered through a 5 – 7 µm porus size cellulose filter paper and the concentration (Ce) was determined by using a Thermo Scientific GenesysTM 10S spectrophotometer and 1 cm thick quartz cells. Measurements were performed against a 1% methanol water blank at a wavelength of 264.2 nm. The percentage of drug removal and the amount of ibuprofen adsorbed per gram of adsorbent q_e (mg/g) were calculated using equations 1 and 2.

$$\% \text{ removal} = \frac{Co - Ce}{Co} x100 \quad (1)$$

$$q_e = \frac{Co - Ce}{m} V \quad (2)$$

Where Co and Ce are the initial and equilibrium concentrations in mg/L, m represents the mass of the adsorbent in grams used in the experiment and V represents the processed volume in liters.

Point of zero charge (PZC).

The point of zero charge (PZC) is the pH at which the adsorbent surface charge is zero, and it depends on the total net surface charge (external and internal) of the particles[8].

The zero charge point is determined using the methodology described by Antunes[9].

A 50 ml solution of a 0.10 mol/L NaCl solution with different pH values (2, 4, 6, 8, 10) is added to 500 mg of solid sample. The pH adjustments are made with 0.1 mol/L NaOH and HCl solutions. The suspensions are stirred at 25 ± 3 °C for one hour. Afterwards, the biosorbent is separated through filtration and the final pH of each solution is measured. The PZC is determined by the convergence point of the plots of the initial pH values against the final pH value of each solution.

A CRISON pH meter, model GLP 21, previously calibrated with buffer solutions of pH 7.00 and 4.01, was used to determine the pH. The method used was the 4500-HB of Standard Methods.

Kinetic studies.

Kinetic studies are a tool that allows the quantification of kinetic parameters in removal processes, being able to determine the adsorption rate of the adsorbate on

Table 1. *Kinetic Models*

Model	Equation	Description
Pseudo-first order. This model assumes that each species is assigned an adsorption site on the adsorbent material.	$q_t = q_e(1 + e^{-k_1 t})$	k_1 = Kinetic rate constant (min^{-1}).
Pseudo-second order. This model assumes that the adsorbate is adsorbed at two active sites on the biomass.	$q_t = \dfrac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$	k_2 = Kinetic rate constant (g/mg min)
Weber y Morris. This model proposes the intraparticle diffusion model to explain adsorption behavior.	$q_t = k_{id} t^{1/2}$	k_{id} = Intraparticle diffusion rate constant. (mg/g min$^{1/2}$)
Elovich model. This model is based on chemisorption processes and assumes that the active sites of the bioadsorbent are heterogeneous with different activation energies. It relies on a second-order reaction mechanism for a heterogeneous reaction process.	$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln\, t$	α = represents the initial adsorption rate (mg/g.min). β = constant related to the surface coverage and the activation energy for chemical adsorption (g/mg).

q_t = amount adsorbed at time (mg/g), q_e = amount adsorbed at equilibrium (mg/g), the sorbent and the influence of the variables on the efficiency of the process. For the study of ibuprofen biosorption with corn cob residues, the pseudo-first order, pseudo-second order, Weber and Morris and Elovich kinetic models were considered (Table 1).

Equilibrium models.

The most widely applied models in biosorption because of their simplicity, predictive ability and quality of fit are the Freundlich and Langmuir models (Table 2). The Freundlich model assumes adsorption of a solute monolayer on the adsorbent surface so that adjacent interactions can be established between the molecules that are adsorbed and a heterogeneous distribution of adsorption sites due to the diversity of binding sites. The Langmuir model assumes an adsorption monolayer with a homogeneous distribution of both adsorption sites and adsorption energies with no interaction between the adsorbed molecules. Biosorption equilibrium experiments were carried out at temperatures of 20, 30 and 40 °C.

RESULTS AND DISCUSSION.

Biomass dosing study.

As shown in Figure 1, the percentage of removal increases as the amount of biomass increases, until it reaches a point where it tends to stabilize at 15 g/L due to the fact that as the biomass increases, the number of active sites of the adsorbent also increases. Other studies indicate that as the adsorbent dose continues to increase, the removal of ibuprofen may be reduced because there is an overlapping or aggregation of the adsorption sites of the adsorbent, which leads to a decrease in its total surface area[10].

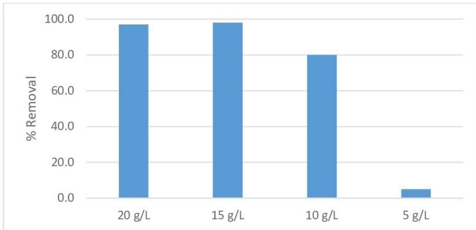


Figure 1. *Influence of Biomass Dose. (Ibuprofen: 20 mg/l, pH:6, temperature: 30°C, stirring time: 1 hour, Parcicle Size 0.419mm)*

Table 2. *Equilibrium Model*

Models Name	Equation	Parameters	Reference number
Isotherm models			
Langmuir	$q_e = \frac{Q^0 b C_e}{1 + bC}$	Q^0-monolayer adsorption capacity (mg/g), b-constant related to net enthalpy of adsorption ($b \propto e^{-\Delta H/RT}$), q_e-solute amount adsorbed per unit weight (mg/g), C_e-solute equilibrium concentration (mg/L). The Langmuir isotherm assumes a homogenous surface, monolayer coverage and no interaction of the adsorbate with neighboring sites.	14
Freundlich	$q_e = K_F\, {C_e}^{1/n}$	K_F-constant indicative of the relative adsorption capacity of adsorbent (mg/g), $1/n$-a constant indicative of the intensity of the adsorption, q_e-adsorption capacity (mg/g), C_e-equilibrium concentration of solute (mg/L). This isotherm is used in the low to intermediate adsorbate concentration range.	14

Influence of particle size.

The influence of particle size is studied as shown in Figure 2.

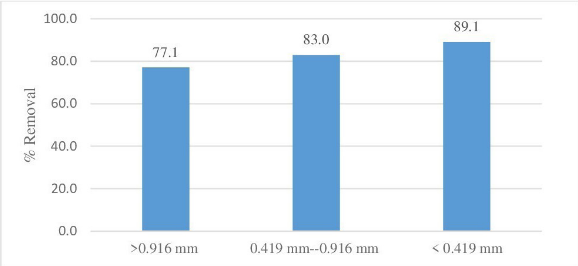


Figure 1. *Influence of Particle Size. (Ibuprofen: 20 mg/l, pH:6, temperature: 30°C, stirring time: 1 hour, Biomass Dose 15 g/L)*

Particles smaller than 0.4191 mm have a higher adsorption, since the surface area increases[10,11].

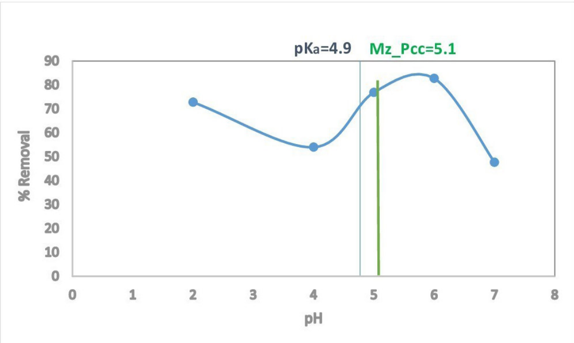


Figure 3. *Influence of pH on the Removal of Ibuprofen (Biomass: 10g/L, Ibuprofen: 20 mg/L, Temperature: 30°C, particle size: 0.4191 mm, stirring Time: 1 hour)*

Figure 3 shows that the pH at the point of zero charge (pH_{PZC}) found according to the methodology described above, for corn cob residues was 5.1. The pKa of ibuprofen is 4.9. The higher adsorption of ibuprofen occurred at pH 2 and 6, which agrees closely with the research developed by Essandoh and co-workers, who assume that at pHs higher than both pK_a and pH_{PZC} the adsorbate is unprotonated (R-COO$^-$) and the biomass surface is negatively charged and therefore creating an electrostatic repulsion between adsorbate and adsorbent. However, there is a region of intermediate pH values where adsorption increases, maximizes and then continues to drop as pH increases. As negative surface charge density is a complex function of pH because carboxylic acids, phenols and surface aliphatic hydroxyls can ionize in different pH ranges Essandoh et al. justified the maximum at pH higher than pH_{PZC} due to the presence of phenolic groups present in the biomass that act as H^+ donors to form hydrogen bridges with ibuprofen carboxylate anion[14]. In this work, when working at pH 6.0 more than 80% removal of ibuprofen was achieved.

At pH = 2, the surface of the corn cob residues is positively charged and the ibuprofen will be in its neutral molecular form, which could represent more than 99% in moles. Possibly, the positive charges of the biosorbent favor the adsorption of the neutral molecule of ibuprofen through hydrogen bonds and other interactions, obtaining a removal rate of 72%. A similar result was obtained in the study reported by Mondal [13], in which 98.37% was removed working with biochar derived from chemically modified ***Parthenium hysterophorus*** which presented a pH_{PZC} of 7.4. In addition, Mestre has experimented with activated carbons achieving a removal of ibuprofen higher than 90%, in which a pH_{PZC} value of 7.5 was determined, working in both studies with pH = 2[12].

Influence of contact time.

The objective of the contact time study is to observe the kinetics of drug biosorption with respect to time. In turn, with these data, kinetic modeling of the ibuprofen biosorption process can be performed. After the onset of agitation, the active sites on the adsorbent surface are empty for binding to the adsorbate molecules; then, the free sites are filled until the equilibrium point is reached. As can be seen in Figure 4, at 10 minutes there is a 50% removal, reaching 80% in 60 minutes. From this point, the adsorption rate changed slightly, remaining constant due to the decrease in the diffusion rate[13]. The initial concentration acts as an important driving force to prevail over the mass transfer resistance of all ibuprofen molecules between the aqueous and solid phases[14].

Mondal and collaborators determined the same behavior in the curve, detecting an optimum time greater than 120 min for the removal of ibuprofen[13].

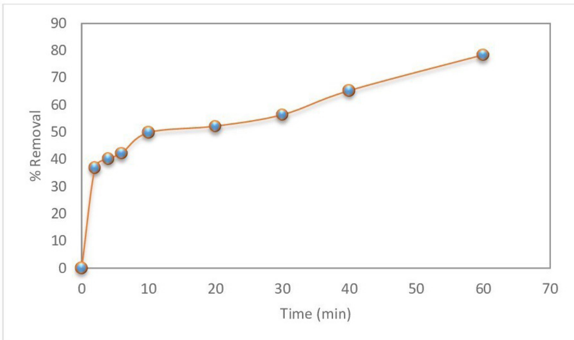


Figure 4. *Influence of Contact Time*

Kinetic study

From the experimental data, the mathematical modeling of the biosorption kinetics was carried out with the following models: pseudo first order, pseudo second order, Weber and Morris and Elovich (Table 1). This was done with the objective of determining which of these models fit the experimental data.

As shown in Figure 5, the pseudo-second order model fits the experimental data, with the experimental and model-calculated adsorbed amounts being very close, yielding a coefficient of determination of 0.982, which means that the adsorbate adsorbs on two active sites in the biomass. Although the Elovich model gives a high

Table 3. *Model Parameters*

Pseudo first order		Pseudo second order				Elovich		
k_1 (min^{-1})	R^2	k2 (g /mg min)	qe cal (mg /g)	q_e exp (mg /g)	R^2	α (mg /g min)	β (g /mg)	R^2
0.038	0.865	0.148	2.005	2.045	0.982	6.249	0.643	0.993

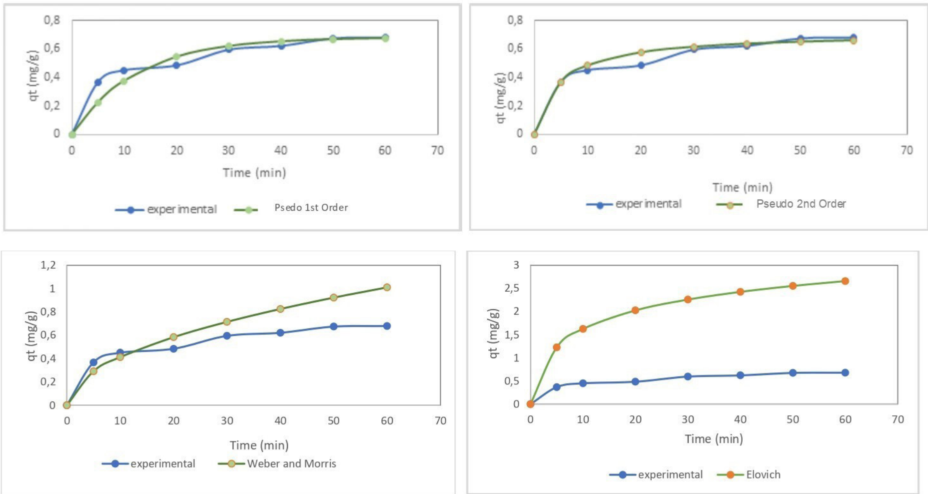


Figure 5. Kinetic Study of Ibuprofen Removal with Corn Cob

Figure 5. *Kinetic Study of Ibuprofen Removal with Corn Cob*

coefficient of determination (0.993), the values of the experimental and model-calculated adsorbed amounts differ. Table 3 shows the pseudo-second order adsorption rate constant $\boldsymbol{k}_2$ of 0.148 g/mg min, and that both calculated and experimental q_e have close values. This model represents chemisorption or chemical adsorption due to the formation of chemical bonds between adsorbent and adsorbate in a monolayer on the surface.

Equilibrium study

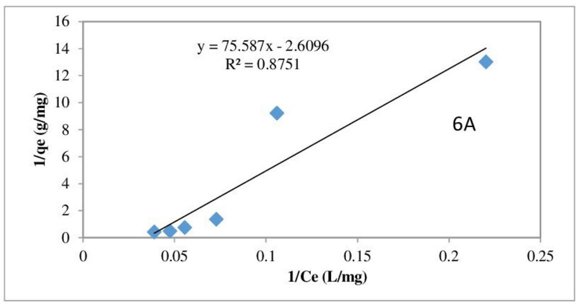
Figures 6A, 6B and 7 show the experimental data at 30°C fitted to the Freundlich and Langmuir models.

According to the results presented in Figure 7, the Freundlich model offers the best fit to the experimental data, so this model is the most appropriate in the representation of the adsorption process equilibrium, since it has a coefficient of determination $R^2 > 0.98$.

The Freundlich model assumes that the surface of the biosorbent is heterogeneous. The sites with the highest affinity are occupied first, and subsequently the rest are occupied. In its application, it is also assumed that the type of binding is a physical one.

$\boldsymbol{K_F}$ 1.367 L/mg, Freundlich constant, is an approximate measure of the adsorption capacity.

n represents the adsorption intensity, $0< \frac{1}{n} <1$ the process is favorable resulting in a value of 0.885.



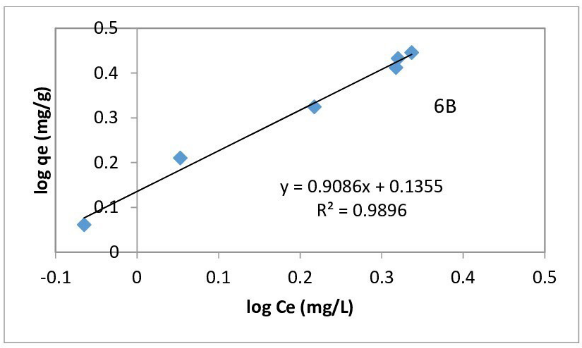


Figure 6A. *Langmuir Model;* **Figure 6B**. *Freundlich Model*

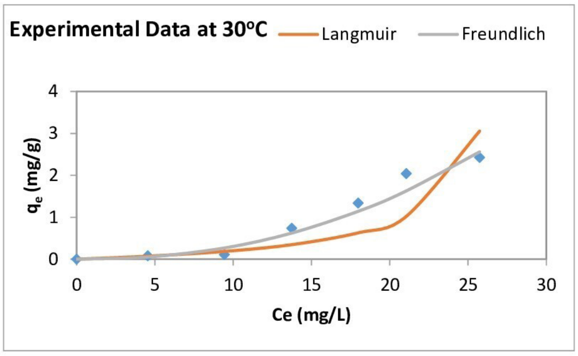


Figure 7. *Equilibrium Study*

Thermodynamic Study

As can be seen in Figure 8, temperature does not have a significant influence on the removal of ibuprofen, although there is a slight decrease with increasing temperature. *Mondal et al.* state that, in the adsorption process, Van der Waals forces and hydrogen bonds are weak. This, as well as an increase in temperature, leads to a decomposition of the adsorption forces, causing a decrease in the elimination of the drug[15].

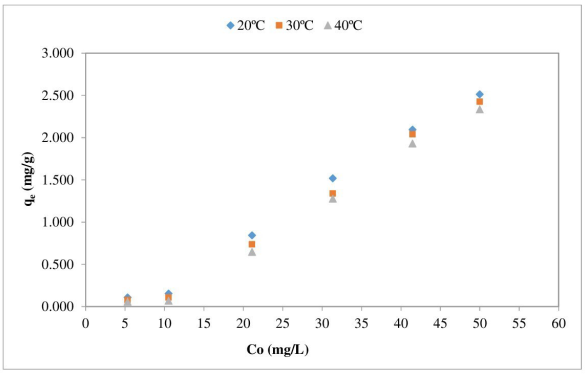


Figure 8. *Thermodynamic Study of Ibuprofen Biosorption with Corn Cob Residues*

CONCLUSIONS.

Corn cob proved to be a good adsorbent in the removal of ibuprofen from synthetic waters with 80% removal. Temperature did not show significant influence on the removal of ibuprofen. The pH that most favored the adsorption of the drug was pH 6.0. The pseudo-second order model best reproduced the experimental results and the adsorption isotherms were well fitted by the Freundlich model. It would be a feasible technology as a tertiary treatment in both wastewater and sewage treatment plants.

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