Journal of Physical Chemistry and Functional Materials (JPCFM)

journal homepage: http://dergipark.gov.tr/jphcfum

Received: 28 July 2018 Accepted: 1 August 2018 Research Article

Investigation of the Availability of Apricot Shell in Adsorption Equilibrium Studies

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Abstract

In this study, adsorption of Cu^{+2}ions from aqueous solution onto apricot stone shell as investigated. First the physicaland chemical characterization of apricot shell was performed, and then the effect of some working conditions on bisorbtion yield was investigated. The fit of the equilibrium results to the adsorption isotherms of Langmuir, Freundlichand Dubinin–Radushkevich (D–R) to data was examined, and it was determined that the best fitted model is Langmuir isotherm.

Key Words: Adsorption, isotherm model, apricot shell.

1.Introduction

The pollution of the environment by heavy metal ions is a serious problem because of their toxic effects on human health and living organisms. Heavy metals do not degrade into harmless product and tend to accumulate in living organisms, causing various diseases and disorders, even theypresentin verylow concentrations. Heavymetals in wastewatershaverisentotoxiclevelsin some regions because of thehumanandindustrialactivities. Mine drainage, metal industries, petroleumrefining, tanning, photographicprocessingandelectroplatingaresome ofthe main industrialsources of heavy metals [1]. Adsorption using naturel adsorbents, which can remove heavy metals from waste water, is an effective purification and separation technique used in industry,especially in water and waste water treatments

In this study, biosorption of Cu^{+2}on apricot stone shell (ASS) was studied in a batch system. The effects of changes in parameters such as time, concentration, temperature, biosorbent amount on the biosorptionperformance were investigated. The fit of the experimental data to Langmuir, Freundlich and Dubinin and Radushkevich(D-R) isotherm models was then examined.

1.1. Adsorption isotherms

Adsorbtion isotherms show the data of the amount adsorbed on the surfaceversus remaining amount in the solution for a given substance in equilibrium at a fixed temperature, and therefore they are called isotherms. The most frequently encountered adsorption isotherm models in adsorption processes are Langmuir, Freundlich and Dubinin-Raduskevichmodels.

Langmuir isotherm describes the formation of a monolayer adsorption with physical interaction, which can be represented by the following equation.

(2)

where C_e is the equilibrium concentration (mg·L^{-1}), $q_e$the amount adsorbed at equilibrium (mg·g^{-1}), $Q_0$the Langmuir constant related to adsorption capacity (mg·g^{-1}), and b the Langmuir constant related to the energy of adsorption (L·mg^{-1}).

Freundlich isotherm model is normally used to describe multilayer adsorption occurring on heterogeneous surfaces of adsorbents.This is used to describe the chemical and physical adsorption that is represented by the following equations[3].

$$\ln q_e = \ln k_f + \left(\frac{1}{n}\right) \ln C_e \quad (3)$$

wherek_f is a constant for the system related to the bonding energy. The 1/n value indicates the relative distribution of high-energy sites and depends on the nature and strength of the adsorption process.

Dubinin and Radushkevich (1947) developed an adsorption isotherm, which is alsocalled D-R isotherm. This isotherm is more general than Langmuir and Freundlich equations.D-R equality[4];

$$\ln q_e = \ln q_s - k_{ad}\varepsilon^2 \quad (4)$$

$$\varepsilon = [RT\left(\ln \frac{1}{C_e} + 1\right)] \quad (5)$$

whereq_s(mg/g) and k_{ad} (mol^2/ kJ^2) are D-R constants.

2. Materials and Methods

2.1. Preparation of bio-adsorbent

As bio-sorbent, the stone shells of the apricot fruit grown for commercial purposes in Malatya province of Eastern Anatolia were employed. Bio-adsorbent was washed, dried and then ground. The particle size range was 0125-0,106 mm.

2.2. Biosorption Experiments

Cu^{+2} solutions were prepared in distilled water at desired concentrations. The bio-sorption experiments were carried out by adding 0.2 g of ASS into 50 mL solution prepared at a desired concentration at the temperatures of 298 K, 313 K , 323 K and 333 K in a thermostatic bath operating at 400 rpm. The amount of Cu^{+2} adsorbed onto AS, q_t ($mg \cdot g^{-1}$), was calculated by the mass balance relation represented by Equation (1) as follows:

$$q_t = \frac{C_0 - C_t}{W} V \quad (1)$$

For the analysis of bio-adsorbate, anRigakuGeigerflex D/MaxB-made XRD, a SEM device made by LECO CHNS-932 and Mattson 1000 FTIR device were employed, and the elemental analysis was performed with LECO CHNS-932 device. The temperature was kept constant by a constant temperature bath. The ion analysis was carried out by a Consort made pH/ion meter.

3.Results and Discussion

3.1. Structural Characterization of Apricot Stone Shell

Theanalysis results of SEM, XRD, FTIR of ASS are given in Fig.1-3.When the figure of SEM is scrutinized, it seems to be dominated by microporosity.

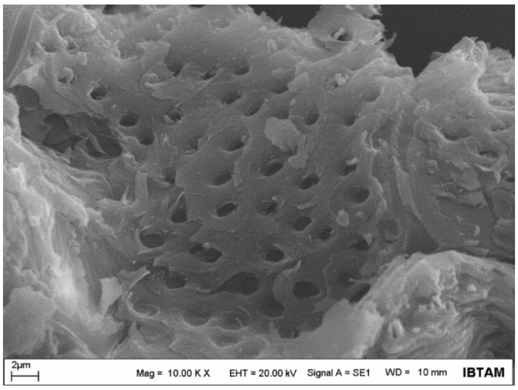

Figure1.SEM Analysis

According to XRD analysis shown in Figure 2, the apricot stone shell has anamorphous structure.

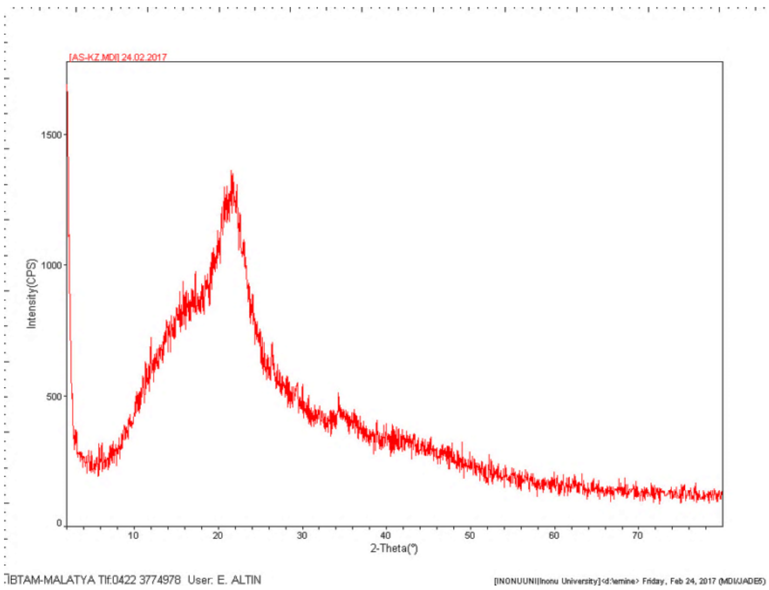

Figure2. XRD Analysis

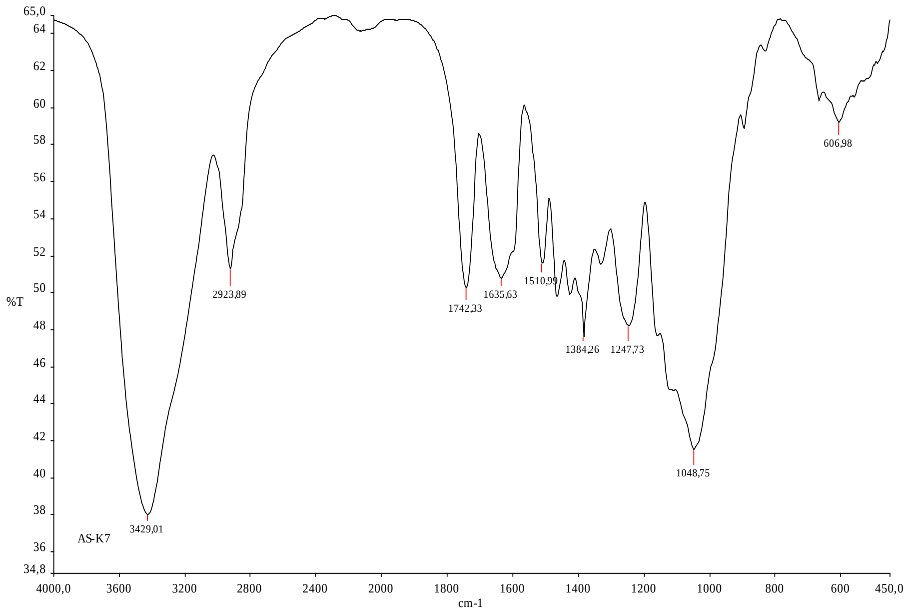

Figure3.FTIR Analysis

FT-IR analysis has an important place in the study of spectrum in complex molecules. When FTIR analysis given in Figure 3 is examined, it seen that it shows the peak of aliphatic group around 2900-3100 cm^{1}.Aromatic hydrocarbon peaks are around 1500-1635 cm^{-1}, and the peak of aldehyde ketone group is around 1700 cm^{-1}.

3.2. Effect of Adsorption Parameters

3.2.1. Equilibrium time

Before carrying out equilibrium measurements, some experiments were performed to determine the equilibrium time. The experiment performed at 298 K and 333 K given in Figure 3 showed that the system reached at equilibrium at about 60 minutes.

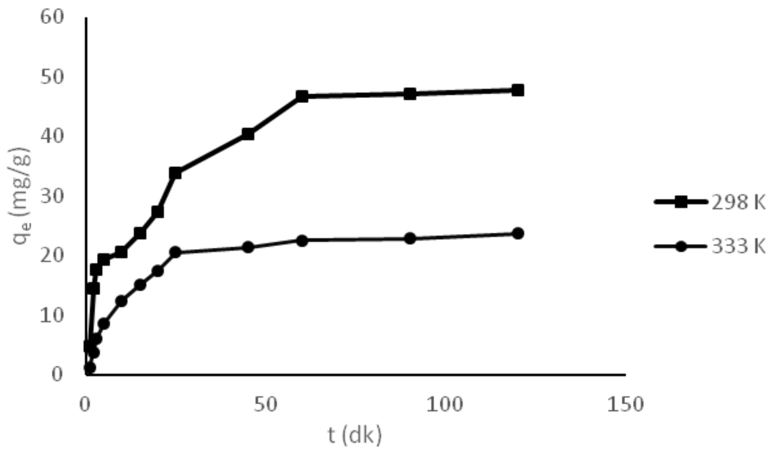

Figure 4. Equilibrium time experiments.

3.2.1. Effect of biosorbent dose

The effect of adsorbent dose on Cu^{+2} biosorption from the aqueous solutions by ASS is shown in Figure 5 as seen from the figure, the biosorption increases rapidly when biosorbent dosage increased from 0.05 g to 0.2 g,and then it exhibits a slow increase.

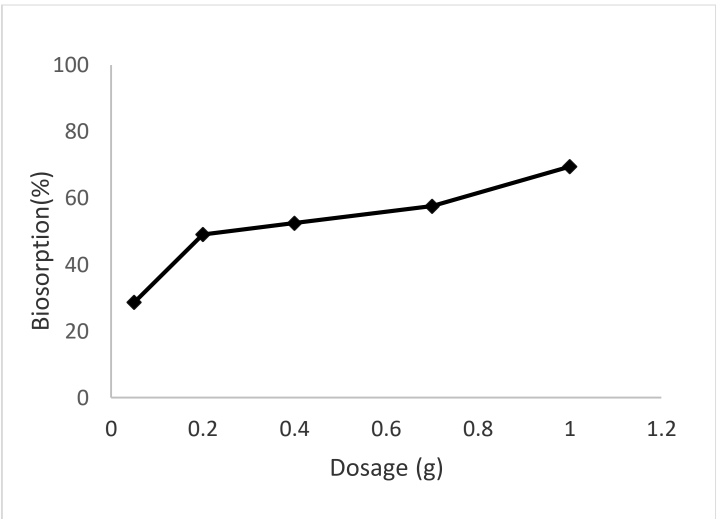

Figure 5. Effect of biosorbent dose.

3.2.3. Effect of initial concentration and temperature of Cu^{+2}

The effect of initial concentration of Cu^{+2} on its removal from the aqueous solutions by ASSis shown in Figure 6. It was found that the removal percentage of Cu^{+2}ions decreases with increasing initial Cu^{+2}concentration for a given amount of biosorbent. This shows that increasing initial Cu^{+2} concentration reduces the biosorptiondue to the diminishing of surface area per amount of initial Cu^{+2} ionpresent.

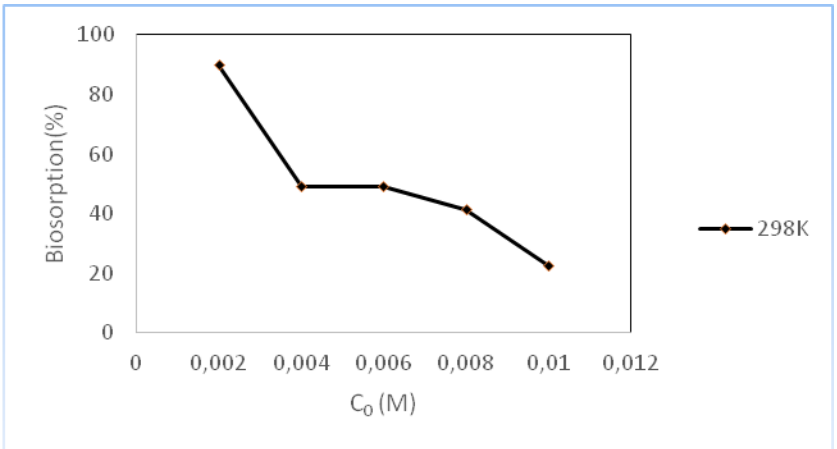

Figure6. Effect of initial concentration of Cu^{+2}

3.3. Analysis of Adsorption Equilibrium Data

To find the best fitting isotherm model to the experimental data, the istatistical and graphical analysis were performed for the Langmuir, Freundlich and D-R adsorption isotherms of Cu^{+2} ions at 298, 313, 323, and 333K. All the parameters of the isotherm model for the adsorption of Cu^{+2} ions onto ASS are illustrated in Table 1. As seen from this table, the adsorption of Cu^{+2} ions onto ASS fits best to the Langmuir isotherm model with R^2 values between 0.913- 0.948. The graph of the experimental results for Langmuir isotherm is given in Figure 7.

Table 1. Results of analysis of experimental data for fitting to someisotherm models.

Isotherm	Ads. and Statistical Constants	Temperature (K)			
		298	313	323	333
Langmuir	Q_0(mg/g) b (L/mg) R^2	43,8590 0,1272 0,9488	37,8787 0,1312 0,9194	37,8787 0,1682 0,9130	36,4963 0,0070 0,9513
Freundlich	n (g/L) K_f (L/g) R^2	7,0422 19,2401 0,5811	4,6794 11,2424 0,5759	2,4697 3,1695 0,7363	2,3369 2,1917 0,9018

D-R	q_m(mol/g)	9,19x10^{-4}	9,861x10^{-4}	1,407x10^{-3}	1,195x10^{-3}
	K_{ad}(mol^2/kj^2)	0,0010	0,0025	0,0049	0,0052
	E_a (kJ/mol)	22,3600	14,1420	10,1010	9,8050
	R^2	0,5761	0,5924	0,7751	0,9115

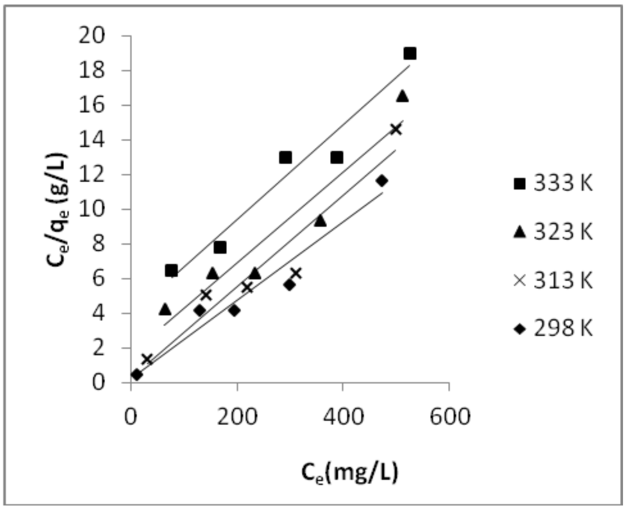

Figure7. Fitting of experimental results to Langmuir Isotherm

4. Conclusion

In this study, biosorption of Cu^{+2} on apricot stone shell was studied at different working conditions. The surface properties of the biosorbent used were characterized by XRD, SEM and FTIR analyses. It has been determined that ASS has a porous character and an amorphous structure, and it contains various functional groups playing role in biosorption process. It was found that increasing particle size, temperature, initial Cu^{+2} concentration decreased biosorption yield while increasing biosorbent dose enhanced the yield of the process. Biosorption experiments were evaluated by taking account three isotherm models, and it was found that the experimental results fitted best to the Langmuir isotherm.

Acknowledgements: This work was supported by İnönü University Scientific Research Coordination Unit, with Project Number: FYL-2017-685

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