Progress in Chemical and Biochemical Research 2022, 5(1), 53-67

Progress in Chemical and Biochemical Research

Journal homepage: www.pcbiochemres.com

Original Research Article

Removal of Copper II from Industrial Effluent with Beta Zeolite Nanocrystals

Bijan Ghanavati*, Alireza Bozorgian

Department of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

ARTICLE INFO

Article history

Submitted: 2022-01-08

Revised: 2022-02-11

Accepted: 2022-03-15

Available online: 2022-04-02

Manuscript ID: PCBR-2202-1213

DOI: 10.22034/pcbr.2022.328704.1213

KEYWORDS

Heavy metals,

Adsorption,

Nanocrystalline zeolite Beta,

Adsorption isotherm

ABSTRACT

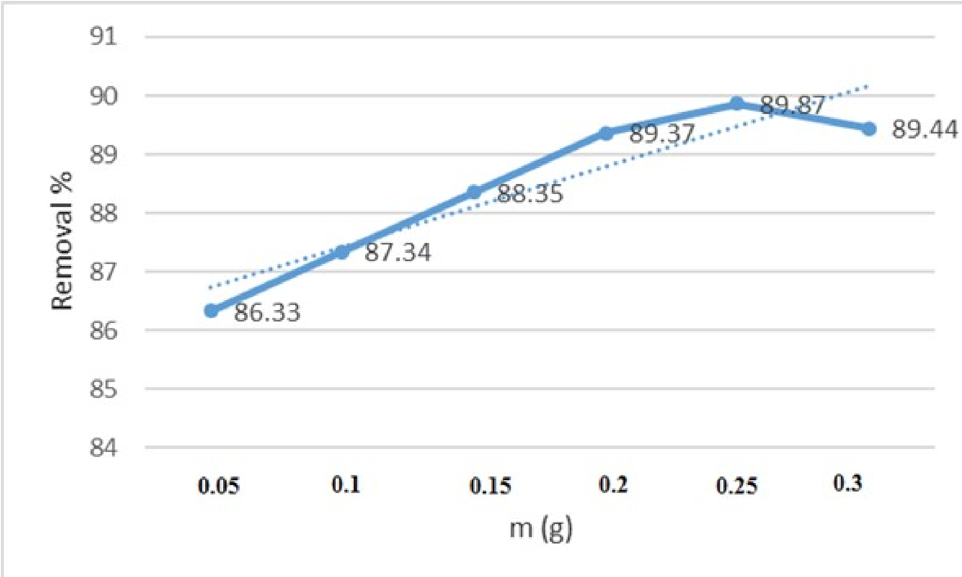
Heavy metals, including copper, are one of the most toxic pollutants in the world today due to the consumption prevalence in industry. There are several ways to remove copper from wastewater, each of which has advantages and limitations. Adsorption is one of the easiest and most commonly used methods to remove heavy metals from aqueous environments. On the other hand, the production of cheap adsorbents using waste from different factories can play an important role in reducing environmental pollution. For this, using copper ion (II) adsorption was investigated using a nanoscale zeolite beta adsorbent through batch adsorption experiments. In the following, various parameters affecting the adsorption process such as pH, initial concentration, temperature, adsorbent amount and contact time were investigated. The highest removal efficiency was observed at pH = 5 at 25 °C for 25 minutes, with a 0.25 g of nanocrystalline zeolite beta in 20 ml of copper solution. The traditional study of copper adsorption by nanocrystalline zeolite beta results in a well-respected second-order pseudo-model. Also, the adsorption thermodynamic studies indicate that the adsorption data is followed by the Doubinin-Raduskovich equivalence model with a correlation coefficient (R2 = 0.9963) at a temperature of C50.

* Corresponding author: Bijan Ghanavati

✉ E-mail: bn.ghanavati@mhriau.ac.ir

☎ Tel number: +989163547899

GRAPHICAL ABSTRACT



Introduction

Increasing the number of heavy metals in water resources has caused serious problems for human health and natural ecosystems because these metals are very stable and have the ability to accumulate in the body of living organisms. Most heavy metals, even in low concentrations, are toxic and cause many problems [1]. Therefore, heavy metal removal methods from contaminated wastewater are of particular importance.

Although conventional methods such as deposition, ion exchange, and electrodialysis are used to remove heavy metals, they are typically economically viable [2]. They are not economical and do not yield to the necessary efficiency for reducing the metal concentration at very low metal concentrations. Adsorption process is one of the most common methods due to its flexibility in design, process, and water production without pollution and suitable for reuse, which can be a reliable method to remove certain types of contaminants by choosing the appropriate adsorbent. Because natural adsorbents have been found in abundance as alternatives to the existing economic adsorbents and are sometimes inexpensive, the adsorption of soluble ions by these materials can be a good way to remove heavy metals from contaminated water and industrial effluents. Today, large amounts of fish waste are discarded, from which the effective sorbents can be extracted by simple and various methods. Beta zeolite nanocrystals have suitable and significant capabilities for the removal of heavy metals and this is due to the presence of reactive surface areas on beta zeolite nanocrystals [3].

Beta zeolite nanocrystals do not have any environmental pollution problems, so they are a better option than the other operations which are expensive and involve complex operations and treatment problems [4]. Today, the adsorption process, especially with the use of activated carbon, has attracted the attention of many scientists; because it is effective for removing small amounts of heavy metals. However, this process is not widely used due to its high cost. For this, the importance of using other adsorbents that have a higher adsorption capacity and are also inexpensive, to remove heavy metals from the effluent can be justified. Beta zeolite nanocrystals have certain abilities to absorb elements such as lead, cadmium, zinc, arsenic, vanadium and uranium due to the presence of various reactive surface areas on beta zeolite nanocrystals [5-9].

The efficiency of copper removal from water using nanocrystals is beta zeolite, which is made and released in laboratory conditions [10]. In the following, the effect of various parameters on the adsorption process such as: pH, initial concentration, temperature, and adsorbent amount, as well as the contact time on the adsorption process will be investigated and finally, traditional studies will be performed on the data [11-15].

Demibas et al. studied the adsorption of copper ions from aqueous solutions by activated carbon prepared from hazelnut shell (HsAc) in a batch adsorption system. The factors affecting the adsorption of copper (II) such as initial concentration (25-25 mg / L), pH (2-6), adsorbent dose (0.5-3 g / L), and temperature (323-293 k) were investigated. Table (1) indicate the data related to pH adsorption (2). The amount of adsorption is increased and the maximum adsorption is obtained at pH = 6, which is the initial pH of the solution. At pH more than 6, copper begins to precipitate in the form of $Cu(OH)_2$.

Table (2) depicts the data about the effect of initial concentration on the adsorption of cu^{2+} from aqueous solution by HASC adsorbent.

Comparison of the traditional model in the rate of adsorption illustrtates that the adsorption system follows the quasi-quadratic synthesis and the adsorption equilibrium data are consistent with the Langmuir model [16].

Zhuang et al. studied lead adsorption by hydroxyapatite magnetic nanoparticles. Its mechanism was determined by X-ray diffraction and photoelectric spectroscopy. The presence of magnetic nanoparticles led to easier separation of the adsorbent from the solution. The maximum absorption was 440 mg/g at pH=3 and the equilibrium time was within 60 minutes. Experimental data were consistent with the Langmuir model and the synthetic results were consistent with the quasi-second-order model. They showed that the ion exchange mechanism causes lead adsorption from the aqueous solution [17].

Materials, equipment and description of tests

In this study, in order to remove copper from the effluent by beta nanocrystal zeolite, first to test the amount of copper adsorption by the adsorbent, solubilization was performed and then, the necessary tests were performe.

Table (1): Effect of pH on removal of cu^{2+} from aqueous solution by HASC adsorbent

pH	2	3	4	5	6
$\mathbf{q_e}$	9.02	14.67	15.02	15.04	15.33

Table (2): Initial concentration on Cu^{2+} uptake by HASC

C_0	25	50	100	200
$\mathbf{q_e}$	8.06	15.33	29.33	36.33

Figure (1): View of the SHIMADZU AA 680 atomic absorption device

Results investigation of the effect of contact time on copper (II) adsorption

The adsorption capacity of beta zeolite nanocrystals and the percentage of copper ion adsorption by it were measured at intervals of 5, 10, 15, 30, 45, 60, and 120 minutes. To investigate the effect of contact on the adsorption of Cu (II) on 7 humans containing 20 cc of 500 ppm solution of Cu (II), 0.1 g of beta zeolite nanocrystalline adsorbent was added and the lids were covered. Then, each of these human beings was stirred at ambient temperature and by the appropriate speed of the stirrer at different times to perform the adsorption operation. The concentration of residual copper (II) in the solution was then measured through an atomic absorption spectrometer.

At the beginning of the adsorption process, there are several voids on the adsorbent. Therefore, the adsorption rate of copper ions is higher at the beginning of the process. Then, after some time of the adsorption process, due to the positions filling up on the adsorbent surface by copper ions and the lack of empty positions, the speed of adsorption process is reduced. According to the results, the optimal contact time equals to 60 minutes, and after this time, the rate of adsorption process has been proven to be due to the fact that the rate of adsorption is equal to the rate of excretion (equilibrium state) and the adsorption capacity is completed (Figures 2 and 3).

Investigation of traditional models of the effect of time on copper (II) adsorption

In this section (Figures 4 and 5), as well as the data, the quasi-first-order traditional models were examined.

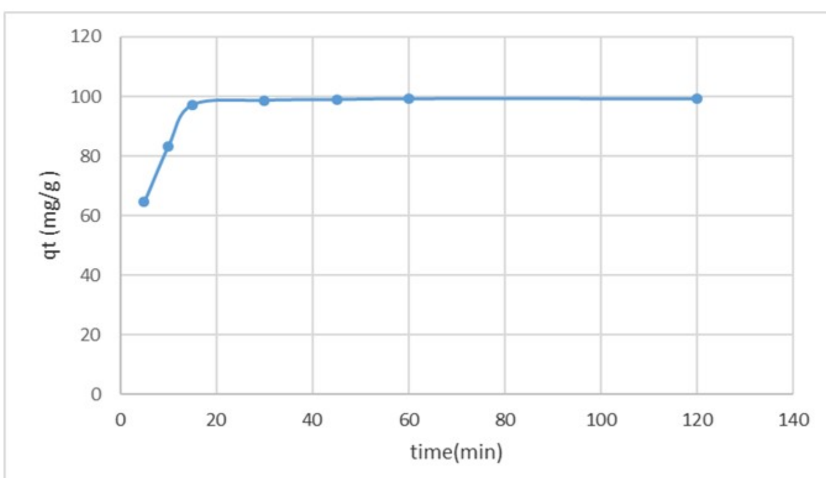


Figure (2): Copper (II) adsorption capacity in terms of time

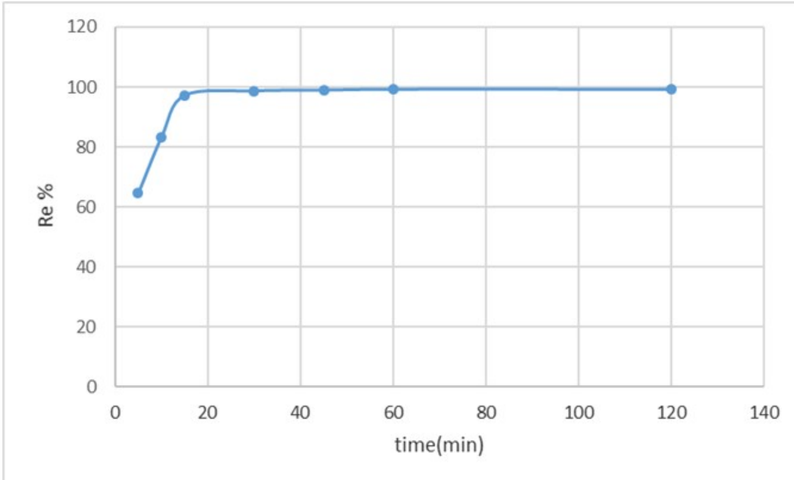


Figure (3): Percentage of copper (II) absorption by time

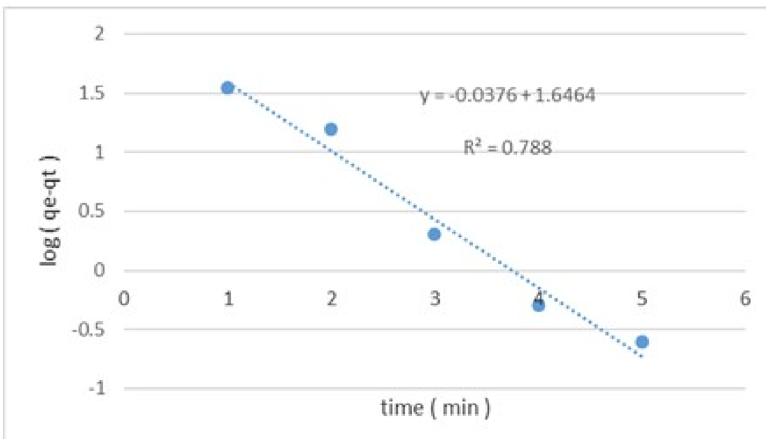


Figure (4): The first quasi-first-order model

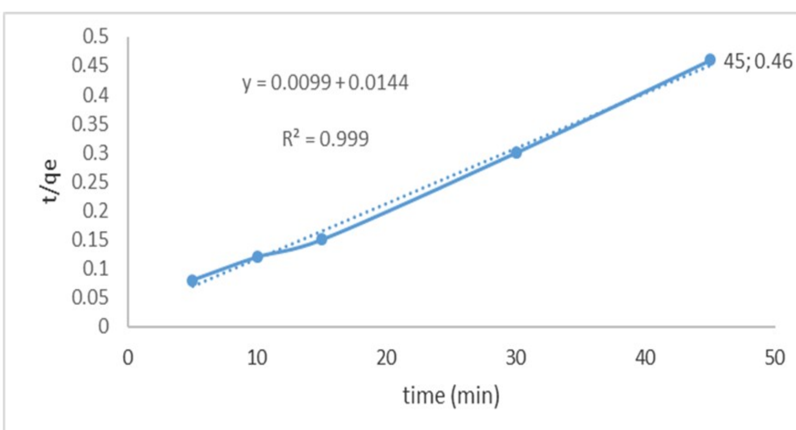


Figure (5): The second-order quasi-second-order model

As can be seen in figures (4) and (5), by drawing a line from the points of the quasi-first and quasi-quadratic graphs, the correlation coefficient (R^2), the line equation along with the slope, and width of the origin are obtained. Table (3) indicates R^2 values for quasi-quadratic and quasi-quadratic traditional models.

Table (3): R^2 values for quasi-quadratic and quasi-quadratic traditional models

Synthetic model	Pseudo-first degree	Quasi-quadratic
R^2	0.7881	0.9995

Given that the R^2 value in the quasi-quadratic synthetic model is greater than 0.95, and is closer to 1.The laboratory data is thus more consistent with this model and follows this model.

Table (4): Proof of quasi-first-order and quasi-quadratic models

Synthetic model	Pseudo-first degree	Quasi-quadratic
K_1	0.08659	_
K_2	_	0.0068
q_e	44.30	101.01

To investigate the amount of adsorbent in the removal of copper (II), 5 people containing 20 cc of 500 ppm solution of copper (II) were added to 0.25, 0.2, 0.15, 0.1 and 0.5-0 g of adsorbent, respectively. Then, the human lid was covered and the stirrer was placed at room temperature and at a suitable speed for 60 minutes, as well. Subsequently, the solutions were filtered and then, their adsorption rate was read by the atomic absorption device.

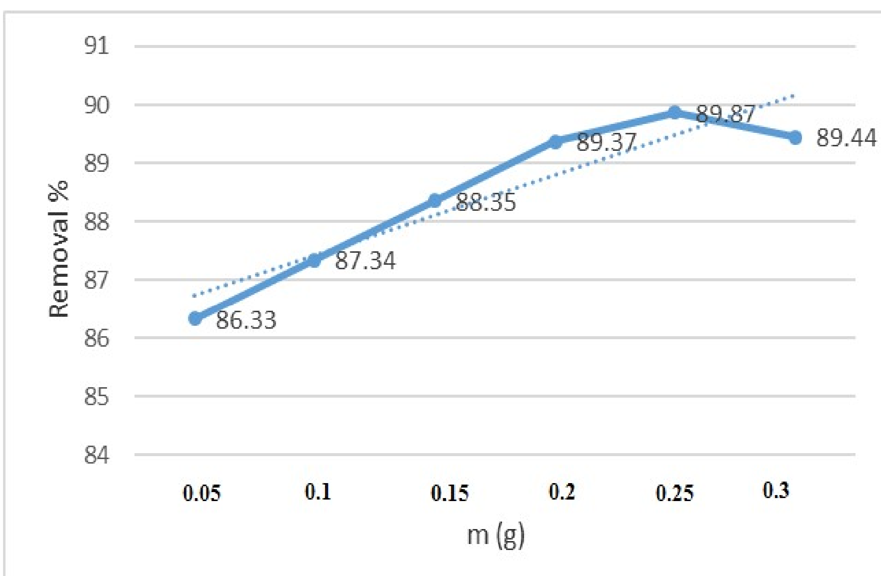


Figure (5): Effect of adsorbent on copper removal percentage (II)

As it is evident in the diagrams, by increasing the amount of adsorbent, the percentage of adsorption of copper ions increased, while its adsorption capacity decreased. Because by increasing the amount of adsorbent, the number of active sites increases and as a result, more copper ions will be removed by beta zeolite nanocrystals. According to figure (5), the optimal amount of adsorbent is equal to 0.25 g and further increasing the amount of adsorbent has no effect on the adsorption process. Because in the optimal amount of adsorbent, most contaminants in the adsorbent solution are adsorbed. Investigation of simultaneous change of temperature and the initial concentration of solution.

In this experiment, 5 samples of copper (II) solution with concentrations of 800-650-500-350-200 ppm were prepared. 0.25 g of beta zeolite nanocrystalline adsorbent was poured into 15 humans and 20 cc of 800-650-500-350-200 ppm solution was added to each human. 5 samples of different concentrations were placed in an ice container at zero °C. 5 samples were placed at 25 °C and the other 5 samples were placed on the heater at 50 °C. All samples were stirred for 60 minutes at a suitable speed. Consequently, the samples were filtered by filter paper and the adsorption rate of samples was measured using an atomic absorption device and the adsorption isotherms were determined. In the following, laboratory data obtained from thermodynamic studies of copper adsorption with adsorbent of beta zeolite nanocrystals are examined for their compatibility with each of the Langmuir, Freundlich, and Dubinin-Radushkovich isotherms.

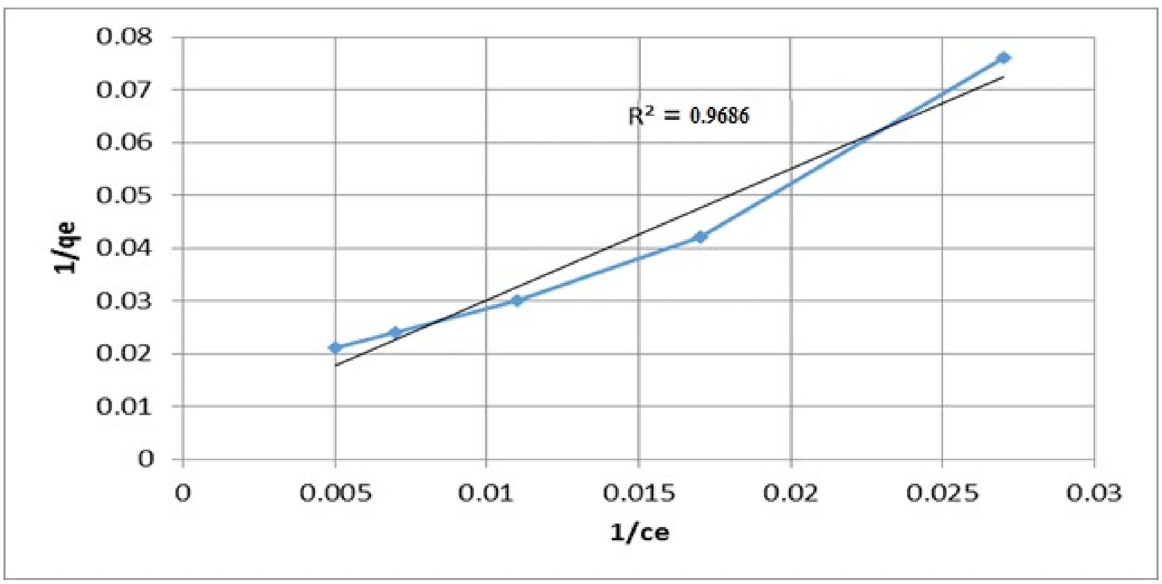


Figure (6): Copper adsorption isotherm based on Langmuir model T = 0 °C

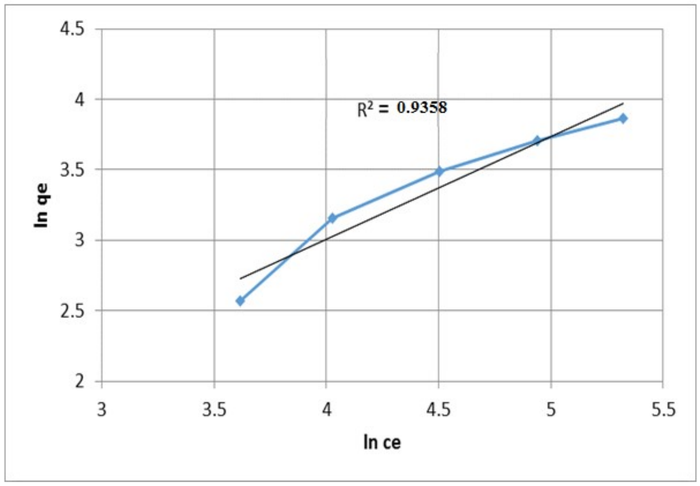


Figure (7): Copper adsorption isotherm based on Freundlich model T = 0 °C

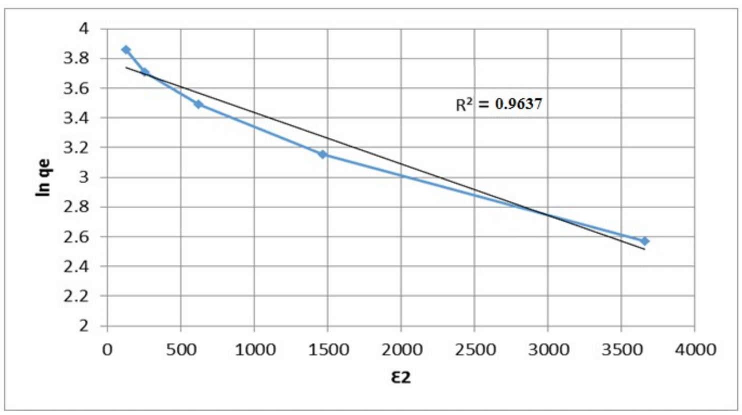


Figure (8): Copper adsorption isotherm based on Dubinin-Radushkovic model T = 0 °C

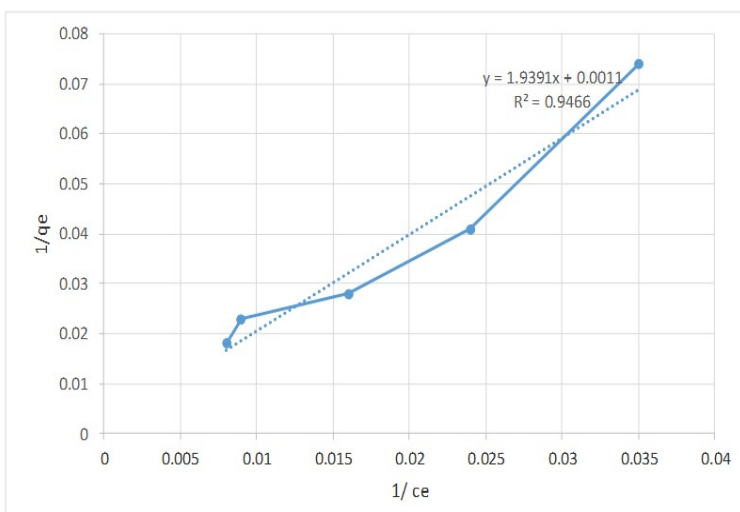


Figure (9): Copper adsorption isotherm based on Langmuir model T = 25 °C

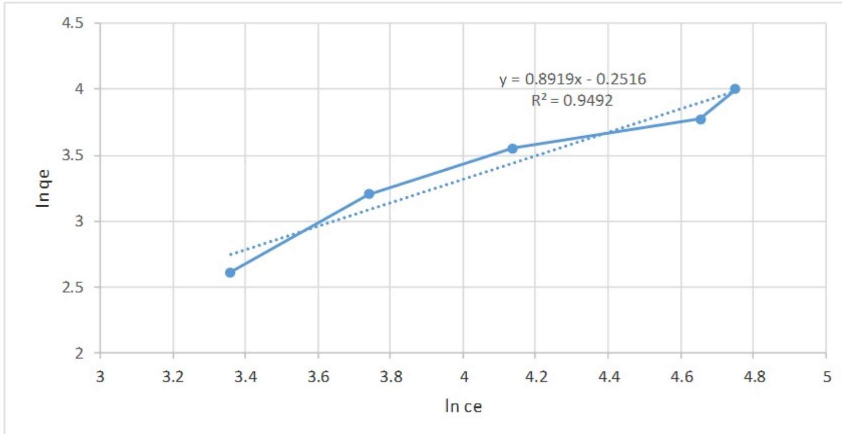


Figure (10): Copper adsorption isotherm based on Freundlich model T = 25 °C

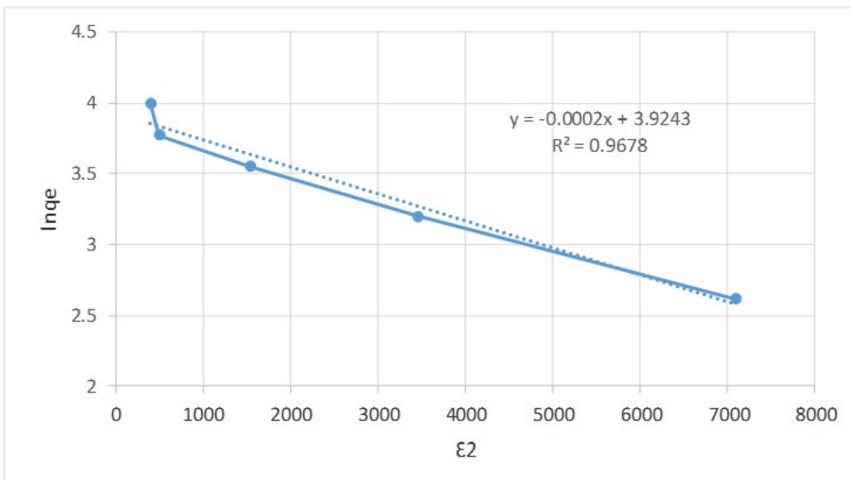


Figure (11): Copper adsorption isotherm based on Dubinin-Radushkovic model T = 25 °C

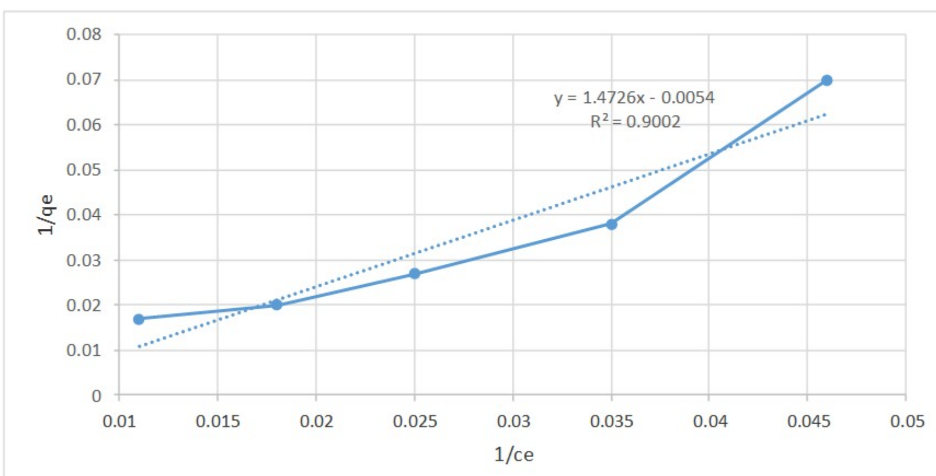


Figure (12): Copper adsorption isotherm based on Langmuir model T = 50 °C

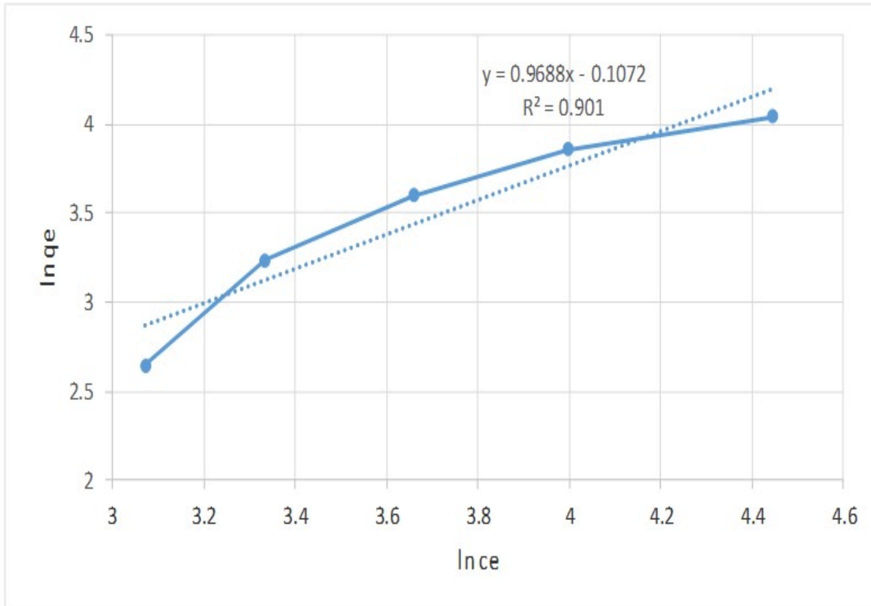


Figure (13): Copper adsorption isotherm based on Freundlich model T = 50 °C

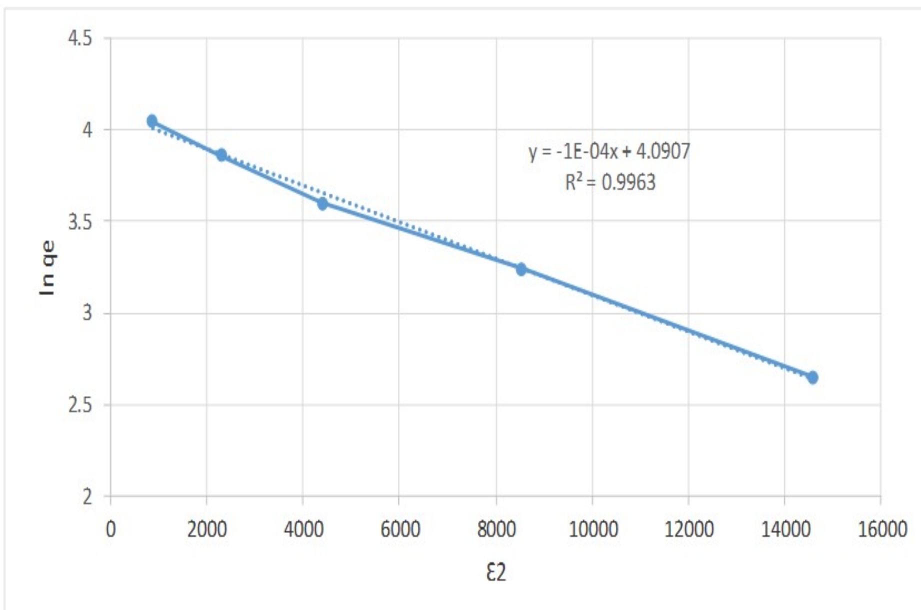


Figure (14): Copper adsorption isotherm based on Dubinin-Radushkovich model T = 50 °C

Due to the larger correlation coefficients of Dubin and Vraduskovich isotherms in all three temperatures, it can be stated that this isotherm is more consistent with the data. The constants of the Langmuir, Freundlich, and Dobinin-Radushkovich isotherms are obtained from the graphs 1/qe in terms of 1/Ce, Ln qe in terms of Ln Ce, and Ln qe in terms of 2ε, respectively

Table (5): Stability of Langmuir, Freundlich, and Dubinin-Radoshkovic isotherms at 0 °C

T=0 °C						
Langmuir		Freundlich		Dubinin-Radushkevich		
q_{max}(mg/g)	K_L (mg / L)	K_f(mg/g)	n	q_D	K	E(kj/mol)
0.403	468	1.101	1.38	43.85	0.0003	0.0408

Table (6): Stability of Langmuir and Freundlich, and Dubinin-Radushkovich isotherms at 25 °C

T=25 °C						
Langmuir		Freundlich		Dubinin-Radushkevich		
q_{max}(mg/g)	K_L (mg / L)	K_f(mg/g)	N	q_D	K	E(kj/mol)
0.516	1762	1.29	1.12	50.62	0.0002	0.05

Table (7): Stability of Langmuir, Freundlich, and Dubinin-Radoshkovich isotherms at 50 °C

T=50 °C						
Langmuir		Freundlich		Dubinin-Radushkevich		
q_{max}(mg/g)	K_L(mg / L)	K_f(mg/g)	N	q_D	K	E(kj/mol)
0.679	273	1.11	1.03	59.78	0.0001	0.0000002

In Langmuir model, a dimensionless coefficient called RL resolution factor is used to express the main feature and characteristic of this isotherm which can be used to evaluate the adsorption process.

Table (8): RL values for the Langmuir isotherm at 0 °C

C_0(mg/L)	200	350	500	650	800
R_L	0.066	0.097	0.176	0.234	0.299

Table (9): RL values for the Langmuir isotherm at 25 °C

C_0(mg/L)	200	350	500	650	800
R_L	0.019	0.028	0.034	0.054	0.066

Table (10): RL values for the Langmuir isotherm at 50 °C

C_0(mg/L)	200	350	500	650	800
R_L	0.068	0.084	0.109	0.155	0.268

Regarding the calculated RL values are between 0 and 1, it was concluded that the adsorption of copper ions from aqueous solutions by beta zeolite nanocrystals is a desirable process [36]. Likewise, from the n value obtained by Freundlich model, it can be concluded that the adsorption of copper ions from aqueous solutions by nanocrystals of beta zeolite is very desirable and the larger the n value, the better the adsorption occurs [38]. E values were calculated. Because the values obtained for E are less than 8 KJ / mol, adsorption takes place physically. [40]

Thermodynamic parameters

The thermodynamic equilibrium constant K0 is obtained by plotting Ln (qe / Ce) in terms of qe and extrapolating qe to zero (Figure (15). The constants and thermodynamic parameters for copper adsorption by nanoparticles of beta zeolite nanocrystals at 50 ° C are indicated in Table (11). Negative changes in the standard free energy Go adsorption illustrate that the adsorption reaction is a spontaneous process.

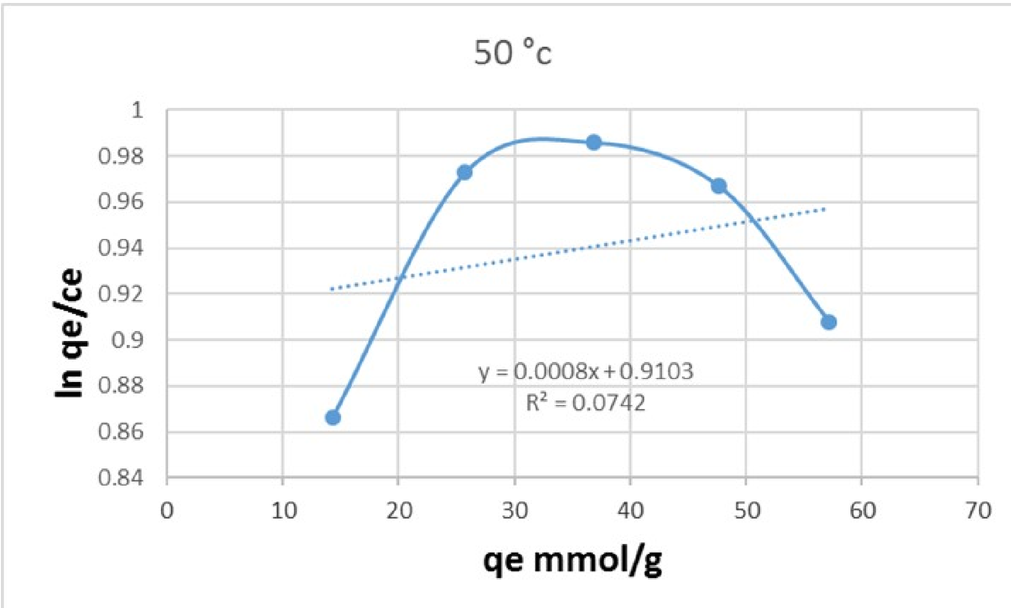


Figure (15): Thermodynamic equilibrium constant for beta zeolite nanocrystals

Table (11): Thermodynamic parameters for copper adsorption by beta zeolite nanocrystals

Beta zeolite nanocrystals	Thermodynamic constants
0.9103	K_0
-252.5	ΔG^0(KJ/mol)

Enthalpy and entropy for the adsorption process is obtained by plotting ^{o}G Δ in terms of T. Enthalpy and entropy for copper adsorption by beta zeolite nanocrystals at 0 °C, 25 °C and 50 °C are depicted in table (12). Negative values ^{o}G Δ at different temperatures indicate the spontaneous nature of the adsorption process and the magnitude ^{o}G Δ between -20 to zero indicates physical absorption and between -80 to -400 kj/mol means chemical adsorption.

Table (12): Calculation of enthalpy and entropy at temperatures of 0 ^{o}C, 25 ^{o}C, and 50 ^{o}C

ΔH (J/mol)	ΔS (J/mol.K)
-2945	-8.23

The negative enthalpy in the adsorption process indicates that this process is exothermic. As the temperature increases, the reaction progresses and, in this case, reduces the maximum adsorption capacity (qmax). The entropy changes in adsorption by the adsorbent are negative, demonstrating a reduction in the solid-solution surface irregularity during the adsorption process and a slight structural change in the adsorbent, results in reversibility of the adsorption operation.

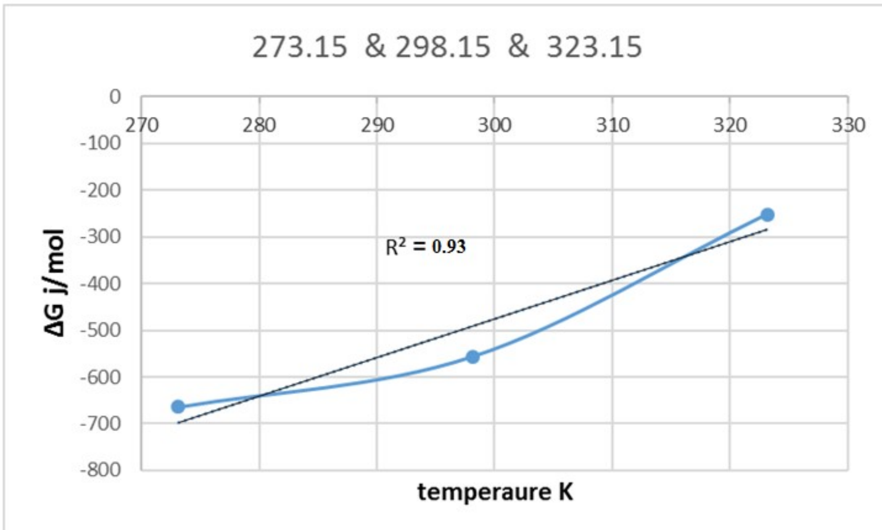


Figure (16): Calculates enthalpy and entropy

PH effect

The effect of pH on four different levels of 2, 3, 4, and 5 on the adsorption of copper (II) metal through beta zeolite nanocrystals was investigated in 60 min, for this purpose, 5 humans were removed and 20 cc of 500 ppm copper (II) solution and 0.1 g of adsorbent was poured into each of them (with an initial pH of 5) to the first, second, and third droplets, respectively, one drop (reached pH= 4) and 6 drops (which reached pH = 3) and 55 drops (which reached pH = 2) 0.1 N hydrochloric acid were added then, the pH values of each of these solutions were measured by pH meter.

In addition, all temperatures were measured in the same laboratory conditions (25 °C) by the pH meter itself. No introduction was added to the fourth human because it initially had a pH of 5. Add drop by drop to increase the pH value and check the conditions at high pH.

The human lids were covered and stirred for 60 minutes at room temperature with a stationary stirrer. Then, the samples were filtered through filter paper and then, the absorbance was measured by an atomic absorption spectrometer. These results indicate that the pH of the solution plays an important role in the adsorption of copper ions. As can be visible in figure (17), increasing pH, the percentage of removal of copper ions by nanoparticles of beta zeolite nanocrystals increases. And the highest percentage and capacity of copper adsorption occurs at pH = 5, which is the pH of initial solution at 25 °C.

At low pHs, H^+ ions compete with free copper ions for adsorption on active adsorbent sites, thus reducing the adsorption of copper ions. In contrast, as pH increases, competition between H^+ and $Cu2^+$ (protons and cations) decreases, leading to more copper adsorption, meaning that there are more negative groups for bonding to metal ions, which leads to more metal adsorption [50, 51]. At pHs over 5, copper begins to precipitate in the form of Cu $(OH)_2$ and cannot be tested at higher pHs. This means that metal cations begin to form hydroxide complexes or deposits of their own hydroxides, which reduce the adsorption of metal ions.

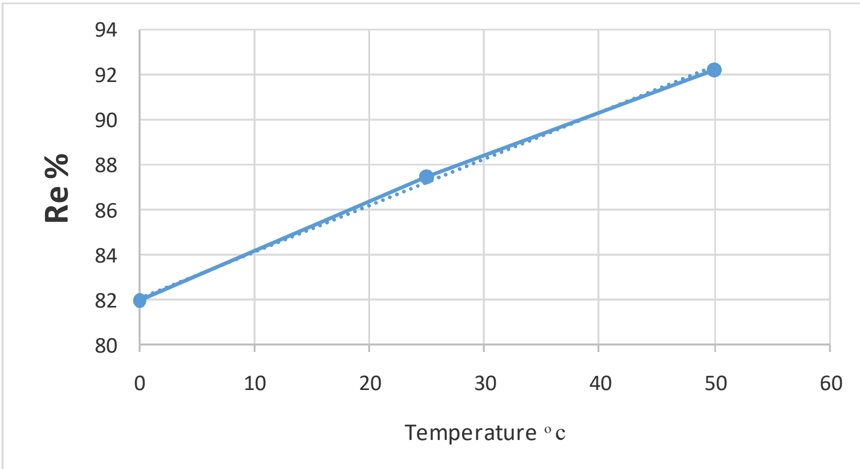


Figure (17): Effect of pH on copper uptake percentage (II)

Conclusion

a. Equilibrium time for copper uptake test (II) by beta nanocrystal zeolite was 60 minutes.
b. Experiments indicated that the percentage of copper removal (II) increases with increasing the amount of adsorbent and the optimal amount of adsorbent is 0.25 g. Adding more adsorbent to the solution has no effect on the adsorption process.
c. The process of adsorption of copper (II) by beta zeolite nanocrystals follows the quasi-second order traditional model.
d. The Dubinin-Radoshkovic model showed that the adsorption process performed by the adsorbent was physical adsorption.
e. The pH test illustrated that the highest percentage and capacity of copper adsorption occurs at pH = 5 and in acidic environments the amount of adsorption decreases.
f. The thermodynamic parameters of the standard free energy confirm the feasibility and spontaneity of the process.

According to the studies conducted in this scrutiny, it was indicated that beta zeolite nanocrystals prepared due to their high adsorption capacity and wide and also distinct application can be applied and be useful for economic and industrial applications in the wastewater treatment industry.

References

1. T. Butter, J. Evison, M. Chancock, I. Holland, F. Matis, K. Philipson, A. Sheike, A. Zouboulis, The Removal And Recavery Of Cadmium From Dilute Aqueous Solutions By Biosorption And Electrolysis At Laboratory Scale, Wat. Res. , 2 (1998) 400-406.
2. A. Bozorgian, S. Zarinabadi, A. Samimi, Preparation of Xanthan Magnetic Biocompatible Nano-Composite for Removal of Ni^ 2+ from Aqueous Solution. Chemical Methodologies. 4 (2020) 477-93.
3. H. Machida, J. Yamazaki.P. Motoi, Role Of Minerals In Carbonaceous Adsorbents For Removal Of Pb(II) Ions From Aqueous Solution, Sep. Purif. Technol ., 46 (2005) 88–94.

4. A. Bozorgian, Investigation and comparison of experimental data of ethylene dichloride adsorption by Bagasse with adsorption isotherm models, Chemical Review and Letters. 3 (2020) 79-85.
5. B. Ganavati., V. A. Kukareko, L. S. Tsybul'Skaya, and S. S. Perevoznikov. "Structural state and tribological properties of Co-P coatings, The Physics of Metals and Metallography, 115 (2014) 1037-1045.
6. A. Bozorgian, Analysis and simulating recuperator impact on the thermodynamic performance of the combined water-ammonia cycle, Progress in Chemical and Biochemical Research, 3 (2020) 169-79.
7. Б. Ганавати, В. А. Кукареко, Л. С. Цыбульская, and С. С. Перевозников, Структурное состояние и трибологические свойства покрытий Co-P." Физика металлов и металловедение 115 (2014) 1100.
8. M. Esmaeili Bidhendi, Z. Asadi, A. Bozorgian,A. Shahhoseini, MA. Gabris, S. Shahabuddin, R. Khanam, R. Saidur, New magnetic Co3O4/Fe3O4 doped polyaniline nanocomposite for the effective and rapid removal of nitrate ions from ground water samples. Environmental Progress & Sustainable Energy. (2020) 13306.
9. Б. Ганавати, В. А. Кукареко, Л. С. Цыбульская, and С. С. Перевозников. ,Структурное состояние и износостойкость покрытий Ni-P., Современные методы и технологии создания и обработки материалов: Сб. научных трудов. В (2014) 68-79.
10. A. Ahmadpoura, AH. Asla, N. Fallahb, Synthesis and comparison of spent caustic wastewater photocatalytic treatment efficiency with zinc oxide composite. Desalin. WATER Treat. 92 (2017) 275-290.
11. A. Leyva, J. Marrero, P. Smichowsky, D. Cicerone, Environmental Science Technology, 35 (2001) 3669.
12. A. Haghighi Asl, A. Ahmadpour, N. Fallah, Photocatalytic treatment of spent caustic wastewater in petrochemical industries. Advances in Environmental Technology. 2017 Apr 22;2(3):153-68.
13. В. А. Кукареко, Б. Ганавати, А. Г. Кононов. "Структура и дюрометрические свойства покрытий Ni-P, подвергнутых низкотемпературному отжигу." Механика машин, механизмов и материалов 3 (2014): 59-63.
14. M. Kalbasi, A. Hedayati, A. Ahmadpour, Optimization of Energy and Production Process Modeling of Zinc. World Applied Sciences Journal. 11 (2010) 228-234.
15. A. Bozorgian, Effect of Additives on Hydrate Formation, International Journal of Advanced Studies in Humanities and Social Science, 9 (2020) 229-240.
16. M. Ahmaruz Demibas, D.K. Sharma, "Adsorption Of Phenols From Waste Water", J. Colloid Inter Face Sci., 14(2005) 287.
17. K. Fuqiang Zhuang, T. Ruiqin, Sh. Wenfeng, Monodisperse magnetic hydroxyapatite /Fe3O4 microspheres for removal of lead(II) from aqueous solution", Journal of Alloys and Compounds, 637 (2015) 531–537.

HOW TO CITE THIS ARTICLE

Bijan Ghanavati and Alireza Bozorgian, Removal of Copper II from Industrial Effluent with Beta Zeolite Nanocrystals, Prog. Chem. Biochem. Res, 5(1) (2022) 53-67.

DOI: 10.22034/pcbr.2022.328704.1213

URL: http://www.pcbiochemres.com/article_147381.html