

Kinetic and Isotherm Studies of Copper Removal by dicalcium phosphate dihydrate

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Abstract— Adsorption of Cu (II) ions by the dicalcium phosphate dihydrate (DCPD) from dilute aqueous solutions was studied. This adsorption is influenced by many physico-chemical parameters like contact time, pH and the initial concentration of the metal ion. The kinetics shows that the extraction equilibrium is fast, it is reached after 45 mn when over than 34% of metal is extracted. The amount of metal adsorbed per unit mass of the support increases with increasing pH of the metal solution and decreases by increasing the initial concentration of Cu^{2+} ions in the supernatant solution. The kinetics data was analyzed with various kinetic models. It was found that the pseudo-second order model using the linear regression method predicted best the experimental data. Furthermore, the adsorption process was modeled by Langmuir isotherm and the removal capacity was 47.61 mg/g. Indeed, the separation factor value ($R_L < 1$) indicates that the adsorption of copper on DCPD is favorable.

Index Terms— water treatment, copper (II), adsorption, liquid-solid extraction, dicalcium phosphate dihydrate .

1 INTRODUCTION

WATER contamination by metallic pollutants is one of the major environmental concerns for many years because their non-biodegradability and their bioaccumulation in organisms may produce undesirable effects on health and ecological environment. The presence of toxic heavy metals in water is mainly rising from mining, metallurgy, abandoned disposal sites and fertilizer industries. Like other metallic ions, copper is included in this class of pollutants even in low concentrations. Its excessive indigestion may cause serious toxicological problems, such as vomiting, cramps, convulsions or even death [1]. International regulations impose a limit content of 1 mg/l of copper [2]. Various treatment technologies for the removal of heavy metals ions from wastewater have been used, including chemical precipitation, filtration, coagulation-flocculation and electroflotation[3]. All these techniques have their inherent advantages and limitations in application. However, in the last decades the adsorption/desorption as much as the ion-exchange processes have received much attention. Activated carbon is the most widely known adsorbent because of its extensive porosity and large surface area. However, due to its high cost, many researchers have focused on cheaper alternates and available adsorbents, such as agricultural by-products, biomass, chitosan, natural zeolite, clay and others [4]. In recent years, the use of phosphate materials such as fixing agents has grown considerably, mainly because of their high capacity to fix a large number of metal ions (Pb^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Sr^{2+} , Cr^{3+} , As^{5+} ...) when they are placed in contact with aqueous solutions [5-8]. Hydroxyapatite is among the heavy metal adsorbents most recently studied, as evidenced by the numerous publications on this subject [9-17]. The present work is to study the adsorption performance of copper on dicalcium phosphate dihydrate.

2. EXPERIMENTAL

2.1 Material Used

Dicalcium phosphate dihydrated $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (DCPD), used as extractant matrix of Cu^{2+} ion was synthesized at the

Laboratory of Electrochemistry and Surface Treatment of the Faculty of Sciences of El Jadida (Morocco). It is in the form of white powder. This ligand has several advantages over other products conventionally used for the extraction of metals:

- It is inexpensive and easy to prepare
- Its extraction implementation is easy
- It has a high chemical stability in a wide pH range.

The quantity of powder placed in contact with the metal solution is selected to have an excess of ligand relative to the metal (DCPD mole / mole metal = 5).

2.2 Preparation of the Aqueous Phase

Copper solutions were prepared. The stock solution to 1000 mg/l is prepared by dissolving 2.1181g of copper chloride (CuCl_2) in 1000 ml of distilled water. The lower concentration of solution is obtained by dilution, pH is adjusted with hydrochloric acid 0.2 N.

2.3 Experimental Protocol

The extraction experiments were performed in a glass cell double walled thermostated at $(25 \pm 0.2)^\circ\text{C}$ and capacity equal to about 150 ml. The cell is provided with a control thermometer with a combined glass electrode and a magnetic stirrer. An amount of 6.9 mg of DCPD support is placed in contact with 100 ml of an aqueous copper solution of concentration and pH known. The amount of the adsorbent matrix was been previously introduced in a bag of dimensions 3cm x 2cm, obtained from filter paper, closed with a wire for his suspension in the solution. This technique has two advantages:

- Avoid crushing grains of DCPD by the magnetic bar during agitation system which has the effect of increasing the exchange surface between the solid phase and the metal solution.
- Make withdrawals, versus time, in the metal solution, without risk of training of the grains of the support (medium) in samples to be measured.

In the case where the support is put directly in contact with the metal solution, stirring is carried over, using a Heidolph RZR engine 2000. When the extraction equilibrium is reached,

the loaded support of metal is separated from the supernatant solution by filtration.

2.4 Instrumentation

The copper in solution was assayed by flame atomic absorption (air / acetylene) at 324.8 nm on a type of spectrometer Unicam 929 AA spectrometer. Calibration of the spectrometer was carried out using metal standard solutions. The calibration range varies between 0.5 ppm and 2 ppm. The correlation coefficient is 0.999.

The extraction yield is calculated by the following relationship:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100$$

C_0 : Represents the initial concentration of metal in aqueous solution

C_e : Represents the concentration of metal in aqueous solution to the extraction equilibrium

The amount of copper adsorbed per unit mass of support (DCPD) q (mg/g) is determined by the following literal expression:

$$q = \frac{C_0 - C_e}{m} \times V$$

C_0 : Initial concentration (ppm).

C_e : equilibrium concentration (ppm).

m : The mass of adsorbent (DCPD) (g).

V : Volume of the solution (l).

3. RESULTS AND DISCUSSION

3.1 Effect of Contact Time on the Adsorption of Copper on the DCPD

The study was carried out by putting in contact a quantity of 6.9 mg of support with 100 ml of copper solution of concentration 10^{-4} M and pH equal to 6, at 25 °C. Samples were made over time in the supernatant solution. Figure 1 shows the simultaneous variations of the copper concentration and the adsorption capacity of the support as a function of contact time. The results obtained show that the amount of metal adsorbed per unit mass of support increases rapidly with increasing contact time, the extraction equilibrium is reached after 45 min of stirring system, indicating that adsorption of copper on the DCPD is rapid for $t < 45$ min. For $t > 45$ min results in a level corresponding to the adsorption equilibrium where q_t adsorption capacity equal to 28.71 mg /g, and the extraction yield is about 34%.

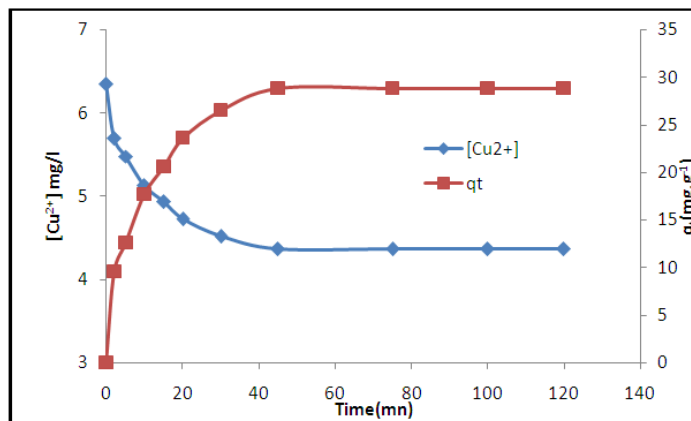


Fig.1. Influence of the contact time on the kinetics of adsorption of copper on DCPD

3.2 Effect of pH

To examine the effect of pH on the retention of copper by dicalcium phosphate dehydrate, we followed the evolution of the amount of metal adsorbed per unit mass of support as a function of initial pH imposed on the metal solution. Aqueous copper solutions were prepared by copper chloride solution in distilled water at a concentration of 10^{-4} M and at different pH values: 3.5; 4.0; 4.5; 5.0; 5.5; 6.0 and 6.5. In 100 ml of each of them, we have introduced a quantity of (DCPD) 6.9mg. Each solution is stirred for 2 hours, sufficient time to reach the equilibrium of extraction. The mixtures were filtered through a fritted glass of porosity 3. Then the samples were taken in each of the filtrate, diluted appropriately with distilled water and then assayed by flame atomic absorption. The results obtained are the subject of Figure 2.

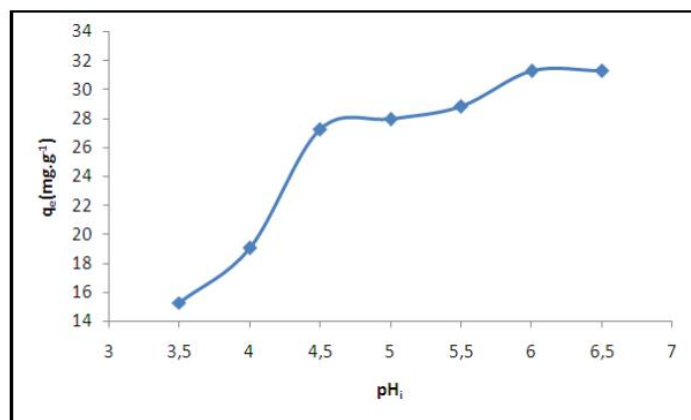


Fig.2. Effect of pH on the adsorption of copper on DCPD

The analysis of these results shows that the amount of Cu (II) adsorbed on dicalcium phosphate dihydrate increases with increasing pH. A very acidic pH the elimination of Cu (II) is very low, this result can be explained by a competition between the copper ions and protons H⁺ in favor of the hydronium cations. At pH less acid the amount of Cu (II) removed from the solution increases rapidly and reaches a maximum at pH equal to 6 where $q_{max} = 31.30$ mg/g. This may be due to the decrease of the concentration of H⁺ ions, which promotes

the adsorption of the Cu (II) on the negative surface of the adsorbent used.

3.4. Effect of the Initial Concentration

To study the effect of the initial concentration of copper on the adsorption of copper Cu (II) by the DCPD, we adopted the same experimental protocol described above, but this time by setting the pH and by varying the initial concentration of copper from 19.8 mg/l to 280 mg/l. The results obtained are illustrated in figure 3.

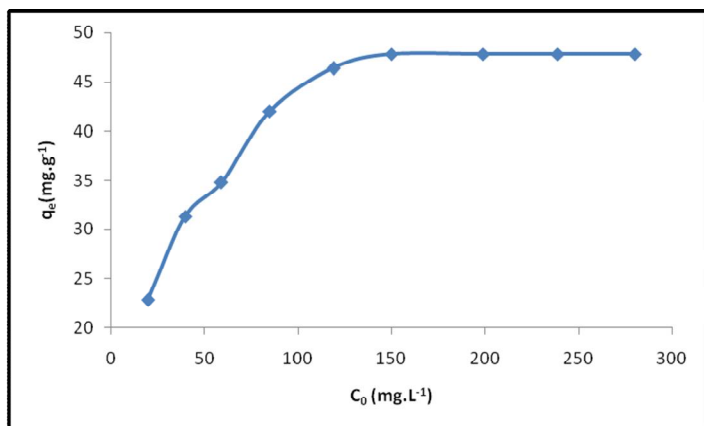


Fig.3. Effect of initial concentration on the adsorption of copper on DCPD.

Examination of these results shows that the amount of copper absorbed per unit mass of support increases with the increase of the initial concentration of copper, from a copper concentration of 150 mg/l is obtained a bearing correspond to the saturation of the support. The rapid step is probably due to the abundant availability of active sites on the material and the adsorption plateau indicating the complete occupancy of these sites.

4. MODELING ADSORPTION KINETICS

To determine the rate constants of adsorption of copper on DCPD, the kinetic data were analyzed using two kinetic models, namely the model of the pseudo-first order and the pseudo-second order. Table 1 shows the different expressions of both kinetic models.

TABLE 1
ADSORPTION KINETIC MODELS

Model	Linear expression	Plot
Pseudo first-ordre [18]	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$ (1)	$\log(q_e - q_t)$ vs. t
Pseudo second-ordre [19]	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ (2)	$\frac{t}{q_t}$ vs. t

Where:

q_t : Quantity of adsorbate adsorbed in time (mg /g)

q_e : Adsorbed amount at equilibrium (mg /g)

k_1 : Adsorption constant rate of pseudo-first-order model

K_2 : Constant adsorption rate of pseudo-second-order model

t : Time (min)

The graphical representation of experimental results for these two kinetic models is shown in Figures 4 and 5.

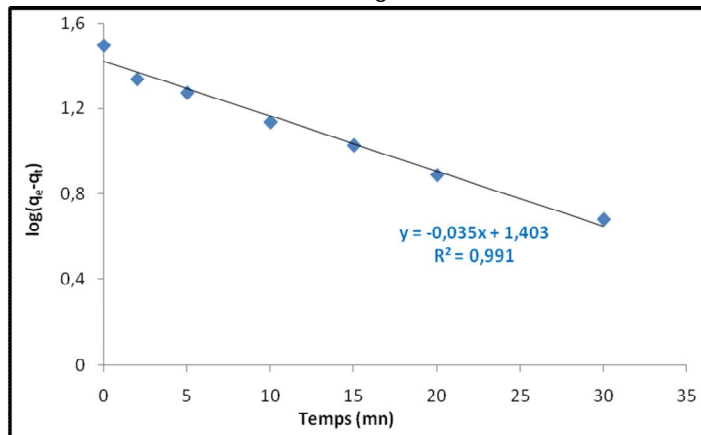


Fig.4. Pseudo-first-order kinetic model

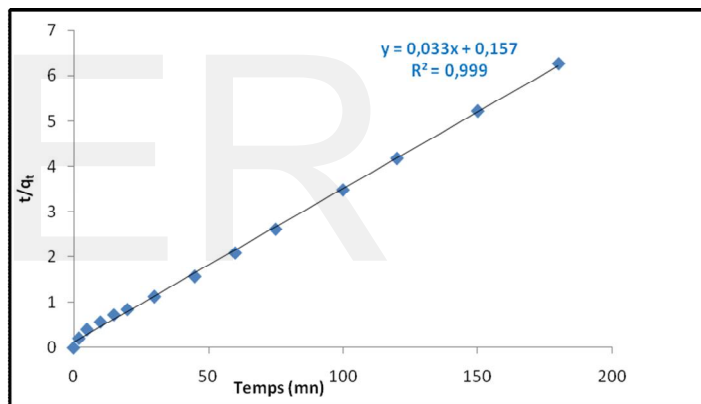


Figure 5: Pseudo-second-order kinetic model

The parameters of kinetic models, pseudo-first order, pseudo-second order, are summarized in Table 2.

TABLE 2
PARAMETERS OF KINETIC MODELS

Pseudo-first order				
$q_{e \text{ exp}} \text{ (mg.g}^{-1}\text{)}$	$q_{e \text{ theo}} \text{ (mg.g}^{-1}\text{)}$	Relative difference (%)	$k_1 \text{ (min}^{-1}\text{)}$	R^2
28,71	25,29	13,52	0,08	0,991
Pseudo- second order				
$q_{e \text{ exp}} \text{ (mg.g}^{-1}\text{)}$	$q_{e \text{ theo}} \text{ (mg.g}^{-1}\text{)}$	Relative difference (%)	$k_2 \text{ (min}^{-1}\text{)}$	R^2
28,71	30,30	5,24	0,0069	0,999

The most representative data model is selected based on the correlation coefficient R^2 . The correlation coefficient R^2 value for the pseudo-second-order adsorption model is very close to

unity ($R^2 = 0.999$), this value is higher than the pseudo-first-order model ($R^2 = 0.991$). In addition, $q_{e,theo}$ was quite similar to $q_{e,exp}$. Therefore, the copper adsorption kinetics on DCPD can be best described by the pseudo second-order model. These results imply that the chemisorption mechanism may play an important role in the adsorption of copper on DCPD.

5. MODELING OF ADSORPTION ISOTHERMS

Equilibrium isotherm equations are used to describe experimental adsorption data. The equation parameters of these equilibrium models often provide some insight into both the sorption mechanism and affinity of the adsorbent. The importance of obtaining the best-fit isotherm becomes more and more significant, because as more applications are developed, more accurate and detailed isotherm descriptions are required for the adsorption system designs. The curve $q_e = f(C_e)$, which is the plot of the quantity of sorbate removed per unit of sorbent (q_e) against the concentration of sorbate in the liquid phase (C_e), is the most used one for this description. The results obtained are the subject of Figure 6.

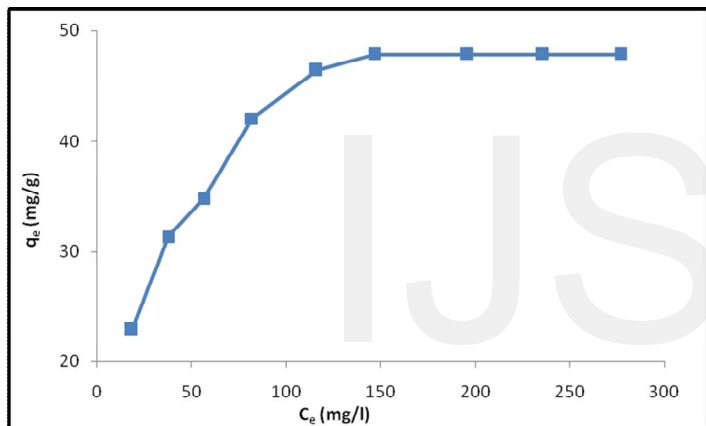


Fig. 6. Isothermal adsorption of copper on DCPD

It is observed that the amount adsorbed (mg/g) of metal on DCPD increases more quickly for low concentrations in solution and then reaches a plateau.

Concerning the isotherm models that were developed, Langmuir and Freundlich have been used in this study. The Langmuir isotherm deals with the unimolecular thick layer of adsorbate upon the surface of an homogeneous adsorbent without having any interactions between adsorbed molecules. The Freundlich isotherm encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. Table 3 describes the different expressions of these models.

TABLE 3
MODELS ADSORPTION ISOTHERMS

Model	Model expression	Linear expression	Plot
Freundlich [20]	$q_e = K_F C_e^{\frac{1}{n}}$ (3)	$\log q_e = \log K_F + \frac{1}{n} \log C_e$ (5)	$\log q_e$ vs. $\log C_e$
Langmuir [21]	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$ (4)	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$ (6)	$\frac{C_e}{q_e}$ vs. C_e

Where C_e is the equilibrium concentration ($mg.l^{-1}$), q_e and q_{max} are respectively the amount and maximum amount of metal ion sorbed at equilibrium per unit weight of sorbent ($mg.l^{-1}$) and K_L is the equilibrium adsorption constant. K_F is multilayer adsorption capacity and n is adsorption intensity for Freundlich isotherm. The parameters of each isotherm are listed in Table 4.

The Langmuir separation factor (R_L) is calculated from the Langmuir isotherm based equation as follow:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

With

C_0 : Initial concentration (ppm).

K_L : constant adsorbate-adsorbent adsorption equilibrium Langmuir ($l.mg^{-1}$).

This factor was applied to estimate either the sorption system [22]:

- Favorable ($0 < R_L < 1$)
- Unfavorable ($R_L > 1$)
- Irreversible ($R_L = 0$)
- Linear ($R_L = 1$)

A temperature studied, the free energy of adsorption ΔG°_{ads} can be calculated by the following equation:

$$\Delta G^{\circ}_{ads} = -RT(\ln K_L + 4.02) \quad (8)$$

ΔG°_{ads} , R , T and K_L represents the free energy of adsorption, the ideal gas constant, the absolute temperature and the Langmuir constant, respectively.

The experimental results for the initial concentrations of copper ranging from 19.8 to 280 mg/l provide isothermal data in Figure (6). These results indicate a form of L type according to the classification [23]. This form is Langmuir isotherm types. The interpretation of this curve must be done with the adsorption isotherm models shown in Figures 7, and 8. Parameters of these isotherms are recorded in Table 4.

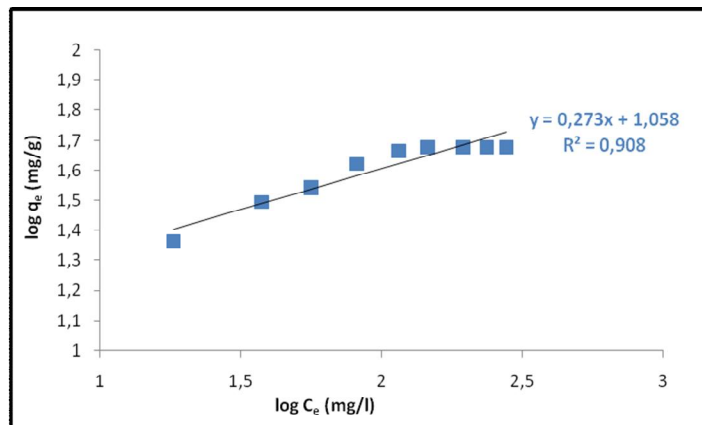


Fig. 7. Freundlich isotherm model

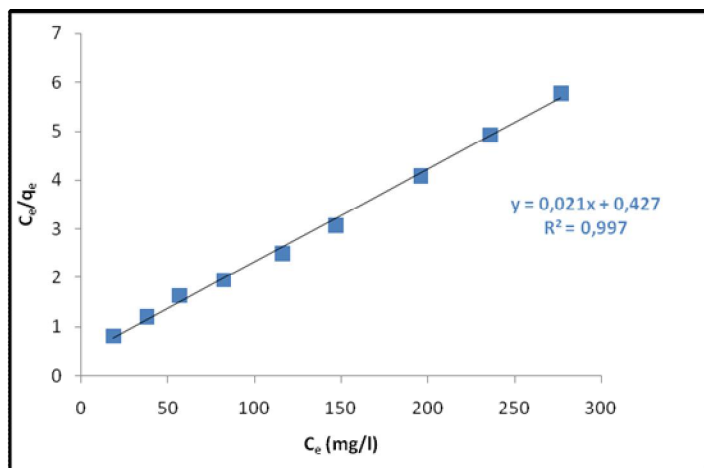


Fig. 8. Langmuir isotherm model

TABLE 4
PARAMETERS OF LANGMUIR AND FREUNDLICH ISOTHERM FOR ADSORPTION OF CU(II).

Freundlich					
$1/n$	K_F	R^2			
0.273	11.42	0.908			
Langmuir					
$q_{m, théo}$	Ecart Relatifs (%)	K_L	ΔG_{ads}° (Kj/mol)	R^2	R_L
47,61	0,43	0,04	-1,98	0,997	$R_L < 1$

According to the correlation coefficients shown in Table 4, the isotherm of copper on the DCPD is well represented by the Langmuir model, the correlation coefficient is very close to the unity $R^2=0.997$, with a maximum value of adsorption capacity (47.61 mg/g) very close the experimental value (47.82 mg/g) and The values of The dimensionless constant separation factor R_L were found to vary between 0 and 1 for initial Cu(II) concentrations ranging from 19.8 to 280 mg/l. It indicated favorable sorption of Cu(II) on DCPD. The results demonstrate the formation of monolayer coverage of copper ion at the outer surface of DCPD and the value of the free energy of adsorption $\Delta G_{ads}^{\circ}=-1.98$ Kj/mol demonstrates the spontaneous nature of the process involved.

6 CONCLUSION

The adsorption of copper on dicalcium phosphate dihydrated, $CaHPO_4 \cdot 2H_2O$ (DCPD) has been studied. The main results are:

1. The study of the evolution of the copper (II) concentration versus time shows that the binding kinetics of the studied medium is rapid, the equilibrium is reached in about 45 minutes of stirring system where $q_m = 47.61$ mg/g.
2. pH measurements during the experiment show that it has a remarkable effect on the adsorption of copper on the DCPD. Indeed, the amount of copper adsorbed per unit mass (q) increases with increasing pH. The optimum ad-

sorption capacity was achieved from pH= 6 where $q_e= 31.30$ mg/g.

3. The study of the effect of the initial concentration of metal shows that the amount of copper adsorbed per unit mass of DCPD increases with the increase of the initial concentration of copper.
4. The kinetic order of the adsorption of copper on the DCPD follows the pseudo-second-order model.
5. The adsorption of copper on DCPD obeys the Langmuir model, indicating that the mechanism involved is an adsorption monolayer which involves identical and independent sites limited.
6. The energy of adsorption (ΔG°) of Cu (II) on DCPD, as calculated from the Langmuir constant was found to be -19.51 kJ/mol. The negative value of ΔG° confirmed the feasibility of the process and the spontaneous nature of sorption of Cu (II) on DCPD.

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