



Elimination of Cadmium (II) in aqueous solution using corn cob (*Zea mays*) in batch system: adsorption kinetics and equilibrium

Eliminación de Cadmio (II) en solución acuosa usando zuro de maíz (*Zea mays*) en sistema por lotes: Cinética y equilibrio de adsorción

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Abstract

The objective of this work was to evaluate in a batch system the effect of temperature, adsorbent dose and particle size in the elimination of Cadmium (II) ions using corn cob (*Zea mays*). A central 22 star composite type experimental design was used. From the characterization of the bio-adsorbent by Fourier Transform Infrared Spectroscopy (FTIR), it was found that its structure has OH, COOH, methyl and amino groups, intervening in the process. It was found that at 55 °C, 0.031 g and 0.6775 mm the maximum adsorption capacity was obtained (210.1 mg/g). From the kinetics, it was established that removal occurs rapidly in the first minutes and equilibrium is reached at 120 min, the data being adjusted by the Pseudo-Second order model. The adsorption equilibrium data is fitted by the Langmuir model, suggesting that it occurs uniformly on the surface of the bio-adsorbent. Corn cob is presented as an effective adsorbent for Cadmium (II) in aqueous solution.

Keywords: Bio-adsorption, kinetics, isotherm; Langmuir, pseudo-second order.

Resumen

El objetivo del presente trabajo fue evaluar en sistema por lotes el efecto de la temperatura, dosis de adsorbente y tamaño de partícula en la eliminación de iones de Cadmio (II) usando zuro de maíz (*Zea mays*). Se utilizó un diseño experimental de tipo compuesto central 22 estrella. De la caracterización del bioadsorbente por Espectroscopia Infrarroja por Transformada de Fourier (FTIR) se encontró que en su estructura cuenta con grupos OH, COOH, metilo y amino, intervinientes en el proceso. Se encontró que a 55 °C, 0,031 g y 0,6775 mm se obtuvo la capacidad máxima de adsorción (210,1 mg/g). De la cinética se estableció que la remoción se da rápidamente en los primeros minutos y el equilibrio se alcanza a los 120 min, siendo los datos ajustados por el modelo de Pseudo-Segundo orden. Los datos de equilibrio de adsorción son ajustados por el modelo de Langmuir, lo que sugiere que se produce de manera uniforme sobre la superficie del bioadsorbente. Se presenta el zuro de maíz como un adsorbente efectivo de Cadmio (II) en solución acuosa.

Palabras clave: Bioadsorción, cinética, isoterma, Langmuir, pseudo-segundo orden.

1 Introduction

The increase in the contamination of water bodies as a result of anthropogenic activities constitutes an environmental problem of broad resonance and research interest, so the search for alternatives for

their removal is a key issue in the management of environmental pollutants (Neris *et al.*, 2019). Among these pollutants, heavy metals such as Mercury (Hg), Lead (Pb), Chrome (Cr), Nickel (Ni), Zinc (Zn) and Cadmium (Cd) are discharged in industrial effluents to water sources (Afroze & Sen, 2018; Abba *et al.*, 2020; Ibrahim *et al.*, 2020; Salazar-Pinto *et al.*, 2021).

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Cadmium (II) is a transition metal, part of group II-B with an atomic weight of 112.41 g/mol. It is obtained as a by-product of the metallurgical treatment of zinc and lead, from cadmium sulphide (Amro *et al.*, 2019), pollutes the environment from smelting and refining, and for its many industrial applications, for its resistance to corrosion, in electroplating, galvanizing and galvanizing, as well as its use in plastics, pigments to create dyes, nickel and cadmium batteries, manufacture of electrical conductors, polyvinyl chloride (PVC) products, photocells, tires, automotive radiators, electronic components, heating elements and fertilizers (Amro *et al.*, 2019; Yuan *et al.*, 2019). It is a toxic, non-biodegradable metal, accumulating in living beings, and its ingestion in small concentrations can produce from stomach irritation, cause bone degradation, inhibit the functioning of the kidneys, liver and lungs, cancer, high blood pressure, destruction of erythrocytes and testicular tissue (Basu *et al.*, 2017; Liu *et al.*, 2019; Mezynska & Brzóska, 2018). The effects of Cadmium (II) toxicity depend on the type of exposure, whether through inhalation of contaminated air, particularly near smelters and incinerators or through cigarette smoke, consumption of contaminated food and water (Martínez *et al.*, 2013).

In the natural environment cadmium is found with 2+ valence, so in solution it forms chemical species such as CdCl_2 , CdOH , CdHCO_3 , CdCl_3^- , CdCl_4^{2-} , $\text{Cd}(\text{OH})_3^-$ and $\text{Cd}(\text{OH})_4^{2-}$ and organic chelates. The solubility of cadmium salts in water is highly variable; halides, sulphate and nitrate are soluble while oxide, hydroxide and carbonate are practically insoluble (Sanchez *et al.*, 2014), (Huang *et al.*, 2017). The concentration of Cadmium in air from industrial areas varies from 9.1 to 26.7 mg/m³ compared to 0.1 to 6 ng/m³ in air from rural areas, with the time spent in soils being up to 300 years and 90% staying unchanged, reaching the soil of agricultural land by air deposition (41%), with phosphate fertilizers (54%), by application of manure fertilizer (5%) and in contaminated soils levels reach up to 1 mg/g and contaminated river water may contain up to 0.14 mg Cd/L (Manjuladevi *et al.*, 2018; Saravanan *et al.*, 2017).

In the study of metal ion adsorption processes, it is important to determine the properties of the adsorbing material, since the surface contact area that will allow contact between active centres and the contaminant

depends on these properties (Ahmad *et al.*, 2012); as well as factors such as pH, contact time, temperature, initial concentration, adsorbent dose, particle size, among others.

The adsorption kinetic study allows determining the useful life of the adsorbent before saturating and the mechanism that controls the process and how the interactions between the adsorbent-adsorbate occur, determining the limiting phase of the process. (Dai *et al.*, 2018; Krika *et al.*, 2016; Rodrigues *et al.*, 2019). The biosorption kinetics describes the speed at which the adsorbate is trapped by the sorbent, determining the contact time between the adsorbent and the treated effluent. For this reason, knowledge of the speed laws that describe the adsorption system is required, which are determined by experimentation and cannot be inferred in any case (Hubbe *et al.*, 2019). In general, the removal of metal ions from aqueous solutions by bio-adsorption depends on the mechanisms that involve the interactions of metal ions with specific active groups associated with the bio-sorbent cell wall (Kulbir *et al.*, 2018). Therefore, the kinetics of bio-adsorption indicate the evolution of each of the stages through which it is carried out and which controls the process (chemical reaction, diffusion, or mass transfer). In this sense, different kinetic models have been proposed to describe the mechanism by which the adsorption process takes place, which is generally complex and may involve chemical reactions between functional groups of the sorbent and the metal ions, ion exchange reactions or the formation of the complex. Also, it is necessary to consider the mass transfer processes such as the transport of species within the liquid phase, diffusion from the liquid phase to the solid surface and diffusion inside macropores or micropores. (Basu *et al.*, 2017). Table 1 shows the equations of different models widely used in the literature, and these kinetic models have been evaluated in different studies. (Wang & Guo, 2020).

The adsorption isotherm is an analytical relationship that correlates the amount of a component adsorbed at an interface with the concentration of this component within the phase. Table 2 presents isotherm models evaluated in different studies. Adsorption isotherms are a graphical representation showing the relationship between the amount adsorbed per unit weight of adsorbent and the amount of adsorbate remaining in a test medium, at a constant temperature, at equilibrium (Yi *et al.*, 2017).

Table 1. Kinetic models of adsorption.

Model	Equation
Pseudo-first order	$q_t = q_e(1 - e^{-k_1 t})$
Pseudo-second order	$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$
Mixed order	$q_t = q_e(1 - e^{-K_3 t}) + \frac{q_e^2 k_4 t}{1 + q_e k_4 t}$
Pseudo-n-th order	$q_t = q_e \left(1 - \frac{1}{[(1 + (n-1)q_e^{n-1} k_n t)]^{1/(n-1)}} \right)$
Boyd's external diffusion equation	$q_t = q_\infty(1 - e^{-k_{\infty} t})$
Frusawa y Smith	$q_t = \frac{C_o}{m_s} = \left(1 - \frac{1}{1 + m_s K} - \frac{m_s K}{1 + m_s K} e^{\frac{1+m_s K}{m_s K} k_{FS} S t} \right)$

Table 2. Adsorption isotherm models.

Model	Equation
Langmuir	$q_e = Q_{max} \frac{b C_e}{1 + b C_e}$
Freundlich	$q_e = K_f C_e^{1/n}$
Henry	$q_e = K_{HE} C_e$
Dubinin-Radushkevich	$q_e = q_s e^{-K_{RD} t}$
Temkin	$q_e = \frac{RT}{b_T} \ln A_T C_e$
Jovanovich	$q_e = q_{max}(1 - e^{k_f C_e})$
Redlich Petersen	$q_e = \frac{K_R C_e}{1 + a_R C_e^g}$
Baudu	$q_e = \frac{q_m b_0 C_e^{1+x+y}}{1 + b_0 C_e^{1+x}}$
Fritz-Schluder	$q_e = \frac{q_m F S K_1 C_e^{\alpha FS}}{1 + K_2 C_e^{\beta FS}}$

Conventional methods for removing cadmium from industrial waters include: chemical precipitation, ion exchange, filtration, reverse osmosis,

electrochemical treatment, among others.; however these techniques can be expensive when removing metal ions at low concentrations(II) (Moreno-Rivas *et al.*, 2016). Thus, bio-adsorption is presented as an effective, economic and environmentally friendly strategy for the removal of heavy metals in solution, due to the fact that materials of plant origin have the capacity to trap metals present in water by their ion exchange capacity, since their cell wall is composed mainly of cellulose, hemicellulose and lignin, which contain functional groups such as hydroxyl, carboxyl, amino, hydrocarbons, among others, which are directly related to the active sites of adsorption (García *et al.*, 2013; Medellín-Castillo *et al.*, 2017; Rinaldi *et al.*, 2018).

Various waste materials have been studied and have the potential to be used as bio-adsorbents in the adsorption of heavy metals with good yields; among these materials are banana peels (Anwar *et al.*, 2010), melon (Manjuladevi *et al.*, 2018), lentils (Basu *et al.*, 2017), cocoa (Vera-Cabezas *et al.*, 2018), orange (Chen *et al.*, 2018; Romero-Cano *et al.*, 2017; Tran *et al.*, 2016), among other (Dai *et al.*, 2018; Neris *et al.*, 2019); This is due to the potential that residues of lignocellulosic origin have as heavy metal adsorbents due to the presence of functional groups that act as active exchange centres (Guedidi *et al.*, 2017). Among the functional groups present in lignocellulosic origin materials,

there are commonly hydroxyl, carbonyl, carboxyl, amines, amides, alcohols, methoxy, alkanes, alkenes and alkynes (Herrera-Barros *et al.*, 2020). These groups are essential in the adsorption process since, due to their anionic nature, they exert electrostatic forces on the metal cations to capture them in their structure (Bisla *et al.*, 2020; Lapo *et al.*, 2020; Patriota *et al.*, 2020).

In Colombia, 1,368.536 tons of corn product/year are produced, and this production generates 1,936,479 tons/year of residual corn biomass (stubble, stalk, and husk) at the national level, and in Bolivar, 218.782 tons/year of this waste are generated, so its use is necessary, because its elementary composition shows that it is a material with a good cellulose content (13.08%), pectin (7.98%) lignin (6.51%) and hemicellulose (6.47%), so its structure would have the presence of functional groups involved in the adsorption process (Núñez-Zarur *et al.*, 2018). The new knowledge about the adsorption properties of post-harvest residues generated in large volumes may be interesting for developing countries with extensive rural areas, such as Colombia. Thus, the objective of the present research was to evaluate the effect of temperature, adsorbent dose, and particle size on the adsorption capacity of Cadmium (II) using corn cob as adsorbent, evaluating the kinetics and isotherms at the best conditions. This work contributes to supporting the current knowledge on the study of cadmium removal by using light cellulosic biomass. In this work, the effectiveness of the adsorption of Cd^{2+} ions from the aqueous solution was studied using biomass-derived from corn to evaluate the effect of temperature, adsorbent dose, and particle diameter.

2 Materials and methods

2.1 Materials, equipment, and reagents

In the present investigation a sieve machine brand Edibon model orto alresa Mod. Vibro was used,

an orbital shaker brand Gemmy Industrial model Shaking incubator IN-666, pH meter brand Thermo Scientific model Star A221, FTIR spectrophotometer brand Perkin Elmer 1660, Atomic Absorption Spectrophotometer brand Unicam model 969 series Solar with flame. 2M Hydrochloric Acid and Sodium Hydroxide solutions for pH adjustment. Merck Millipore Cadmium Sulfate (CdSO_4) analytical grade was used to prepare the synthetic solutions.

2.2 Design of experiments

The effect on the adsorption capacity (mg/g) of the independent variables: temperature ($^{\circ}\text{C}$), amount of adsorbent (g) and particle size (mm) was evaluated. For this, a continuous linear factor experimental design was followed, in response surface type 22 central compound: Star made in Statgraphics Centurion XVI.II. The levels of variation of the factors are shown in Table 3. Subsequently, under the best experimental conditions obtained, the kinetic and equilibrium study will be carried out.

2.3 Preparation and characterization of the adsorbent

The corn cob was obtained in a farm located in the department of Córdoba, selecting the best state to guarantee the quality of the adsorbent, obtaining a total of 430 g. Then, it was washed to eliminate impurities, and dried in the sun to a constant mass. Finally, the size was reduced and selected according to the design of experiments, for subsequent storage. The adsorbent material was characterized in order to evaluate the physical and chemical characteristics that allow and support its use in the adsorption of Cadmium (II) in aqueous solution. Fourier Transform Infrared Spectroscopy analysis was performed to determine functional groups present in the materials, making 128 scans in the range of $400\text{--}4000\text{ cm}^{-1}$ and at a wavelength of 540 nm.

Table 3. Experimental range and levels of factor variation.

Independent variables	Unit	Range and level				
		$-\alpha$	-1	0	+1	$+\alpha$
Particle size	mm	0.135	0.355	0.677	1	1.21
Amount of adsorbent	g	0.031	0.15	0.325	0.5	0.619
Temperature	$^{\circ}\text{C}$	29.8	40	55	70	80.2

Scanning Electron Microscopy (SEM) analysis was also performed to obtain morphological, topographical, and compositional information of the samples; for this, a JEOL model JSM 6490-LV with an Energy Dispersive Spectroscopy Detector was used. (Chen *et al.*, 2012).

2.4 Adsorption test

For the adsorption tests, a solution of Cadmium(II) at 100 ppm was prepared through the addition of 0.1555 g of cadmium sulfate (CdSO_4) in 1 L of deionized water. Cadmium(II) adsorption tests were performed individually in a batch system, in the shaker placing 100 mL of solution in contact with the adsorbent, at the different doses established in the design of experiments (Table 3), at 200 rpm per 24 h at pH 6 (Herrera-Barros *et al.*, 2018). The final concentration of contaminant was determined by atomic absorption at 228.8 nm.

The analysis of the results was carried out using the Statgraphics Centurion XVI.II software, to determine the incidence of the independent variables on the adsorption process. For this purpose, an analysis of variance, Pareto chart, estimated response surface and the evaluation of this response were carried out in order to maximize the adsorption capacity.

2.5 Kinetics and adsorption isotherm

Kinetics was done during 24 hours at the best conditions determined in the analysis of results, taking samples at 5, 10, 20, 30, 60, 120, 240, 480, 960 and 1440 min. The experimental data were adjusted to the pseudo-first order, pseudo-second order and

Elovich kinetic models by maximizing the R^2 using the software OriginPro 8®, in order to establish the phases that control the process.

The isothermal tests were performed at different initial adsorbate concentrations, under the best experimental conditions found, taking a single sample after contacting the contaminated solution with the adsorbent for 24 h. The experimental data of the adsorption equilibrium were adjusted using the Langmuir and Freundlich isotherms (Yu & He, 2018).

3 Results and discussion

3.1 Characterization of the bio-adsorbent

Figure 1 shows the FTIR analysis of the biomass under study. In the spectrum, the C=O and C-O stretching in the bands around 1600 cm^{-1} is observed, which indicates the vibration of the carboxyl groups belonging to pectin, hemicellulose and lignin in corn cob and reported in the previous characterization of the material (Tejada-Tovar *et al.*, 2016). The vibration of the OH groups and secondary amines between 3200 and 3600 cm^{-1} corresponding to the hydroxyl of the ligno-cellulosic molecules (Tejada-tovar *et al.*, 2019). The peak observed around 2900 cm^{-1} can be attributed to the C-H vibrations of methyl, methylene and methoxy groups. The peak of about 1400 cm^{-1} could be due to the presence of (C-H) aliphatic and aromatic groups in the plane of deformation (Ahmad *et al.*, 2012; E. D. Asuquo & Martin, 2016; Rinaldi *et al.*, 2018).

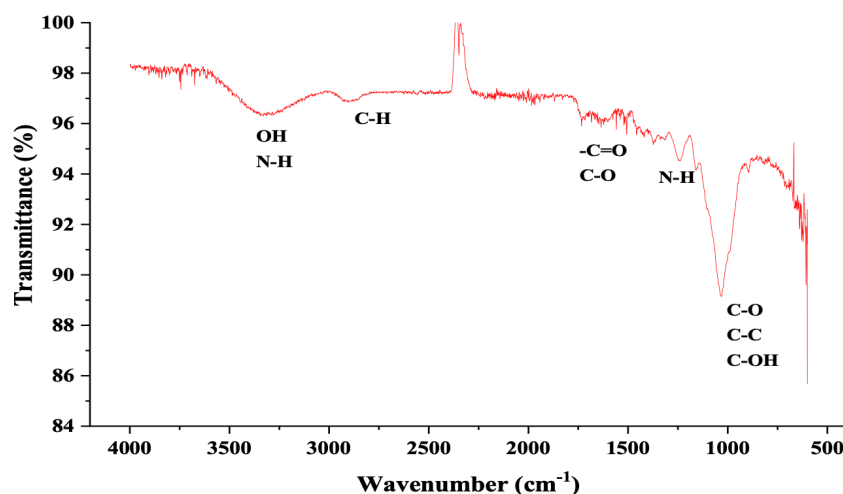


Fig. 1. FTIR spectrum of the corn cob.

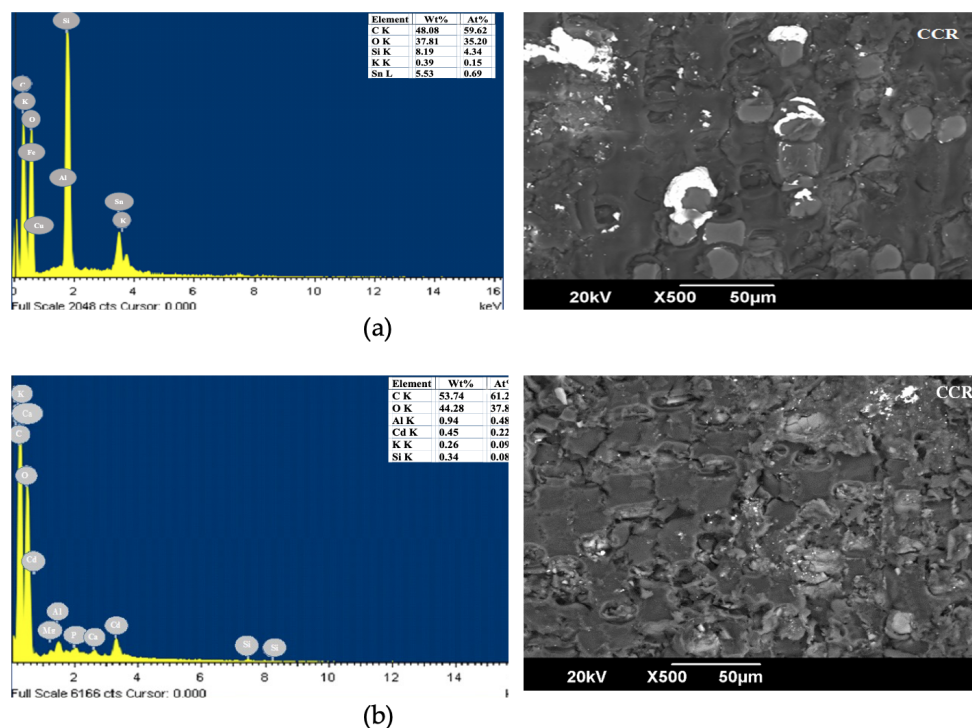


Fig. 2. EDS spectra and -SEM micrographs for corn cob: a) before and b) after adsorption.

It has been previously reported for corn residues that the presence of these absorbance peaks corresponds to esters, amines, hydroxyl, and alcoholic groups (Carreño-De León *et al.*, 2017). These are attributed to the majority presence of cellulose (13.08%), hemicellulose (6.47%) and lignin (6.51%) in the structure of the biomaterial (Herrera-Barros *et al.*, 2018).

Figure 2 shows the SEM-EDS analysis results before and after the adsorption of the Cd^{2+} ions, developed to identify the morphology and elemental composition of the biomaterial. As seen in the SEM micrograph, the corn residue exhibits a smooth, porous surface. Such molecules in the amorphous region have been reported to contain hydroxyl groups (Warui *et al.*, 2020). SEM micrographs before and after adsorption show luminous and non-luminous regions, which are attributed to organic minerals such as calcium, magnesium, and potassium in the biomass matrix (Deng *et al.*, 2018).

Furthermore, the EDS spectrum confirmed the presence of these characteristic peaks attributed to these elements; before adsorption, no signal was recorded for cadmium ions. Likewise, he showed that carbon and oxygen are the elements that most affect the composition of the bio-sorbent before ion removal as follows: C (48.08% w), O (35.2% w),

and Si (8, 19% by weight). The biomass showed the disappearance of Si at 1.9 keV and of K at 3.3 keV, with Cd's appearance near 2.8 keV. Likewise, the conservation of Ca in the 1.3 keV peak occurred in most cases. This fact is due to the conservation of the variation of the equivalent charges between Cd^{2+} and $\text{Ca}^{2+} / \text{K}^{+}$, so that the adsorption of Cd^{2+} is more competitive for the functional groups, resulting in the ion exchange process (Xia *et al.*, 2015). The increase in the atomic percentage of and P, Mg, Al, O and K in the surface structure of the biomaterial, after the adsorption of Cd^{2+} , illustrates that the formation of precipitation in the form of calcium sulphate and phosphate on the cell surface, which observed in SEM micrographs, it was another probable biosorption mechanism. The adsorption mechanisms of heavy metals in lignocellulosic biomass can include ion exchange, microprecipitation, complexation, and coordination due to functional groups such as hydroxyl, carboxyl, amides, and phenols in lignocellulosic materials (Basu *et al.*, 2017). In this work, the cation exchange mechanism and the microprecipitation mechanism were identified as crucial in the biosorption of Cd^{2+} by the evaluated bio-sorbent (Huang *et al.*, 2017; Mahdi *et al.*, 2018).

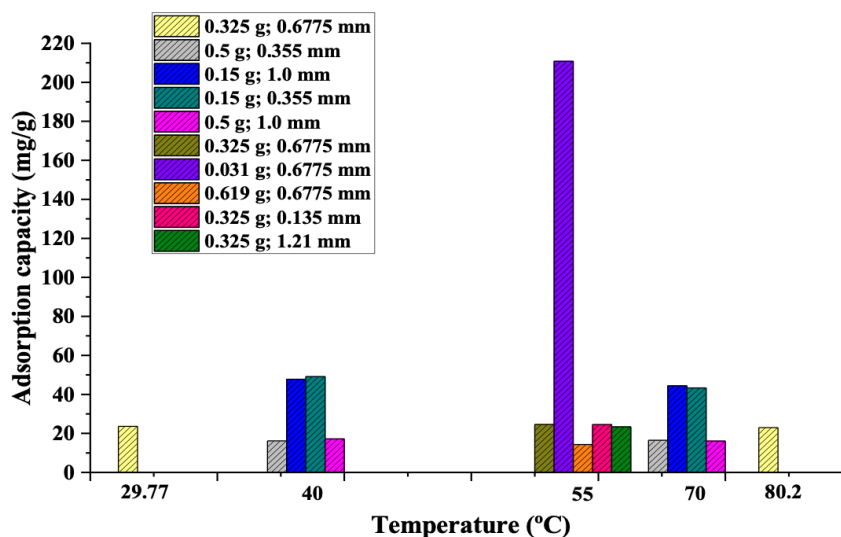


Fig. 3. Adsorption capacity of Cd (II) with corn cob.

3.2 Removal of Cd^{2+}

After carrying out the Cadmium(II) adsorption tests using corn cob, the effect of particle size, adsorbent dose and temperature was evaluated by calculating the Cadmium(II) adsorption capacity. Figure 3 shows the results of adsorption capacity and percentage removal at each of the conditions studied. A maximum adsorption capacity of 210.81 mg/g at 0.6775 mm, 0.031 g and 55 °C was obtained.

The effect of the particle size is shown in Figure 4; this is an important parameter in the adsorption, since the process occurs on the external surface of the adsorbent, where the functional groups are present which can be responsible for the adsorption (Haro *et al.*, 2016; Tejada-Tovar *et al.*, 2016). The best performance of the adsorbent was presented at the intermediate particle size evaluated (0.6775 mm), which can be explained due to the nature of the adsorbato-adsorbent interactions and the presence of functional groups containing oxygen on the surface of the biomaterial, since this determines the presence of active centers of biomass/ion exchange (Mahdi *et al.*, 2018). Previously, similar results were obtained when using foxtail millet shells (Peng *et al.*, 2018), ballota undulata biomass (Al-Shannag *et al.*, 2017) and activated carbons from coconut, walnut and almond (Ayub *et al.*, 2019), in the removal of Cd^{2+} ions.

The effect of the dose on the adsorption capacity of Cadmium (II) is shown in Figure 5; there is a

decrease in the adsorption capacity of the metal as the amount of adsorbent increases, which may be due to the low availability of ions, so the bio-adsorbent is not saturated, which is a result of the high availability of active sites in the bio-adsorbents by the presence of the hydroxyl, carbonyl, amine and unsaturated hydrocarbon groups characteristic of lignocellulosic materials, shown in Figure 1 (Mushtaq *et al.*, 2016). It was found that 0.5 mm particle diameter offers the best results, which is due to the interactions of sorbate-sorbent on the surface. This behaviour can be attributed to the relationship between the effective specific surface area of the adsorbent particles and the size of the particles (Al-Shannag *et al.*, 2017; Peng *et al.*, 2018).

Temperature is a significant physicochemical parameter as it changes the adsorption limit of the adsorbent. According to Figure 6, the adsorption capacity increases with increasing temperature up to 55 °C, and decreases from there to the maximum evaluated temperature, which is due to the interaction of adsorption-adsorbent bonding or the formation of new effective sites for adsorption (Hernández *et al.*, 2018). The decrease observed in the adsorption capacity with an increase in temperature, up to 55 °C, indicated that the low temperatures favour the elimination of Cadmium (II) ions, due to the tendency of the ions to escape from the solid phase to the mass phase with an increase in the temperature of the solutions, this suggests that the process is endothermic (Medellín-Castillo *et al.*, 2017).

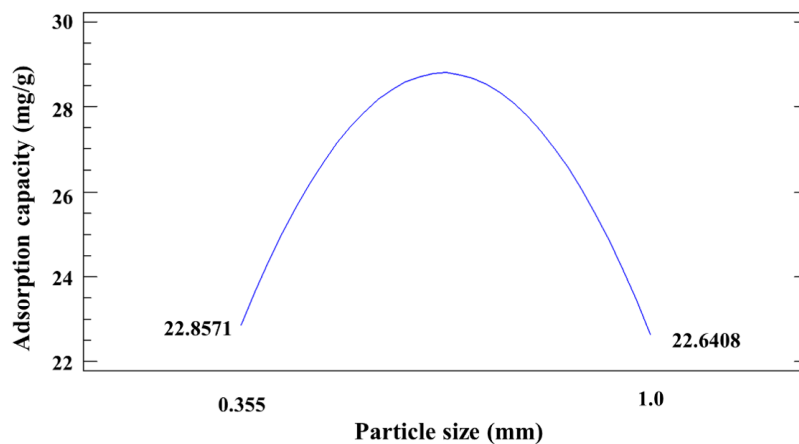


Fig. 4. Effect of particle size on Cd (II) adsorption.

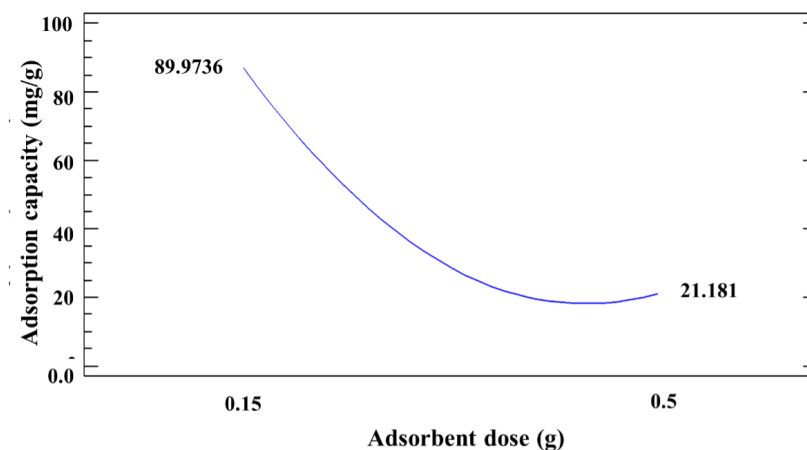


Fig. 5. Effect of adsorbent dose on Cd (II) adsorption.

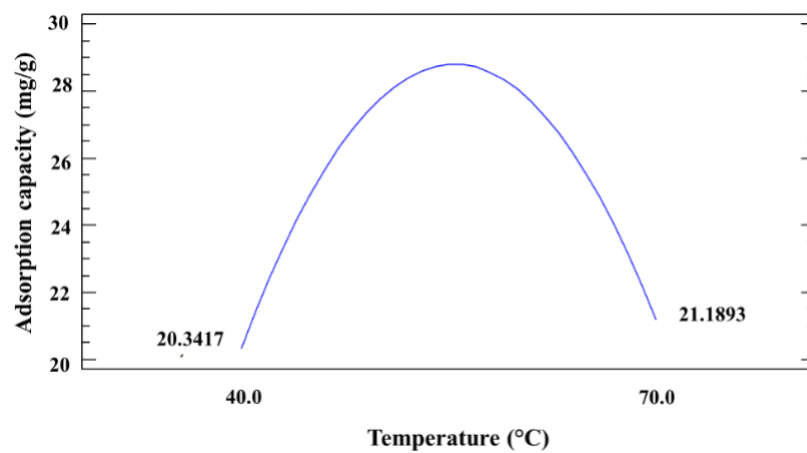


Fig. 6. Temperature effect on Cd (II) adsorption with corn cob.

Table 4. Analysis of Variance for adsorption capacity with corn cobs.

Source	Sum of Squares	GI	Medium Square	F-Ration	P-value
Cd (II) Model	3031.58	15	202.105	28.13	0.0071
A:Temperature	2.45	1	2.45	0	0.97
B:Adsorbent Dose	14779	1	14779	9.39	0.028
C:Particle size	0.16	1	0.16	0	0.9924
AA	391.19	1	391.19	0.25	0.6393
AB	8.86	1	8.86	0.01	0.9431
AC	0.12	1	0.12	0	0.9934
BB	3865.94	1	3865.94	2.46	0.1779
BC	0.1	1	0.1	0	0.9939
CC	221.98	1	221.98	0.14	0.7227
Total error	7871.88	5	1574.38		
Total (corr.)	33948.6	14			

An endothermic process assumes an energetic need to supply and increase the electrostatic interaction forces between the active centres of the material and the ions (Guedidi *et al.*, 2017). The favourable effect of temperature on Cadmium(II) adsorption may be due to the increased ionization of the lignocellulosic components. They act as adsorption sites, thus promoting the increased rate of diffusion of the cation through the outer boundary layer into the pores (Mushtaq *et al.*, 2016; Renugadevi *et al.*, 2009). The reduction in adsorption capacity at temperatures > 55 °C is attributed to the tendency of the process to desorb due to the addition of unnecessary heat to the system. Thus, more cadmium ions escape from the solid phase, according to what was reported by Cheriak & Louhab (2018) and Naseem *et al.* (2019). It has been found that at high temperature, the thickness of the boundary layer decreases due to the expanded inclination of the metallic particle to escape from the surface of the biomass to the disposition stage, which causes a decrease in adsorption as the temperature increases (Akinyeye *et al.*, 2020). Increasing the temperature can reduce the adsorption powers between the adsorbate and the adsorption destinations on the biomass surface, causing a reduction in the adsorption limit. This phenomenon is observed in the results presented in this study, as well as in others when using various biomasses such as bamboo stems (Akinyeye *et al.*, 2020), microalgae *Parachlorella* sp. (Dirbaz & Roosta, 2018), and *Aphanothece* sp. (Satya *et al.*,

2020) for the Cd⁺² removal. Comparing this finding with previous publications for the removal of heavy metal ions using biomasses such as the selected in this work. At pH 6, the same evaluated in the present investigation, were reached adsorptions capacities of 17.7 mg/g using oil palm residual biomass (A. Herrera-Barros *et al.*, 2020), 14.77 mg/g with cork biomass (Krika *et al.*, 2016), and 21.28 mg/g over rice husk (Kumar *et al.*, 2010). The capacities reached in this work are within the range observed for lignocellulosic biomasses under similar conditions of temperature and pH.

Analysis of variance (ANOVA) was performed for the independent variables and their effect on adsorption capacity (Table 4); the dose of adsorbent was found to have a P-value less than 0.05, indicating that they are significantly different from zero at a 95.0% confidence level; as is summarized in the Pareto diagram (Figure 7), which shows that the lower dose of adsorbent favoured the adsorption process, and that temperature and particle size had little influence on the process. The R² statistic indicates that the model explained 76.81% of the variability in percentage of removal. Regarding the percentage of Cadmium(II) removal, from Table 4, it can be seen that the F-value of the model is 28.13 and the P-value of 0.071, which means that the model is statistically significant (Equation 1). None of the model's terms were significant.

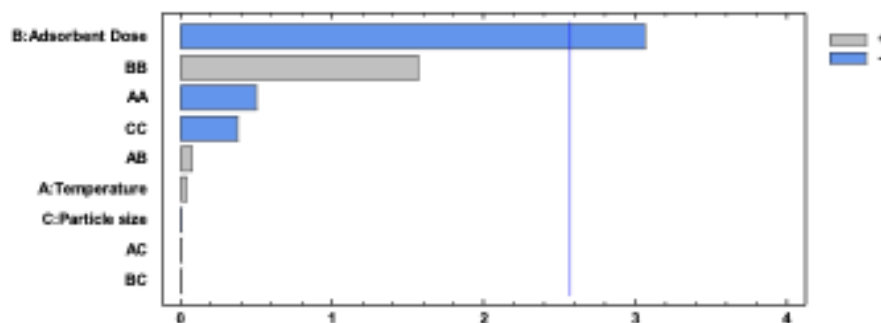


Fig. 7. Pareto diagram for Cd adsorption capacity (II).

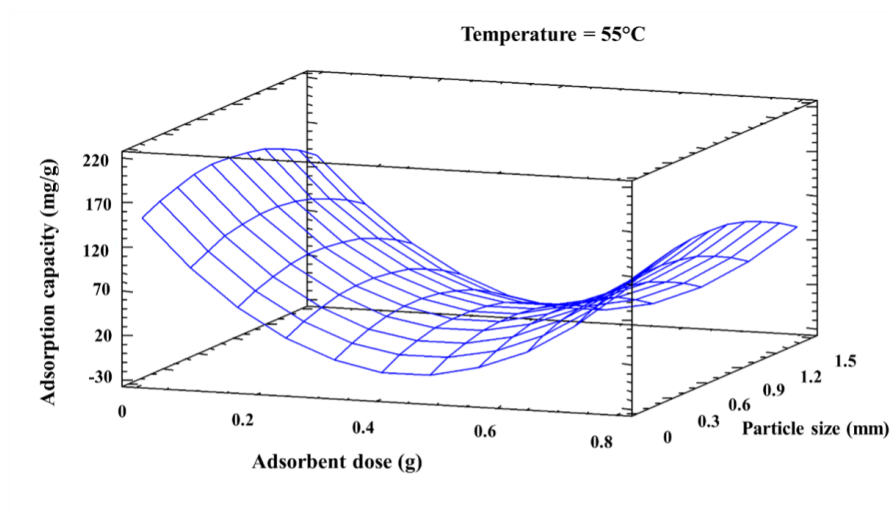


Fig. 8. Surface response for Cadmium adsorption.

Using the Response Surface Method (Figure 8) in order to predict the response of the process, shows the regression equation that fits the experimental data of Cadmium(II) removal on corn cob. This equation showed a fit of more than 85%. From the statistical results obtained, it can be seen that the model was adequate to predict the removal of Cadmium(II) within the range of the variables studied. A correlation coefficient between the real data and those predicted by the model of 99.26%.

$$q_t = 49.4755 + 39.81 * T - 747.77 * D + 76.5197P - 0.0357 * T^2 + 0.4 * T * D + 0.025 * T * P + 825.224 * D^2 + 1.99 * D * P - 58.2255 * P^2 \quad (1)$$

where q_t is the adsorption capacity (mg), D the adsorbent dose (g), T the temperature ($^{\circ}\text{C}$) and P the particle size (mm).

3.3 Modelling of adsorption kinetics

Figure 9 shows the fit of the experimental data to the Pseudo-First Order, Pseudo-Second Order and Elovich kinetic models, in order to identify the mechanisms controlling the process of removal of Cadmium(II) from corn cob. Rapid adsorption was obtained in the first 60 min, which is due to the availability of large sorption sites during the initial period (Villabona-Ortíz *et al.*, 2020), and balance was reached after 120 minutes.

The results of the adsorption of Cd^{2+} by corn cob, it can be established that the adsorption capacity of the metal on the biomass is dependent on the contact time, with a high speed in the initial minutes of contact; removal of $> 90\%$ of the metal was achieved in the first 30 min. Likewise, the trend suggests that this ion's union may be through interactions with functional groups such as the carboxyl or hydroxyl groups located on the surface of the biomass, according to what is presented in Figure 1.

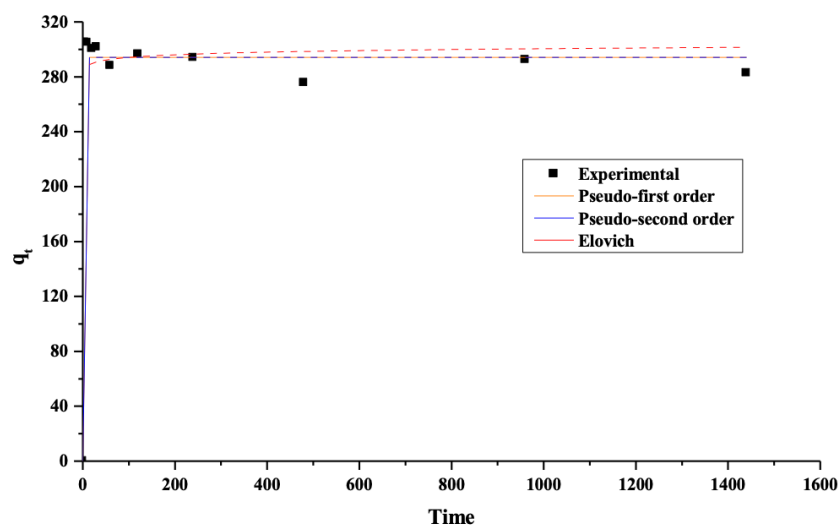


Fig. 9. Non-linear adjustment the adsorption kinetics of Cd (II) to the kinetic models.

Table 5. Adjustment parameter of Cd (II) kinetic adsorption.

Kinetic model	Parameter	Corn cob
Pseudo-First Order	k_e	443.1831
	q_e	294.0682
	SS	3.02
	R^2	0.98
Pseudo-Second Order	k_e	2.05×10^{15}
	q_e	294.0682
	SS	5.08
	R^2	0.98
Elovich's Equation	α	0.3624
	β	5.44×10^{44}
	SS	6.89
	R^2	0.97

The positive effect of increasing the contact time on the metal ion adsorption capacity has been reported using different biomasses, such as blue agave in lead adsorption (Romero-González *et al.*, 2007), Chromium on banana residues and oil palm bagasse (Villabona-Ortíz *et al.*, 2020) and copper on chitosan-cellulose cryogel (García-González *et al.*, 2016).

From the fit shown in Figure 9 and the parameters in Table 5, it was evident that the models evaluated satisfactorily predict the fit of Cadmium (II) kinetics on corn cob, with the Pseudo-Second Order model being the one that best describes the process. Therefore, it can be said that the limiting step of

Cadmium (II) removal on the bio-sorbent under study is the chemical reaction between the ion and the active centres of the material (Krika *et al.*, 2016; Obike *et al.*, 2018). It could be said, the process happens by chemisorption in the system, in which the adsorption rate is limited by valence forces given by the exchange of electrons between the adsorbate and the adsorbent due to the non-homogeneous surface of the solid (Castro *et al.*, 2018; Obike *et al.*, 2018; Villabona-Ortíz *et al.*, 2020).

3.4 Adsorption isotherm

Adsorption isotherms are determined in order to establish the relationship between the initial solute concentration and the nature of the interaction forces between the adsorbate and the adsorbent, at constant temperature. The equilibrium data of Cadmium (II) adsorption on corn cobs were adjusted to the better conditions found in Langmuir and Freundlich's models (Figure 10); the adjustment parameters are presented in Table 6.

As can be seen, the model that best describes the isotherm is that of Langmuir, which suggests that adsorption occurs on a homogeneous surface by monolayer (Mutongo *et al.*, 2014). This means that there are individual fixed sites and that each one also adsorbs only one Cadmium (II) molecule. Furthermore, the model assumes uniform energies of adsorption on the surface and no transmigration of the adsorbate (Leizou *et al.*, 2018).

Table 7. Summary of biomasses used in cadmium ions adsorption.

Biomass	Experimental conditions	Q_{max} (mg/g)	Reference
Powdered activated carbon from palmae	pH= 6; 40 g/L of bio-adsorbent, at 25 °C	9.98	(Egirani <i>et al.</i> , 2020)
Granular activated carbon from palmae		9.96	
Corn cob modified with alumina nanoparticles	pH= 6; particle size 0.5 mm, 5 g/L of adsorbent at 25 °C	3.2	(A Herrera-Barros <i>et al.</i> , 2018)
Bamboo stem powder	pH= 5; 0.1 g/L of adsorbent at 25 °C	12.34	(Akinyeye <i>et al.</i> , 2020)
Aphanothece sp. enriched with CO ₂	pH= 8; 0.1 g/L of adsorbent at 30 °C	60.24	(Satya <i>et al.</i> , 2020)
Litchi peel	pH=5; particle size 43 μ m; 25 °C	18.87	(Ansari <i>et al.</i> , 2020)
Corn cob	pH=6; particle size=0.6775; 3.3 g/L of adsorbent at 55 °C	541.51	Present study

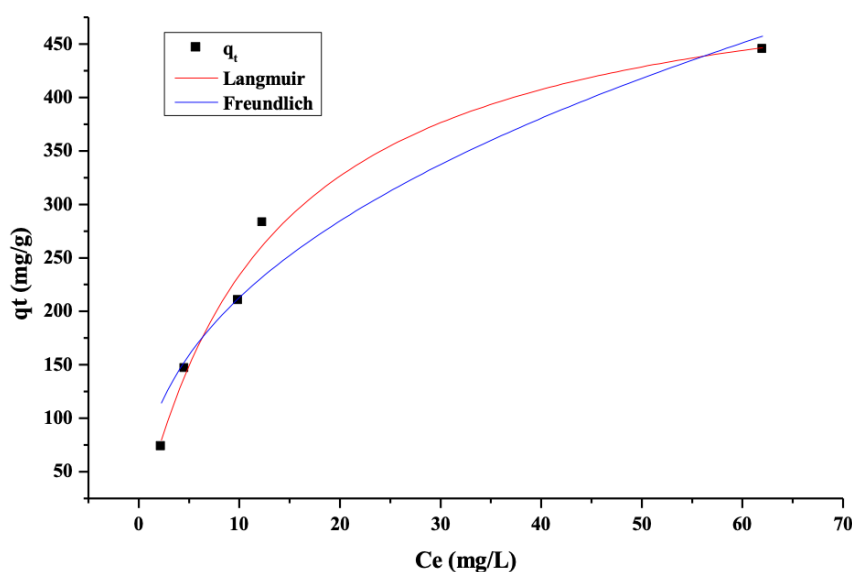


Fig. 10. Adjusting the adsorption balance to the Langmuir and Freundlich isothermal models.

The trend of parameter b to zero indicates that active adsorption sites in the fungal biomass are equivalent and that the ability of metals to bind to the surface is independent of the existence or non-existence of nearby occupied positions (E. Asuquo *et al.*, 2017; Obike *et al.*, 2018). It has been reported that the presence of OH, COOH and amines groups contribute to the metal ion uptake process in the lignocellulosic matrix of bio-adsorbents, which

favours interaction with the active centres due to their anionic nature (Herrera *et al.*, 2020). In the adsorption of Cd^{+2} on cocoa mesocarp, it was found that the functional groups involved in the removal process were those that have Oxygen in their structure, such as ethers (aromatic, olefinic or aliphatic), esters, amines, hydroxyl, and aliphatic hydrocarbons (Herrera-Barros *et al.*, 2020).

The adsorption process is controlled by different mechanisms and is attributed to intervening factors such as particle size, pH, temperature, initial concentration of the adsorbate, is highly dependent on the nature of sorbate-sorbent interactions and the presence of functional groups on the surface of the adsorbent (Neris *et al.*, 2019). Surface complexation, ion exchange, electrostatic attraction, hydrogen bridges, among others, are mechanisms that often control the process and depend on the presence of functional groups on the surface of the biomass such as OH, COOH, CO, CH, which are present on the surface of the corn cob due to its high lignocellulosic content and its shown at Figure 1 (Asuquo & Martin, 2016). The presence of lignin in corn cob enhances the presence of carboxylic acids in its structure, which are active centres of ion exchange that promote metal removal (Núñez-Zarur *et al.*, 2018). Similarly, the presence of Silicon, Calcium and Magnesium in the bio-adsorbent, promotes cationic exchange with Cadmium (II) (Dai *et al.*, 2018; Pardavé-Livia *et al.*, 2020).

In Table 7, results of the Langmuir Q_{max} parameter obtained previously for different biomasses of lignocellulosic origin are summarized. It is observed that, under the conditions evaluated in the different studies, the corn biomass presented excellent results, which is an advantage, since its high cadmium removal capacity contributes to the remediation of water and the mitigation of the impacts caused by pollution from poor disposal of these post-harvest residues.

Conclusions

The FTIR analysis showed the presence of OH groups, COOH, tertiary amines and methyl, which are functional groups present on the surface of the material. An adsorption capacity of 210 mg/g at 55 °C, 0.031 g and 0.6775 mm was achieved, with the dose of adsorbent being the most statistically influential factor in the process. ANOVA showed the dose of adsorbent had a P-value less than 0.05, indicating that they are significantly different from zero at a 95.0% confidence level. The Pareto diagram revealed that the lower dose of adsorbent favoured the adsorption process and that temperature and particle size had little influence on the process. The adsorption kinetics was adjusted by the Pseudo-Second Order model, reaching a steady state at about 120 min, and the isotherm was described by

the Langmuir model, so the process is controlled by chemical adsorption and occurs in a single layer over the adsorbent. Corn cob is presented as an effective Cadmium (II) adsorbent in aqueous solution.

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Nomenclature

q_t	Adsorption capacity in a time t
q_e	Adsorption capacity at equilibrium
k_1	Lagergren constant
α	initial adsorption rate
β	Constant related to surface coverage and chemisorption energy
Q_{max}	Maximum pollutant adsorption, corresponding to the active centres
k_2	pseudo-second order constant
b	relationship between adsorption/desorption rates
k_f	Freundlich constant
n	represents the intensity of adsorption
C_e	Residual metal concentration in solution
rpm	Revolutions per minute
k_3	First-order constant of the mixed-order model (min ⁻¹)
k_4	Second-order constant of the mixed-order model (g ⁻¹ *min ⁻¹)
n	nth order rate constant (gn ⁻¹ *mg ¹⁻ⁿ *min ⁻¹)
k_n	The relationship of q_t y q_∞
k_∞	Reaction rate constant (min ⁻¹)
m_s	Mass of adsorbent per unit volume of solution (g/L)
k_{FS}	Mass transfer coefficient between the bulk liquid and the surface of the adsorbent (cm/h)
S	Outer surface of adsorbent per unit volume (cm ⁻¹)
C_0	Initial adsorbate concentration (mg/L)
K	Partition coefficient of the linear model (L/g)
K_{HE}	Henry's isotherm model adsorption constant
q_s	Theoretical isotherm saturation capacity (mg/g)

g	Redlich-Peterson exponent that lies between 0 and 1
K_R	Redlich-Peterson isotherm constant (L/g)
K_{RD}	Reaction rate constant of Dubinin-Radushkevich
R	Universal gas constant (8.314J/mol K)
T	Temperature (K)
a_R	Redlich-Peterson isotherm constant (1/mg)
q_m	Capacity at monolayer coverage of the Baudu model (mg/g)
b_o	Baudu isotherm equilibrium constant
q_{mFS}	Fritz Schlunder maximum adsorption capacity (mg/g)
β	FS Fritz-Schlunder isotherm model parameter
α	FS Fritz-Schlunder isotherm model parameter
b_T	Temkin isotherm constant which is related to sorption heat (J/mol)

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