Research in Marine Sciences
Volume 5, Issue 2, 2020
Pages 718 - 730

Nickel metal organic framework efficiency in Cadmium removal from wastewater entering the Caspian Sea using response surface model

Leila Azizi Fard[1], Lida Salimi[2,*], Gholamreza Nabi-Bidhendi[3], Hossein Gafourian[4], and Majid Baghdadi[5]

[1]Ph.D Student, Department of Marine Environmental Engineering, North Tehran Branch, Islamic Azad University, Tehran, Iran

[2]Assistant Professor, Department of Marine Environmental Engineering, North Tehran Branch, Islamic Azad University, Tehran, Iran

[3]Professor, School of Environment, College of Engineering University of Tehran, Tehran, Iran

[4]Professor, Department of Marine Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

[5]Associate Professor, School of Environment, College of Engineering University of Tehran, Tehran, Iran

Received: 2020-02-22 *Accepted: 2020-05-30*

Abstract

In recent years, cadmium in wastewater and Industrial sludge has distributed in marine ecosystem and it has created many hazards to human and aquatics. Given this situation, present study aims to investigate the possibility of using Nickel based metal- organic framework as an efficient way to remove heavy metal cadmium from water. Additionally, the influence of important factors such as pH, time, and dose of absorbent has been examined in present study. The result demonstrates that all three elements have direct and significant influences on absorption process and the highest amount of cadmium removal is observed in pH =5.36 reaction time of 16.35min and absorbent dose of 0،03gr. In fact, pH plays a key role in the absorption of the element, and its interactions with the absorption time and dose can greatly increase the effectiveness of this method. According to the findings, increasing the contact time reduced the rate of adsorption efficiency and the adsorbent dose up to certain levels could have a significant effect on increasing the efficiency of the adsorption process. Also, Langmuir

*Corresponding Author's email: L_Salimi@iau-tnb.ac.ir

isotherm model has demonstrated highest conformity with laboratory results and the increase in absorbent is shown due to increase in contact surface between absorbent and adsorbate. Moreover, the application of Nickel-based metal organic framework is a cost-effective, practical, and suitable method to remove heavy metals ions like cadmium from marine ecosystems.

Keywords: Absorption; Nickel; Wastewater; Metal-organic frameworks; Pollution.

1. Introduction

The present paper was carried out to study the possibility of using nickel-based metal organic frameworks in absorption of cadmium toxic element in wastewater and to reduce the rate of heavy metals entering Caspian Sea in 2018. Nowadays, the environment pollution by different types of heavy metals entering to human and animal food Cycles has created serious challenges to the globe and its living organisms. Different experiments on various chemical industrial wastewaters in coastal area of Caspian Sea in Mazandaran province have shown significantly high concentration of cadmium. Thus, the main purpose of present study is to detoxify and remove cadmium from waste water and contaminated water entering Caspian Sea. The widespread industrial activities, excessive consumption of toxic materials, chemical fertilizer and waste water discharges into the environment are among the most important manifestations of this type of pollution. Unfortunately, it is increasingly growing in Iran. On the other hand, the aquatic environments like sea and oceans are not exceptions to these hazards. In parallel with the worldwide industrial and economic growth great deal of pollutants have entered into these aquatic environments whose disastrous effects will remain for a long period of time (Essien *et al*., 2009). Accordingly, Caspian Sea is one of the most unique enclosed aquatic ecosystems in the world that is of great importance for Iran. Since the last decades' heavy metals have been considered as the most important pollutant sources (Sohrabi *et al*., 2010). These heavy metals have threatened the health of human and aquatics living in the sea based on their toxicity, sustainability and the amount of their transformation into food chain (Ganjavi *et al*., 2010) Additionally, they entered to the sea through agricultural and industrial activities, excavations and fossil fuel transportation (Saeedi *et al*., 2010). Also, they can be highly influential in the quality of seawater. The dominant off-shores flows from Azerbaijan coast to Iran, oil industry activities and the presence of oil tarball can be considered as the factors affecting the increase in concentration of some of metals in seawater (Nasrabadi *et al*., 2010). Meanwhile, various methods are used to remove heavy metals from contaminated Waters. These methods can be generally divided into three physical, chemical, and biological categories. Among these methods, adsorption using a proper absorbent, being a physical method to remove heavy metals, have brought about very favourable results. It has been influential in removal of these elements from water and contaminated wastewaters. In this method, the area and porosity absorbent surface are considered effective elements in increasing the efficiency of absorption process. In the meantime, the porous nano-structures including nano-adsorbent and metal-organic frameworks drawing attention of researchers due to the large pore size, surface area and selective absorption of small molecules (Keenan, 2014). Additionally too much little inaccessible concentrated volume in metal-organic is among the most important properties of these materials (Noorpour *et al*., 2017). Although large surface area has been reported for active carbon and zeolits, a very little volume in frameworks has been shown with highest porosity (Morsali, 2013). The results of different studies indicates the high efficacy of metal organic framework, for instance, Sohrabi (2014) indicated that porous metal-organic frameworks including Thiol_functionalized nano-particles, copper, and trimesic acid compounds are useful for removing Mercury. In another study carried out by Zhu *et al*. (2012), it was found that Fe_ BTC metal organic framework synthesis using simple solvothermal method can be used as a suitable absorbent to remove arsenic from water samples. This group of materials which is classified as coordination polymers are hybrid organic mineral crystal. They are formed by linking metal ions including metals accompanied by organic ligands like carboxylate letrozolate and sulphoxylate through coordination bonds. In fact, three-dimensional polymers have permanent porosity known as metal-organic frameworks. They have gained more attention due to the inclusion of molecules with multiple functions inside their networks. In addition, metal ions with secondary structures or organic networks cannot only diversify the topology, but also the pores in the walls can serve multiple functions including catalytic applications, hydrogen storage, mechanism separating molecule from gaseous or liquid compounds (David *et al*., 2009; Soleimani, *et al*., 2016).

Given the intense necessity of heavy metals removal from aquatic ecosystems and high efficiency of metal-organic frameworks, the present study is carried out to investigate the application of these structures to remove toxic elements Cadmium. It has been viewed as one of the most dangerous heavy metals for human health entering into the Caspian Sea through various wastewaters.

2. Method and materials

Response surface methodology was used to design the experiments. This method is used in cases where the desired response is influenced by multiple variables. The main purpose is to optimise the response (Zhang *et al*., 2009; Ramakrishna and Susmita, 2012). Additionally, Central Composite Design (CCD) method was used to do experiments on Cadmium heavy metal absorption. Thus, the main advantage of using response surface method is the reduced number of experiments required to evaluate the effects of process variable and their interactions and response (Jeong and Park, 2006). Thus, the synthetic wastewater consisted of Cadmium was built.

At first, to prepare Cadmium standard solution 1.6g of cadmium Nitrate powder was dissolved in 10cc of 69% concentrated Nitric acid and then the solution was brought up to the volume into 1000ml volumetric flask. Therefore, 1000mg/lit Cadmium standard solution was synthesized and subsequent solutions were prepared at desired concentration by diluting the certain volume of original solution (Karimi Takanlu *et al*., 2014).

In present study, Ni_MoF was synthesized by dissolving 2.27mmol Cyanoguanidine linker and 3.56mmol Nickel nitrate hexahydrate in

Table 1. Investigated variables

Investigating variables	Numerical values
Contact time (min)	6.59, 10, 15, 20, 23.41
pH	3/3, 4, 5, 6, 6/67
Absorption does (gr)	0/013, 0/02, 0/03, 0/04, 0/046

25mmol water and the mixture was transferred to autoclave. Heating was carried out in heating furnace at 110c for 22h.Then, the solution was washed out by distilled water, and finally the resulting product dried in the oven at 60c for 24h (Zhao *et al.*, 2018).

In this study, there were three numerical variables including adsorbent, contact time, adsorbent dose and pH, the effect of each of which on the adsorbent Nickel-based metal organic framework and subsequently the rate of Cadmium separation from synthetic wastewater was investigated. Thus, in designing the experiments the desired response was Cadmium separation. The variables studied in these experiments can be seen in Table 1. It should be noted that each of these parameters and the range considered for use in the reaction of Cadmium adsorption from wastewater was selected based on the result of similar studies by other researchers like Gatabi *et al*. (2016) and Feng *et al*. (2010) and preliminary experiments. Given the above-mentioned materials (Table 1), fewer experiments are required than full factorial design. After analysis, the results of final experiments efficiency presented using design _expert software. The suggested model by this software was based on the highest degree and the correlation coefficient higher than quadratics. In addition, Freundlich and Langmuir isotherm models (Feng *et al*., 2010; Gatabi *et al*., 2016) were used to describe the experimental data and adsorbent_adsorbate behaviour that shows the relationship between the amount of metal in solution and metal absorbed on adsorbent in a constant temperature.

The results of this study were evaluated as interactions between variables. So, when one factor at another level causes different changes in response, then, there is an interaction between two factors. The existence of this interaction also means that they can affect the response both independently and simultaneously, although the simultaneous effect of factors on the response has a different effect from the effect of an independent factor on the response (Anderson, 1987; Millar and Millar, 2000).

3. Results and Discussion

According to the results of Figure 1, the simultaneous effect of pH and contact time on a fixed dose of Nickel metal-organic adsorbent frames indicates that the rate of Cadmium removal increased with increasing solution pH and contact time under certain absorbent dose. With increased contact time, Nickel-based metal organic framework shows higher removal efficiency in aqueous medium. As it is evident, removal rate is stronger, therefore, contact time has a significant effect on cadmium removal on Nickel-based metal organic framework, and plot performance is more like a saddle form.

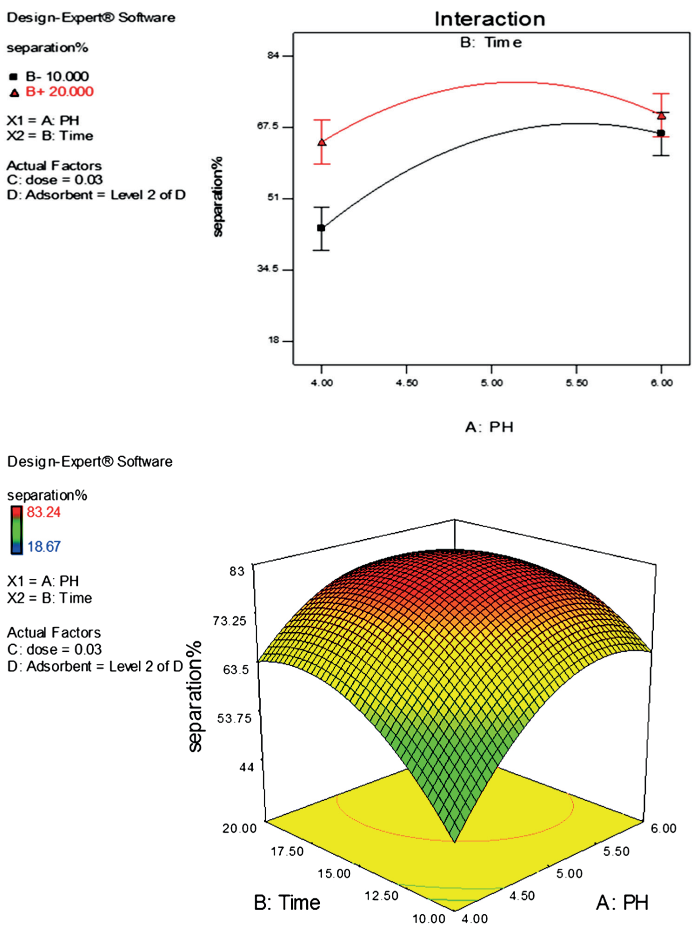

Figure 1. The interaction of PH and time on Cadmium ion adsorption amount by Nickel-based metal organic framework

Chart of interactions between major factors is a way to better understand the interactions between agents. Figures 1 to 3 show the interaction between the main factors. When one factor at the other agent level causes different changes in response, then there is an interaction between two factors. Interaction means that factors can affect the response both independently and simultaneously. The simultaneous effect of factors on response has a different effect than the effect of an independent factor on response. Non-parallel lines and curved surfaces in three-dimensional scales indicate strong interaction between agents and almost parallel lines, X-shaped and non-curved surfaces indicate poor interaction between agents. Another conclusion that can be drawn from these diagrams is that the effect of one factor on the response in the presence of another factor also depends on the level of that factor (Anderson 1987; Millar and Millar, 2000).

According to the findings of present study, the final concentration of Cadmium decreased very rapidly with increasing pH, but it decreased very slowly with further increasing pH up to 5, and final concentration increased. Absorption efficiency decreased at pH above 5. In fact, the competition between Hydroxide ion present in the solution and absorbent sites for cadmium metal ion deposition actually creates metal organic frameworks bonds which resulted in a steady state in the metal present in the solution and it in turn reduced metal transfer to absorbent and reduced adsorption efficiency (Kadirvelu and Namasivayam, 2003). Therefore, it can be said that binding of metal ions by functional group is strongly affected by pH, so the pH of aqueous solution is a very important parameter in adsorption process.

Determination of optimum pH for adsorption of metal ions is dependent on the type of ion and adsorbent used. The effect of this parameter is directly dependent on the ability of the hydrogen ions to compete with the adsorbent ion on the active sites of adsorbent surface. Figure 2 shows the effect of PH and adsorbent dose in constant time for the Nickel-based metal organic framework absorption. With increase in pH and adsorbent does during a specific time of absorption, Cadmium removal is decreased. However, the increase is more significant for contact time and variation curve will be subsequently in saddle form.

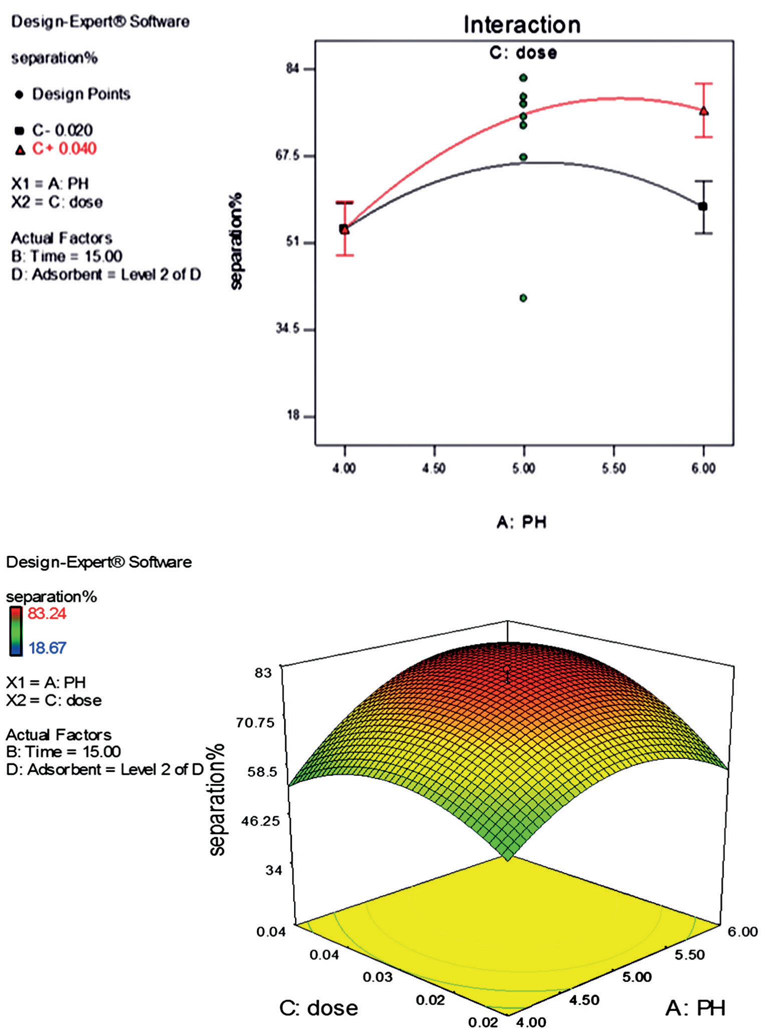

Figure 2. The interaction of PH and adsorption dose on Cadmium ion adsorption amount by Nickel-based metal organic framework

Additionally, the increase in absorption dose will to some extent result in increasing cadmium removal efficiency. It has been also observed that increasing the adsorbent dose in the feed increased the concentration gradient between the fluid and solid mass which results in an increase in rate of mass transfer and Cadmium removal in aqueous medium.

Adsorbent dose has been viewed as an important parameter in adsorption and the determination of optimal adsorbent amount will reduce waste water treatment cost and pollution and sludge (Kadirvelu and Namasivayam, 2003). Regarding Cadmium ion absorption by Nickel metal organic framework the gradual increase in adsorbent reduces the secondary concentration of cadmium ion and subsequently absorption efficiency is increased. However, further increase in absorbent is accompanied by cadmium removal rate increase and the increase takes place with less asleep and speed and further absorbent increase will not result

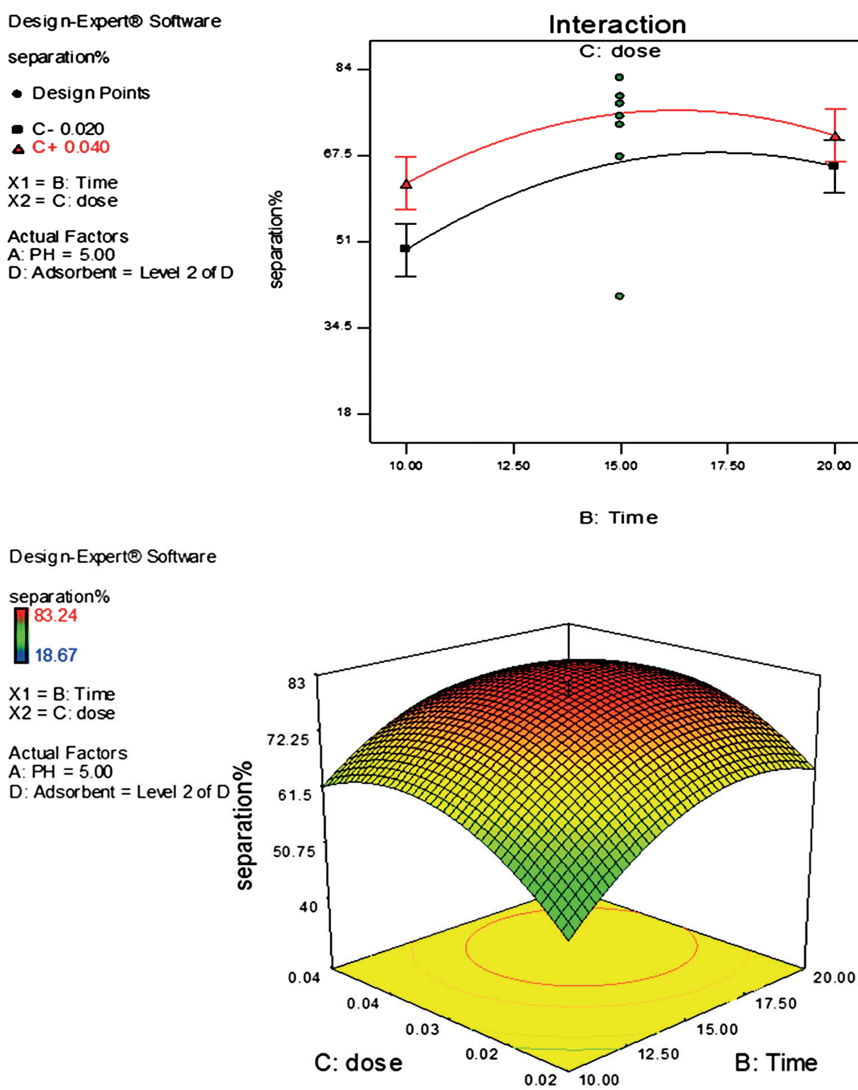

Figure 3. The interaction of adsorbent dose and time on Cadmium adsorbent by nickel based metal organic framework

in more efficiency. It can be said that the reason for increased efficiency with increasing absorbent mass is that more sites are available for absorbent (Kadirvelu and Namasivayam, 2003). However, more adsorbent causes active sites of absorbent experiences a small degree of overlap. Subsequently, it reduces the number of active sites. Increase in absorbent concentration results in increase in number of unsaturated sites. Another reason for the decrease in adsorption capacity or decrease in percentages of cadmium removal from the aqueous medium is reduction in contingency of adsorbent collision with adsorbate. The contingency was due to the aggregation of adsorbent which eventually reduces the surface area and increases the energy distribution path length (El-Ashtoukhy *et al.*, 2008).

As it is shown in Figure 3, with the increase in adsorbent dose and contact time at a constant pH, cadmium removal rate of Nickel-based metal-organic framework is constantly increased. However, the increase is more noticeable for time changes at a specific pH. Meanwhile, the removal efficiency is increased with adsorbent dose. According to the figure, at a particular pH, cadmium removal variation range is changed with contact time changes and it is continuously increase with contact time it indicates that contact time. In addition, it is continuously increased with contact time. Considering absorbent dose, it indicates that contact time factor is significant.

According to the results, Cadmium ion adsorption process on absorbent surface is divided into a slow and fast categories, where the first phase is a slowly carried out for metal ion internal penetration. In the second phase, active bonding groups are placed on adsorbents particles cell walls with more speed. Thus, the high initial adsorption speed is due to surface bonds between these active groups with metal ions and active sites frequency reduction result in metal absorption efficiency speed. Furthermore, metal ion quick phase by adsorption is the result of a lot of pores and cavity and the structure of pores existing in adsorbent which allows rapid penetration for metal adsorption on bonding sites (Saeed *et al.*, 2005).Therefore, in heavy metals adsorption the efficiency is decreased with contact time increase. On the next stage, the goal was to find the model which describes experimental data behaviors, to this end Freundlich _

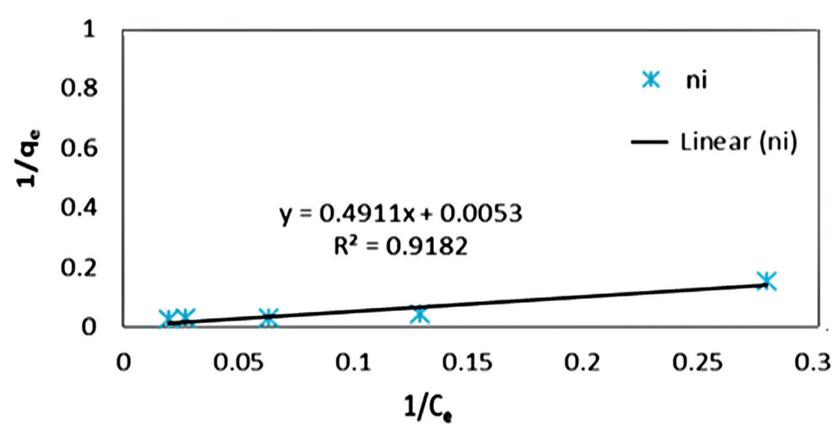

Figure 4. Langmuir isotherm model with experimental data for cadmium ion adsorption on Nickel-based metal organic framework

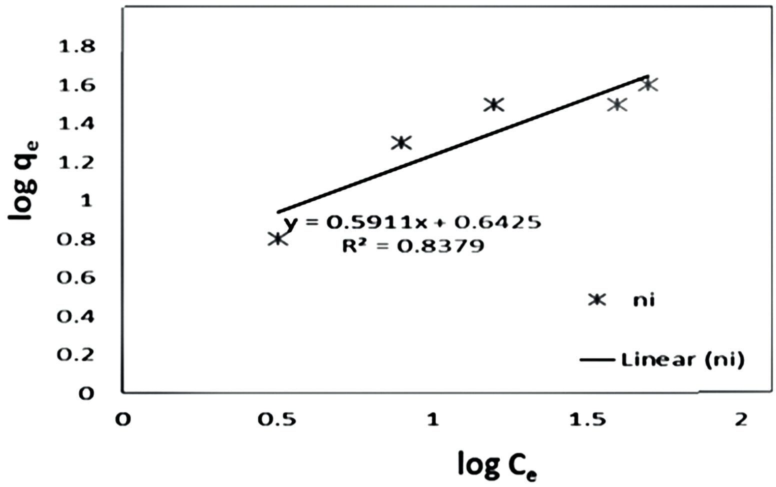

Figure 5. Freundlich isotherm model with experimental data of Cadmium adsorption on Nickel-based metal _organic framework

langmuir isotherm models were used to explain adsorbent_adsorbate behavior. According to Figure 4, the balanced experimental data in vitro with pH =6, contact time of 15 minutes, 15 mg/l adsorbent, and temperature of 25 ºC showed great consistency with relatively high correlative coefficient on Langmuir linear plot. Moreover, it can be argued that Langmuir isothermal is a suitable model to describe cadmium adsorption mechanism on adsorbent on the other hand it indicates that Langmuir theorem govern on homogeneous distribution of active sites on Nickel-based metal organic framework and monolayer coverage of Cadmium ion on the surface.

In addition, according to Figure 5, balanced experimental data in laboratory condition of pH=6, contact time 25 min, adsorbent dose 15mg/l and temperature 25 ºC showed acceptable agreement with good correlation coefficient on Freundlich linear plot. Therefore, it can be concluded that Freundlich isothermal is a suitable model to describe cadmium adsorption mechanism on Nickel based metal organic framework.

To kinetically study of metal ions adsorption on different adsorbent 25ml of Cadmium solution with respectively 6 and 5 mg/l concentrations and pH=6 was dissolved with 15 mg of different adsorbent and the mixture was stirred for 1 to 25 minutes. Then, the sample suspension was centrifuged and the amount of ion adsorbed on different adsorbents was calibrated. The speed of metal ions adsorption was measured based on kinetic equations psudeo first order (Equation 1) and psudeo second order.

$$1n\ (q_e - q_t) = 1n\ (q_e) - k_1 t \qquad (1)$$

$$t / q_t = 1/ h + 1/ q_e t \qquad (2)$$

One of the most important factors to design absorprion system is the prediction of absorprion speed process controlled by system kinetics. Absorprion kinetics depends on the physical and chemical properties of absorbent substance and absorbent which affect adsorption mechanism .Given the results of psuedo first order kinetics based on Langmuir equation, it has been indicated that experimental data with pseudo first order kinetics are not completely overlapped. On the same line, therefore they have lower correlation coefficient. As it is shown in fig 6 psuedo second order kinetics, given the equation of cadmium ion adsorprion, displays better performance on different absorbents. Additionally, experimental data are aligned on one line and show higher correlation coefficient. Thus, it can be concluded that the adsorption is carried out chemically and it follows pseudo second order kinetics. Actually, pseudo second order kinetics is able to explain different factors including liquid components penetration, adsorption, and

Table 2. Data used for kinetic analysis of pseudo first order (left) second order (right) to adsorb cadmium on Nickel-based metal organic framework

Time	Log ($q_e - q_t$)	t/q_t
1	0.91	0.19
3	0.71	0.32
5	0.65	0.63
6	0.61	0.82
10	0.38	1.04
15	0.35	1.54
20	0.19	1.86
25	0.003	2.31

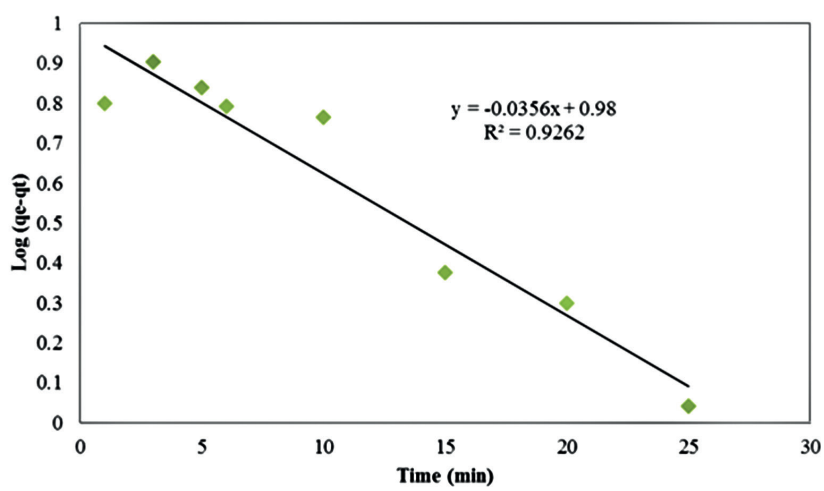

Figure 6. psuedo first order kinetic model with experimental data using nickel based metal organic framework in 25 °C and pH=6 for Cadmium ion.

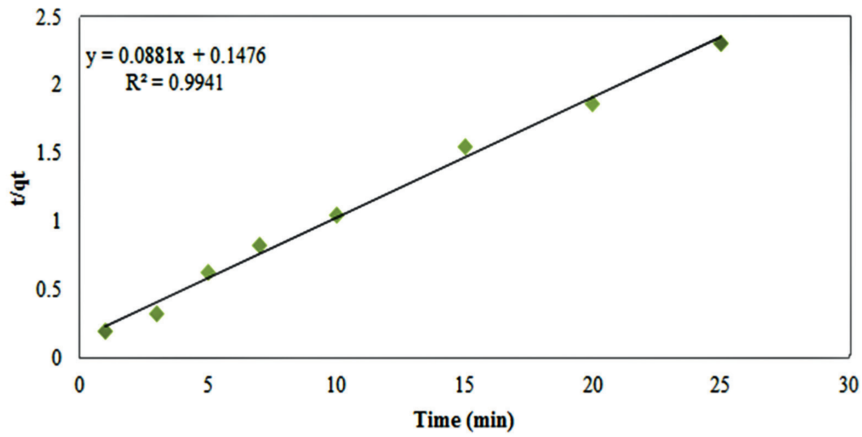

Figure 7. Psuedo second order exprimental data using nickel based metal organic kinitic model with framework in 25 °C and pH = 6 for Cadmium ions.

internal penetration of particles. Therefore, it improves our understanding of cadmium absorption mechanism by absorbent.

Table 2. Data used for kinetic analysis of pseudo first order (left) second order (right) to adsorb cadmium on Nickel-based metal organic framework

Conclusion

In recent years, the entrance of different wastewater in to the sea and consequently contamination of aquatic ecosystems by different heavy metals including cadmium has been intensely growing. Thus, the use of new methods like metal _organic frameworks can play significant role in adsorption of these heavy metals in waste water and contaminated water. The results of present study indicate that Nickel _based metal_organic frameworks play an important role in cadmium removal from contaminated waste water. Factors like pH, absorbent dose, and type of absorbent have direct relationship with adsorption efficiency. The higher solution pH, the better is adsorption efficiency. Also, the ideal efficiency is possible at pH=5.36 The highest amount of removal has been reported at interaction time of 16.35min and absorbent dose 0.03gr.According to the results the extreme increase of absorbent round and its duration has a negative influence on adsorption process. In Addition, adsorption process obeys Langmuir isotherm model which indicates monolayer adsorption. It shows positive effect of nickel -based metal_organic frameworks of absorbents to remove cadmium ions. The kinetic analysis of cadmium ion adsorption by this type of adsorbent showed that the adsorption process follows the second-order synthetics.

References

Anderson, R. 1987. Practical Statistics for Analytical Chemists. New Jersey: Princeton.

David, F., Aguado, S., and Pinel, C. 2009. Metal–organic frameworks: opportunities for catalysis. Angewandte Chemie International Edition 48.41: 7502-7513.

El-Ashtoukhy, E. S., Amin, N. K., and Abdelwahab, O. 2008. Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. Desalination, 223(1-3): 162-173.

Essien, J., Antai, S., and Olajire, A. 2009. Distribution, seasonal variations, and eco toxicological significance of heavy metals in sediments of cross river estuary mangrove swamp. Water Air and Soil Pollution, 197: 91-100.

Feng, Y., Gong, J. L., Zeng, G. M., Niu, Q. Y., Zhang, H. Y., and et al. 2010. Adsorption of Cd (II) and Zn (II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents. Chemical Engineering Journal, 162(2): 487-494.

Ganjavi, M., Ezzatpanah, H., Givianrad, M. H., and Shams, A. 2010. Effect of canned tuna fish processing steps on lead and cadmium contents of Iranian tuna fish. Food chemistry, 118(3): 525-528.

Gatabi, M. P., Moghaddam, H. M., and Ghorbani, M. 2016. Efficient removal of cadmium using magnetic multi-walled carbon nanotube nanoadsorbents: equilibrium, kinetic, and thermodynamic study. Journal of Nanoparticle Research, 18(7): 189-195.

Jeong, G.T., and Park, D.H. 2006. Response surface methodological approach for optimization of enzymatic synthesis of sorbitan methacrylate. Enzyme and Microbial Technology, 39: 381-386.

Kadirvelu, K., and Namasivayam, C. 2003. Activated carbon from coconut coirpith as metal adsorbent: adsorption of Cd (II) from aqueous solution. Advances in Environmental Research, 7(2): 471-478.

Karimi Takanlu, L., Farzadkia, M., Mahvi, A. H., Esrafily, A., and Golshan, M. 2014. Iranian Journal of Health and Environment, 7: 171-184.

Keenan, L. 2014. Post-synthetic modification of metal-organic frameworks (Doctoral dissertation, University of Bath).

Millar, J., and Millar, J. 2000. Statistics and Chemometrics for Analytical Chemistry. Statistics and Chemometrics for Analytical Chemistry.

Morsali, A. 2013. The porous metal-organic frameworks.Tarbiat Modares University publications.

Nasrabadi, T., Bidhendi, G. N., Karbassi, A., and Mehrdadi, N. 2010. Evaluating the efficiency of sediment metal pollution indices in interpreting the pollution of Haraz River sediments, southern Caspian Sea basin. Environmental monitoring and assessment, 171(1-4): 395-410.

Noorpour, Z., Qanbari Pakdehi, Sh., and Rashidi, A. 2017. A review on metal organic nano_adsorbents and their application in Dehumidification process .Gas Engineering Journal, 5: 29-39

Ramakrishna, G., and Susmita, M. 2012. Application of response surface methodology for optimization of Cr (III) and Cr (VI) adsorption on commercial activated carbons. Research Journal of Chemical Sciences, 2(2): 40-48.

Saeed, A., Akhter, M. W., and Iqbal, M. 2005. Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. Separation and purification technology, 45(1): 25-31.

Saeedi ,M., Abesi, A., and Jamshidi, A. 2010.The investigation of heavy metal contamination and oil pollutant in surface sediments in Caspian Sea southeast using existing indice.Ecology Journal, 36 (53): 21-38.

Sohrabi, M. R. 2014. Preconcentration of mercury (II) using a thiol-functionalized metal-organic framework nanocomposite as a sorbent. Microchimica Acta, 181(3-4): 435-444.

Sohrabi, T., Ismail, A., and Nabavi, M. B. 2010. Distribution and normalization of some metals in surface sediments from South Caspian Sea. Bulletin of environmental contamination and toxicology, 85(5): 502-508.

Soleimani, H. A., Meftahi, M., and Nikfarjam, R. 2016. Metal_Organic framework as a new generation of Heterogeneous catalysis and the study of catalyst effect of these compounds in ocidation of alkanes ,alcohol and organic solfid. The first national conference of future of engineering and technology, University of science and culture, Iran.

Zhang, Z., Peng, J., Qu, W., Zhang, L., Zhang, Z., Li, W., and Wan, R. 2009. Regeneration of high-performance activated carbon from spent catalyst: optimization using response surface methodology. Journal of the Taiwan Institute of Chemical Engineers, 40(5): 541-548.

Zhao, X., Pachfule, P., Li, S., Simke, J. R. J., Schmidt, J., and Thomas, A. 2018. Bifunctional Electrocatalysts for Overall Water Splitting from an Iron/Nickel-Based Bimetallic Metal–Organic Framework/Dicyandiamide Composite. Angewandte Chemie International Edition, 57(29): 8921-8926.

Zhu, B. J., Yu, X. Y., Jia, Y., Peng, F. M., Sun, B., Zhang, M. Y., and et al. 2012. Iron and 1, 3, 5-benzenetricarboxylic metal–organic coordination polymers prepared by solvothermal method and their application in efficient As (V) removal from aqueous solutions. The Journal of Physical Chemistry C, 116(15): 8601-8607.