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Adsorption Isotherm Study of Cd (II), Ni (II) and Cu (II) Removal in Ternary System Using Nano ϒ-Al2O3

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Abstract

The adsorption of Cd (II), Ni (II) and Cu (II) ions on nano ϒ-Al_2O_3 isotherms study indicate that (Langmuir, Freundlich and Elovich) be the most excellent model described removal of Cu (II) ion. Jovanovic and Harkins-Jura were found to be the most excellent one described removal of Ni (II) ions and the all models are less suitable for Cd (II) ions. All these were noted from the correlation coefficients values. The highest removal percentages obtained for ions were 92.045 % of Cd (II), 93.175 % of Ni (II) and 93.685% of Cu (II). FESEM was measured to find out the average particle size of nanoparticles and EDXA was used for measuring purity.

Keywords: Langmuir, Freundlich, Elovich, Jovanovic, removal, ternary, Cd (II), Ni (II), Cu (II) ions.

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دراسة ايزوثيرمات الامتزاز لإزالة Cd (II) و Ni (II) و Cu (II) في النظام الثلاثي باستخدام ألألومينا النانوية

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الخلاصة

تشير دراسة موديلات ايزوثيرم امتزاز أيونات الكادميوم (II)، والنيكل (II) والنحاس (II) على السطح النانوي- Al2O3 إلى أن (Langmuir، Freundlich، Elovich) هو أفضل نموذج لوصف أزالة أيونات Cu (II) وأن Jovanovic، Jura - Harkins هو الأكثر تميزا لوصف إزالة أيونات Ni (II) وأن جميع النماذج أقل ملاءمة لأيونات Cd (II) ، وقد لوحظ كل ذلك من قيم معاملات الارتباط. كانت أعلى نسب إزالة للأيونات 92.045٪ من الكادميوم (II)، 93.175٪ من النيكل (II) و 93.685٪ من النحاس (II). تم قياس FESEM لمعرفة متوسط حجم الجسيمات النانوية وقياس EDXA من أجل معرفه النقاوة.

الكلمات المفتاحية: لانكماير، فريندليش، ايلوفك، جافونوفك، ثلاثي، أزالة، النيكل الثنائي، النحاس الثنائي، الكادميوم الثنائي.

Introduction

Millions of people die from communal diseases transmitted through water or human waste [1]. The adsorption process is similarly considered as one of the real process technologies that have been used successfully to remove discoloration and it has been proven to be one of the most real methods physical and chemical methods for treating fabric wastewater [2] [3]. Also is one of the most significant or a major method used in the chemical and petrochemical industries [4]. Al2O3 is used as a sorbent to remove heavy metals from the aqueous solution [5]. ϒ-Al2O3 is a material with advantages such as dielectric constant, excellent stability, favorable thermal conductivity, high hardness, and low refractive index. It can be synthesized in several methods, including chemical vapor deposition, electron beam evaporation, colloidal

solution gel process, pulsed laser deposition, and atomic layer deposition [6]. The adsorption isotherm is designed to measure the concentration of the adsorbent in the medium before and after the adsorption process, at a constant temperature which represents the relationship between the amount of adsorbent at a specific surface and substance concentration or pressure adsorbed at equilibrium by constant temperature to study the interaction between the adsorbent and surface of the adsorbent and to know the structure of absorbed layer [7].

Experimental Work

Materials

1. Adsorbent: Standard stock solutions were prepared from Cd (II) Ni (II) and Cu (II), ions (1000 mg / L) of $Ni(NO_3)_2.6H_2O$, $CdSO_4.8H_2O$ and $CuSO_4.5H_2O$ and in deionized water. Numerous concentrations (20, 40, 60, 80 and 100 mg / L) were ready from this standard stock for each metal ions. The absorbance of these solutions was measured with a wavelength (λ max) 228.8 nm for cadmium, (324) nm for copper and 232 nm for a nickel, in order to regulate metal concentrations by atomic absorption.

2. Adsorbent: Alumina was used from US research nanomaterials, Inc. Made in USA, assay 99.5%.

Experiment of adsorption isotherm

The adsorption isotherm for nickel, cooper and cadmium ions removal in ternary systems on (ϒ-Al_2O_3) at temperature of 298 K, pH of 6, 0.05 g adsorbents and stirring speed 185 rpm, the contact time of (45 minutes) for three metals ions on alumina surface. In ternary systems (30 ml), initial concentration, varied from (20-100 mg/L).In all experiments the equilibrium metal concentration was measured using atomic absorption spectroscopy. The adsorption quantity of adsorbent nanoparticles was calculated using the equation [8,9]:

$$Qe = \frac{(C_o - Ce) \times v}{m} \quad (1)$$

Where: ($\mathbf{Q_e}$), the adsorption quantity of the surface nanoparticles at equilibrium (mg/g), ($\mathbf{C_o}$) means the initial adsorbent concentration (mg/L). (**C**), the equilibrium concentration of metals after adsorption has occurred (mg/L), (V), volume of aqueous solution (L), (m), weight of metal oxide nanoparticles (g).

Results and discussion

1. Field Emission Scanning Electron Microscopy (FESEM)

FESEM was used for the morphological assessment of obtaining Al_2O_3-NPs depicted in figure (1).As per the FESEM images, the nanoparticles predominantly appear to be spherical in shape with little shape variation. The high-resolution images clearly show the features of the tapered surface as the distribution of the nanoparticles can be seen over the entire surface. These very impressive surface features allow the nanoparticles to have higher active sites compared to other shapes. FESEM images revealed that the average size of aluminum oxide nanoparticle is (32.805) nm [10].

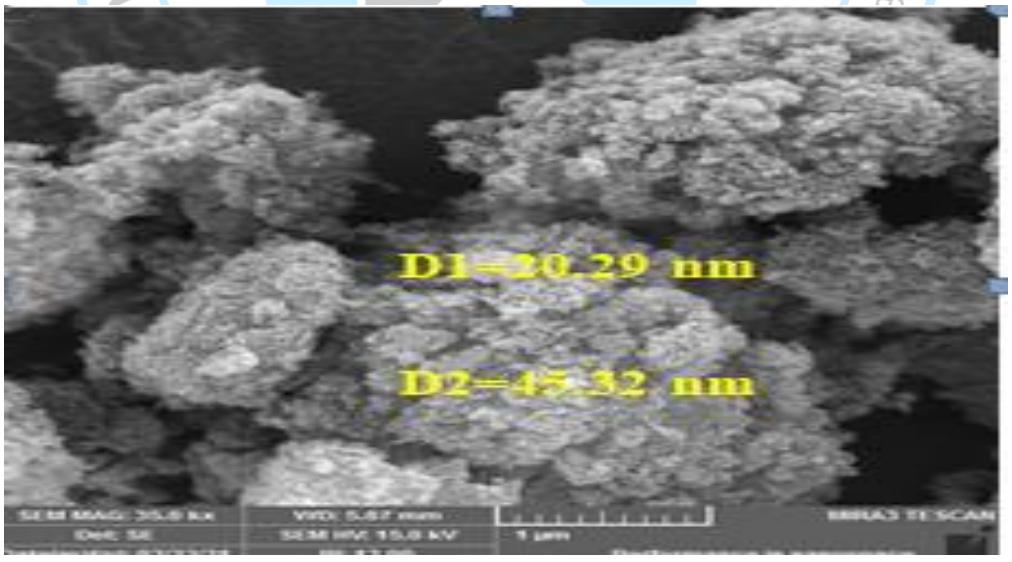

Figure 1: FESEM image of ϒ- Al_2O_3 oxide nanoparticles

2. Energy – dispersive X-ray Analysis Spectroscopy (EDXA)

EDX were used in order to determine the elements that present in the sample of Al_2O_3-NPS. Result revealed in figure (2) that the EDX data was composed of Al (50.8 %) and O (49.2%) were major. This results has confirms that the ϒ-Al_2O_3-NPs has high purity. Similar finding was also found in previous studies that obtained strong peaks related to Al and O in aluminum oxide nanoparticles and these values are very close to the theoretical one for Al (52.9%) and O (47.1%) [11].

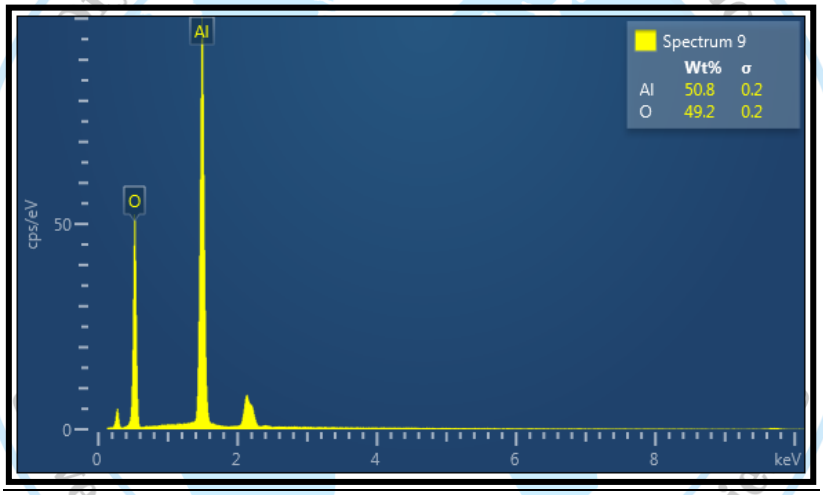

Figure 2: EDX spectrum of nano ϒ-Al_2O_3

3. The adsorption isotherm of ternary metals ions systems

The adsorption isotherm data studied of Cd (II), Ni (II) and Cu (II) ternary systems from an aqueous solution on (ϒ-Al_2O_3) surface at ideal condition(T=298K, wt =0.05 g, 185 rpm and contact time of 45 minutes) are listed in table (1). The results are represented by the initial concentration (C_o) of cadmium, nickel and copper ions, and the equilibrium concentration (C_e) measured at equilibrium state and the adsorption capacity (Q_e) values are calculated from the experimental data by using equation 1.

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Table 1: Adsorption parameters values of Cd (II), Ni (II) and Cu (II) ions of the ternary solution by (ϒ-Al_2O_3) surface at ideal condition

Metals	C_o (mg/L)	Ce (mg/L)	Qe (mg/g)	log Ce	log Qe	ln Ce	Ce /Qe	Q_e/C_e	ln Q_e/C_e	lnQe	1/ Ce	ln1/ Ce	Qe^2	$1/Qe^2$
Cd (II) ions	20	1.591	11.0454	0.2016	1.0431	0.4643	0.1440	6.9424	1.9376	2.4020	0.6285	-0.464	122	0.0081
	40	3.681	21.7914	0.5659	1.3382	1.3031	0.1689	5.9199	1.7783	3.0815	0.2716	-1.303	474	0.0021
	60	5.911	32.4534	0.7716	1.5112	1.7768	0.1821	5.4903	1.7029	3.4798	0.1691	-1.777	1053	0.0009
	80	7.957	43.2258	0.9007	1.6357	2.0740	0.1840	5.4324	1.6923	3.7664	0.1256	-2.074	1868	0.0005
	100	10.247	53.8518	1.0105	1.7312	2.3269	0.1902	5.2553	1.6592	3.9862	0.0975	-2.327	2900	0.0003
Ni (II) ions	20	1.375	11.175	0.1383	1.0482	0.3184	0.1230	8.1272	2.0952	2.4136	0.7272	-0.318	124	0.0080
	40	3.501	21.8994	0.5441	1.3404	1.2530	0.1598	6.2551	1.8333	3.0864	0.2856	-1.253	479	0.0020
	60	5.431	32.7414	0.7348	1.5150	1.6921	0.1658	6.0286	1.7965	3.4886	0.1841	-1.692	1071	0.0009
	80	7.573	43.4562	0.8792	1.6380	2.0245	0.1742	5.7383	1.7471	3.7717	0.1320	-0.311	1888	0.0005
	100	9.703	54.1782	0.9869	1.7338	2.2724	0.1790	5.5836	1.7198	3.9922	0.1030	-2.273	2935	0.0003
Cu (II) ions	20	1.263	11.2422	0.1014	1.0508	0.2334	0.1123	8.9011	2.1861	2.4196	0.7917	-0.233	126	0.0079
	40	2.801	22.3194	0.4473	1.3486	1.0299	0.1254	7.9683	2.0754	3.1054	0.3570	-1.030	498	0.0020
	60	4.429	33.3426	0.6463	1.5229	1.4881	0.1328	7.5282	2.0186	3.5068	0.2257	-1.488	1111	0.0009
	80	6.271	44.2374	0.7973	1.6457	1.8359	0.1417	7.0542	1.9536	3.7895	0.1594	-1.836	1956	0.0005
	100	8.068	55.1592	0.9067	1.7416	2.0879	0.1462	6.8367	1.9223	4.0102	0.1239	-2.088	3042	0.0003

Langmuir isotherm

The Langmuir adsorption isotherm is used to predict the different performance of the absorbent materials, and it is based on the premise that the absorption occurs on a homogeneous surface by means of a monolayer absorption can be expressed by the following equation

$$\frac{Ce}{qe} = \frac{1}{bQm} + \frac{Ce}{Qm} \qquad (2)$$

Figure 3 shows the calculation of the constant related to the adsorption energy from the slope and intercept of the sectors (C_e / Q_e) versus (C_e) and is shown in table (2).

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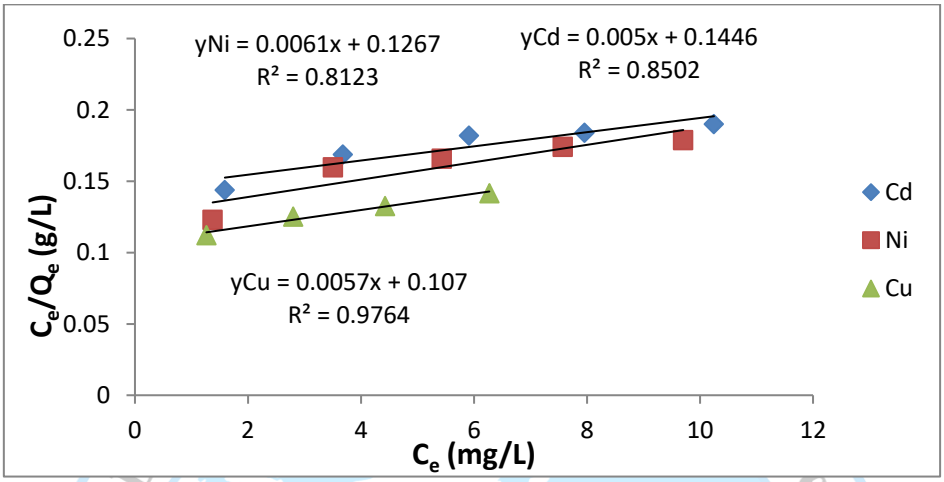

Figure (3): Linear Langmuir isotherm of Cd (II), Ni (II) and Cu (II) ions in ternary system adsorption on (ϒ-Al_2O_3) surface at various initial concentrations

2. Freundlich isotherm

Expressing the surface heterogeneity and the exponential distribution of the active sites and their energies, can be expressed by the following equation

$$\log Qe = \log Kf + \frac{1}{nf} \log Ce \qquad (3)$$

Freundlich (K_f) which is the adsorption capacity of the adsorbent, and (n) is the adsorption intensity which is calculated from the slope and the intersection of the segment (log Q_e) versus (log C_e) as in figure 4, with the results presented in table (2).

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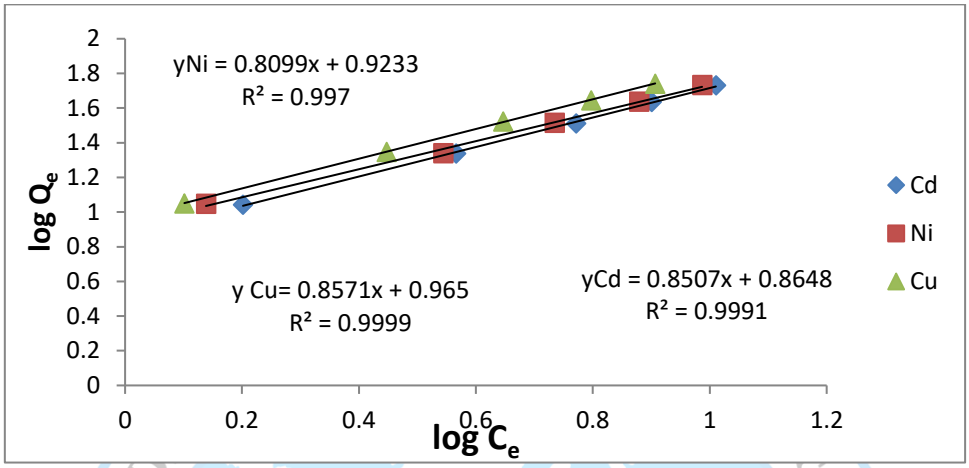

Figure 4: Linear Freundlich isotherm of Cd (II), Ni (II) and Cu (II) ions in ternary system adsorption on (ϒ-Al_2O_3) surface at various initial concentrations.

3. The Elovich isotherm

The equation of the Elovich model is based on a kinetic principle, assuming that the adsorption site increases exponentially with adsorption, implying a multi-layer adsorption. It can be expressed by the following equation

$$\frac{qe}{qm} = KECe\, e^{-\frac{qe}{qm}} \quad (4)$$

The Elovich isothermal constant (K_E), which is the equilibrium link constant (L / mg), if the adsorption is subject to the Elovich equation the maximum absorption capacity and the Elovich constant can be calculated from the slopes and intersections of the plot of ln (q_e / C_e) versus q_e as in figure 5. The results are shown in tables (2).

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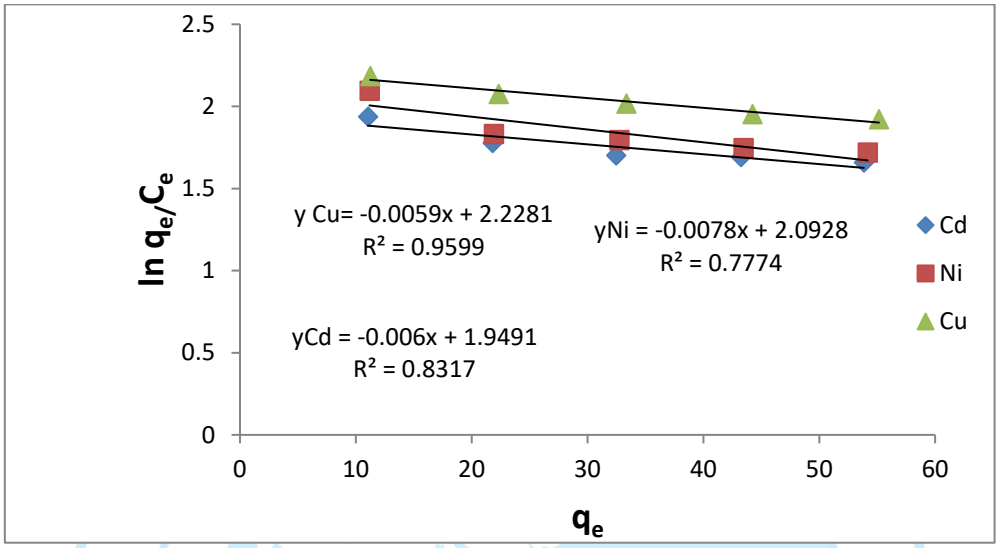

Figure 5: The Elovich isotherm of Cd (II), Ni (II) and Cu (II) ions in ternary system adsorption on (ϒ-Al_2O_3) surface.

4. The Jovanovic isotherm

This model is similar to the Langmuir model, except that the allowance was previously intended for surface binding vibrations of amalgamated species. It is expressed in the following relationship

$$qe = qm\left(1 - e^{kjCe}\right) \quad (5)$$

The Jovanovic isothermal constant (K_J), which is the equilibrium link constant (L / mg), the maximum Jovanovic adsorption capacity and the Jovanovic constant can be calculated from the slopes and intersections of the plot ln (q_e) versus Ce as in the figure 6. The results are shown in tables (2).

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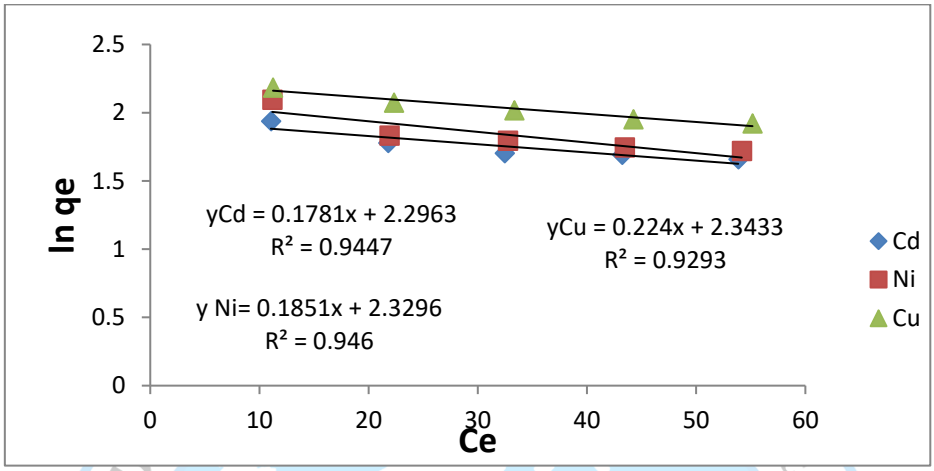

Figure 6: The Jovanovic isotherm of Cd (II), Ni (II) and Cu (II) ions in ternary system adsorption on (ϒ-Al_2O_3) surface.

5. Harkins-Jura Isotherm

The Harkins-Jura isothermal model basically describes multilayer adsorption which can be expressed in the following relationship:

$$\left[\frac{1}{qe^2}\right] = \left[\frac{BHJ}{AHJ}\right] - \left[\frac{1}{AHJ}\right]\log(Ce) \qquad (6)$$

B_{HJ} and A_{HJ} are the Harkins-Jura constants. Both B_{HJ} and A_{HJ} can be realized from the slope and linear plan intercept based on 1 / q_e^2 versus log (C_e) as shown in figure 7. The results are shown in tables (2).

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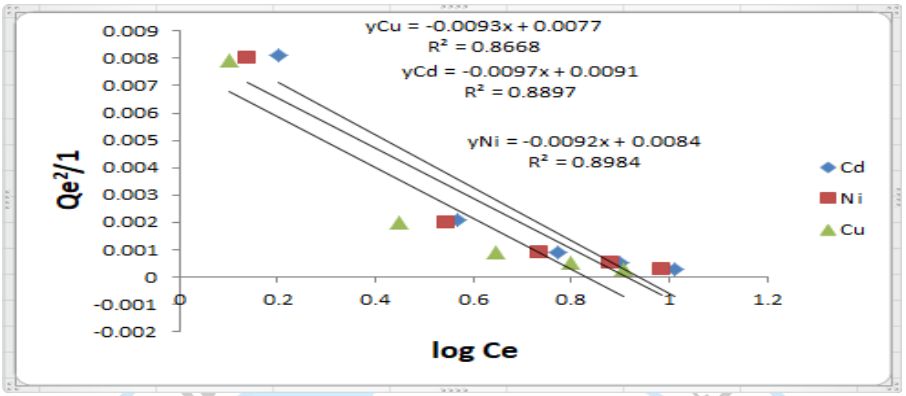

Figure 7: The harkins-Jura isotherm of Cd (II), Ni (II) and Cu (II) ions in ternary system adsorption on (ϒ-Al_2O_3) surface.

Table (2): Isotherm constants

Langmuir	a (mg/g)	b (L/g)	R^2
Cd (II)	200	0.0436	0.8502
Ni (II)	163.93	0.0481	0.8123
Cu (II)	175.43	0.0532	0.9764
Freundlich	n	K_f (mg/g)	R^2
Cd (II)	1.175	7.324	0.9991
Ni (II)	1.234	8.381	0.997
Cu (II)	1.166	9.225	0.9999
Elovich	q_m (mg/g) theoretical	K_E (L/mg)	R^2
Cd (II)	166.66	0.042	0.8317
Ni (II)	128.2	0.063	0.7774
Cu (II)	169.49	0.0547	0.9599
Jovanovic	K_j(L/mg)	q_m (mg/g) theoretical	R^2
Cd (II)	0.1781	9.937	0.9447
Ni (II)	0.1851	10.273	0.946
Cu (II)	0.224	10.415	0.9293
Harkins-Jura	A_{HJ}	B_{HJ}	R^2
Cd (II)	103.09	0.938	0.8897
Ni (II)	108.69	0.912	0.8984
Cu (II)	107.52	0.827	0.8668

In order to optimize the design of an adsorption process for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various

isotherm equations like those of Langmuir, Freundlich, Elovich, Jovanovic, and Harkins-Jura mentioned in the table (2) for the ternary systems were [111]. Langmuir isotropic absorption was used predicts the performance of various absorbents and is based on assuming the absorption occurs homogeneously on the surface by absorption of a monolayer R^2 values were 0.8502 for Cd (II) ion, 0.8123 for Ni (II) ion and 0.9764 for Cu (II) ion. The Freundlich isotherm adsorption, gives the surface heterogeneity and the exponential distribution of the active sites and their energies, the correlation coefficient value R^2 (0.9991 for Cd (II) ,0.9970 for Ni (II) and 0.9999 for Cu (II)ion) is higher for isotherm Langmuir. Further the value of n lies between 1 and 10, which indicates adequate adsorption and the obtained K_f values were 7.324 mg/g, 8.381 and 9.225 indicating positive adsorption process. The equation defining the Elovich model is based on kinetic principle assuming increased adsorption sites exponentially with adsorption, which means multiple layers adsorption. The value the regression coefficient, R^2 (0.8317 for Cd (II) ion, 0.7774 for Ni (II) ion and 0.9599 for Cu (II) ion) was lower than the Langmuir values. Jovanovich's isothermal model corresponds to another model adduction of the localized monolayer absorption without adverse reactions. This model is similar to Langmuir's model and had higher than other isothermal models. For Harkins-Jura the values of R^2 (0.8897 for Cd (II) ion, 0.8984 for Ni (II) ion and 0.8668 for Cu (II) ion) . These reveal that the adsorption performance is against the rule of multi-layer adsorption. Which may be attributed to the heterogeneous distribution of the multilayer activation and adsorption sites [13,14].

Conclusion

FESEM results revealed that average size of aluminum oxide nanoparticle is (32.805) nm which is similar to (20.29) nm reported before. EDXA results has confirmed that the ϒ-Al_2O_3-NPs has high purity. Similar finding was also found in previous studies that obtained strong peaks related to Al and O in aluminum oxide nanoparticles and these values are very close to the theoretical one for Al (52.9%) and O (47.1%). Modelses isotherm (Langmuir, Freundlich,,

Elovich,) was found to be the best one described removal of Cu (II) ions, and Jovanovic, Harkins-Jura was found to be the best one described removal of Ni (II) ions and the models are less suitable for Cd (II) ions .

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