

# PRECONCENTRATION OF Ni (II) ION FROM AQUEOUS SOLUTIONS BY MODIFIED SYNTHETIC COPOLYMER WITH ADSORPTION ISOTHERM STUDIES

Tahir Javadzade<sup>1,2</sup>, Fidan Bahmanova<sup>1</sup>, Famil Chiragov<sup>1</sup>

<sup>1</sup>Baku State University, chemistry, analytical chemistry, Baku, Azerbaijan

<sup>2</sup>Khazar University, chemistry, Baku, Azerbaijan

*Received: 16 november 2024*

*Accepted: 09 december 2024*

*Published: 24 december 2024*

---

This work is dedicated to adsorption study of Ni (II) ions by synthetic adsorbent based on maleic anhydride styrene copolymer and 1,4-bis[2-(prop-1-enil) fenoksi]butan modified with N, N'-diisopropyl thiourea. During work different parameters affecting adsorption process were investigated: influence of pH, contact time, ionic strength and initial metal ion concentration. It was found that maximum adsorption capacity is observed at pH=3 and is equal to 19.5 mg/g. In order to describe adsorption process different adsorption isotherm models were studied and the results were found to be consistent with the Langmuir model. Dubinin-Raduskhevic model was investigated to show that physical adsorption takes place in the system adsorbent-adsorbate. The present work also includes desorption studies.

**Keywords:** adsorption, Ni (II), copolymer, isotherm, preconcentration

---

## INTRODUCTION

Water is a vital natural resource for nature yet in our time pollution is as a deadly concern and a serious worldwide issue [1, 2]. Inorganic contaminants, particularly heavy metals, stand out from the others [3]. Thus, due to their high toxicity and inability to be broken down and removed biologically, this category of inorganic pollutants is always under scrutiny[4]. The widespread usage of these metals in a variety of agricultural and industrial applications has polluted the environment. This group of metals also contains nickel. Nickel is widely utilized in a variety of industrial processes, including electroplating, ceramic product painting, mineral processing and stainless steel manufacture, batteries, nonferrous metal coinage, metal alloys, and so on [5,6]. Nickel's ubiquitous use results in enormous releases into the aquatic environment via industrial waste and nickel-containing compounds in wastewater [7].

One of the biggest challenges facing humanity today is the development of new methods for removing nickel from aqueous media. Adsorption is one of the most efficient, cost-effective, and effective ways to remove heavy metals from solution. Adsorption has demonstrated remarkable efficiency in the separation of metal ions, including nickel. Adsorption is already employed in a variety of industrial processes, including the separation of nickel from wastewater, due to its low cost, speed, simplicity of application, and efficiency even at low concentrations [8].

The goal of the present research is to investigate the sorption of Ni(II) ions from aqueous solutions using a polymer chelating sorbent based on a copolymer of maleic anhydride and 1,4-bis[2-(prop-1-enil) fenoksi] butan with styrene, and to modify this sorbent with a novel thiourea derivative to increase its sorption capacity. The features of sorption were investigated, particularly pH, duration, ionic strength, and the starting concentration of metal

ions. The desorption process was also examined, and the best eluent was identified. Various adsorption isotherms have been investigated.

## MATERIALS AND METHODS

**Devices.** The optical densities of the solutions were measured with a KFK-3 spectrophotometer using 1 cm thick quartz cuvettes. The pH values of the solutions were measured using a pH-meter equipped with a pH-121 standard solution with a glass electrode. Distilled water was obtained through a-10 device.

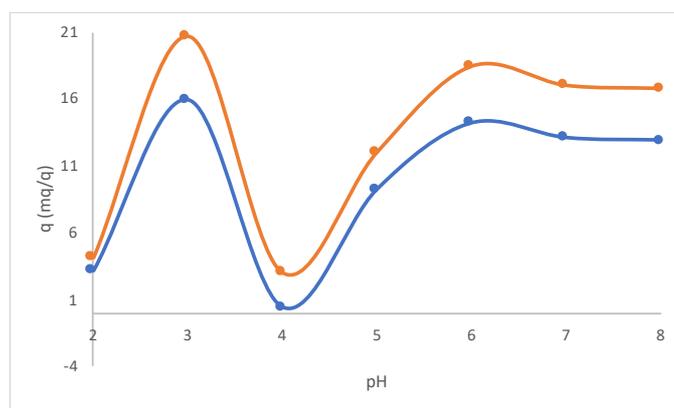
**Preparation of solution.** All the reagents used are of high purity. The  $10^{-2}$  M solution of nickel was obtained by dissolving 0.2628 g of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  in 100 ml of distilled water. Different concentrations of Ni(II) solution was prepared by diluting  $10^{-2}$  stock solution. The buffer solutions (pH 3-8) used during the experiment were obtained by mixing appropriate amounts of 0.1 M  $\text{CH}_3\text{COOH}$  and  $\text{NH}_4\text{OH}$  and for pH 1-2 HCl was used.

**Sorption experiments.** Ni (II) ion sorption tests were conducted at room temperature. In each experiment, 50 mL conical flasks were filled with 2 mL of a known concentration of metal ions ( $5 \cdot 10^{-3}$  mol/L). Each flask was treated with 30 mg of sorbent and the proper pH. After storing the combination for 24 hours, filter paper was used to separate the liquid phase from the solid phase.

Then 1 ml of sample was taken from each flask and diluted with a buffer solution of pH 5. The final concentration of Ni (II) ions was 2,2',2'',2'''-((1,1-Dioxo-2,1λ6-benzoxathiole - 3,3(1H)-diyl)bis[(6-hydroxy-5-methyl-3,1-phenylene)methylenenitrilo])tetraacetic acid reagent (R) was measured using KFK-3 photoelectrocolorimeter at wavelength  $\lambda=580$  nm .

## RESULTS AND DISCUSSIONS

**Effect of pH on the sorption of Ni (II).** The pH of the solution is an essential factor influencing the sorption capacity of Ni(II), since it influences the stability of nickel in the solution and can vary its forms in the solution; for example, at different pH values, nickel in solution takes the  $\text{Ni}^{2+}$ ,  $\text{Ni}(\text{OH})^+$ ,  $\text{Ni}(\text{OH})_2$ , and  $\text{Ni}(\text{OH})^{3-}$  forms [9]. Furthermore, it can alter the electrical characteristics of the sorbent surface. At pH levels over 8,  $\text{Ni}^{2+}$  is the most common type of nickel detected. The pH of the original solution was set between 2.0 and 8.0 to avoid hydroxide production during sorption. The image below (Fig. 1) shows the influence of solution pH on nickel sorption.



**Fig.1.** Effect of pH

The experiment revealed that the largest proportion of Ni (II) ions were captured from the solution at pH 3 same as after modification. So, all future investigations utilized this pH value.

**Effect of time on the sorption of metal ions.** The study found that by 60 minutes, the sorption had already stabilized for both cases.

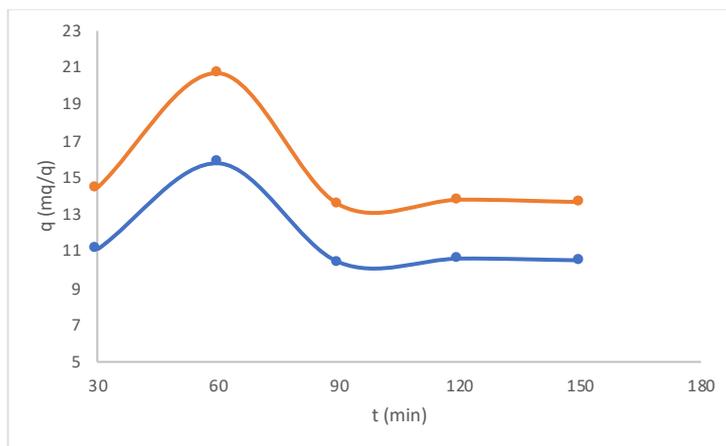


Fig.2. Effect of time

**Desorption process.** In this research, we have studied the effect of different acids and its concentration on the desorption process. The desorption study was carried out using  $0.5 \text{ mol}\cdot\text{L}^{-1}$  solutions of  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{CH}_3\text{COOH}$  acids. The research results showed that the maximum desorption capacity on Ni(II) ions is  $0.5 \text{ mol/L}$   $\text{HNO}_3$  solution.

**Adsorption isotherm.** For a better understanding of the adsorption process, the relevant adsorption equilibrium must be used in the study. The nature of the adsorbate-adsorbent interaction is described by adsorption equilibrium. In the present study the equilibrium data were analyzed using the Langmuir, Freundlich and Dubinin-Radushkevich isotherms.

**Langmuir isotherm.** The Langmuir equation is commonly used to determine the sorption equilibrium. The Langmuir isotherm assumes that all portions of the sorbent's surface are comparable, or homogenous. In this scenario, metal ion sorption takes place on a homogenous surface with no interaction between evenly deposited ions. presupposes that a molecule's capacity to adsorb at a specific site is independent of the occupancy of nearby sites, that adsorption is reversible, and that the adsorbed molecule is incapable of migrating over the surface or interacting with its neighbor [11].

The main characteristic of the Langmuir isotherm can be represented by a separation factor called the equilibrium parameter ( $R_L$ ) and has the following form:

$$R_L = \frac{1}{1 + bC_0}$$

Here,  $b$  is the Langmuir constant ( $\text{L}/\text{mmol}$ ),  $C_0$  is the initial adsorbate concentration ( $\text{mmol}/\text{L}$ ). The  $R_L$  value indicates the type of isotherm. A value between 0 and 1 indicates a favorable adsorption process.

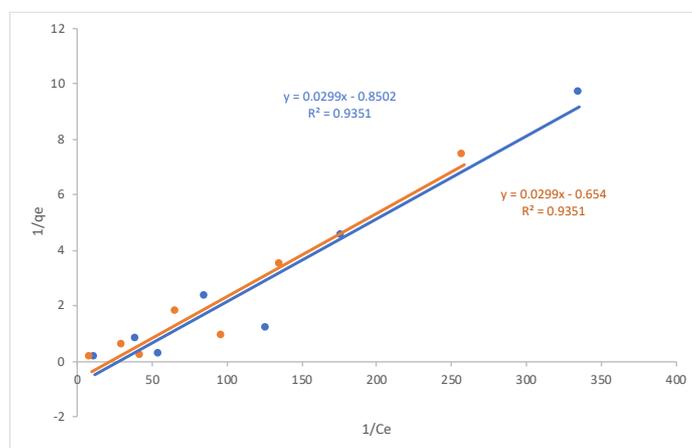
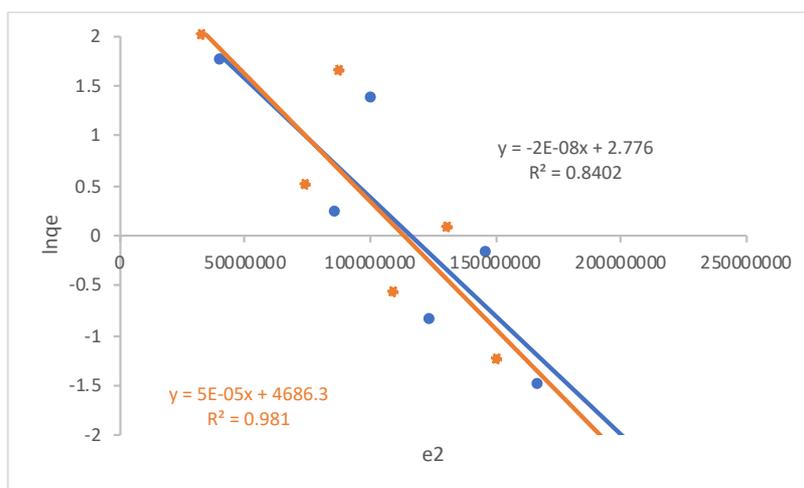


Fig.3. Langmuir isotherm model

The results show that the  $R_L$  is between 0 and 1 and equal to 0.99 when only sorbent is used and after modification, which indicates that the adsorption is favorable under the experimental conditions determined by the Langmuir model. Also, the value of the regression coefficient is  $R^2=0.9351$  for both cases indicating that this isotherm model is in good agreement with the experimental adsorption data (Fig.3).

**Dubinin-Radushkevich (D-R) isotherm.** The Dubinin-Radushkevich (D-R) isotherm model is applied to estimate porosity, free energy, and sorption characteristics. It is successfully applied for the adsorption of heterogeneous system including solid and liquid. This model is considered more general than the Langmuir model, because in its derivation a homogeneous surface and a constant sorption potential are not assumed [14].

The  $R^2$  value is equal to 0.8402 and 0.981. From the isotherm plot we can calculate that in our both case there the physical adsorption (Fig. 4).



**Fig.4.** Dubinin-Radushkevich (D-R) isotherm

## CONCLUSION

Subsequently the results of our experiments suggest that this unique functionalized sorbent may effectively remove nickel from water. Adsorption capacity rises by roughly 20% following sorbent modification. Several models were used to analyze adsorption isotherms, and the Langmuir model was found to suit the data best.

## REFERENCES

- [1] Xu, X., Yang, H., Li, C. Theoretical Model and Actual Characteristics of Air Pollution Affecting Health Cost: A Review. *Int. J. Environ. Res. Public Health*, 2022, <https://doi.org/10.3390/ijerph19063532>
- [2] Lin L, Yang H., Xu X. Effects of Water Pollution on Human Health and Disease Heterogeneity: A Review. *Front. Environ. Sci.* 10:880246. <https://doi:10.3389/fenvs.2022.880246>
- [3] Wasewar, K., Singh, S., Kansal, S.K. Process intensification of treatment of inorganic water pollutants. *Inorganic Pollutants in Water 2020*, P.245-271. <https://doi.org/10.1016/B978-0-12-818965-8.00013-5>
- [4] Yu S., Tang, H., Zhang, D., Wang, S., Qiu, M., Song, G., Fu, D., Hu, B., Wang, X. M. Xenex as emerging nanomaterials in water purification and environmental remediation. *Science of The Total Environment* Vol.811, 10 March 2022, <https://doi.org/10.1016/j.scitotenv.2021.152280>
- [5] Montazer-Rahmati, M.M., Rabbani, P., Abdolali, A., Keshtkar, A.R. Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact

- and chemically modified brown algae, *J. Hazard. Mat.* 185, 401–407, 2011. <https://doi.org/10.1016/j.jhazmat.2010.09.047>
- [6] Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J. Heavy Metal Toxicity and the Environment. In: Luch, A. (eds) *Molecular, Clinical and Environmental Toxicology. Experientia Supplementum*, vol 101. Springer, Basel. [https://doi.org/10.1007/978-3-7643-8340-4\\_6](https://doi.org/10.1007/978-3-7643-8340-4_6)
- [7] Islam, A., Awual, R., Angove, M.J. A review on nickel (II) adsorption in single and binary component systems and future path. *Journal of Environmental Chemical Engineering* Vol. 7, Issue 5, Oct. 2019. <https://doi.org/10.1016/j.jece.2019.103305>
- [8] Topare, N., Vinayak, S., Wadgaonkar, S. A review on application of low-cost adsorbents for heavy metals removal from wastewater. Volume 77, Part 1, 2023, Pages 8-18. <https://doi.org/10.1016/j.matpr.2022.08.450>.
- [9] Gonsalvesh, L., Marinov, S.P., Gryglewicz, G., Carleer, R., Yperman, J. Preparation, characterization and application of polystyrene based activated carbons for Ni (II) removal from aqueous solution. *Fuel Processing Technology*. Volume 149, August 2016, Pages 75-85. <https://doi.org/10.1016/j.fuproc.2016.03.024>
- [10] Akpomie, K., Dawodu, F., Adebowale, K. Mechanism on the sorption of heavy metals from binary-solution by a low cost montmorillonite and its desorption potential. *Alexandria Engineering Journal*. Volume 54, Issue 3, September 2015, Pages 757-767. <https://doi.org/10.1016/j.aej.2015.03.025>
- [11] Atul Kumar Kushwaha, Neha Gupta, M.C. Chattopadhyaya. Dynamics of adsorption of Ni(II), Co(II) and Cu(II) from aqueous solution onto newly synthesized poly[N-(4-[4-(aminophenyl)methylphenylmethacrylamide])]. *Arabian Journal of Chemistry* Volume 10, Supplement 2, May 2017, Pages S1645-S1653. <https://doi.org/10.1016/j.arabj.2013.06.007>
- [12] Anah, L., Astrini, N. Isotherm adsorption studies of Ni(II) ion removal from aqueous solutions by modified carboxymethyl cellulose hydrogel. *IOP Conf. Series: Earth and Environmental Science* 160 (2018). <https://doi.org/10.1088/1755-1315/160/1/012017>
- [13] Aharoni, C., Ungarish, M. Kinetics of activated chemisorptions. Part 2. Theoretical models, *J. Chem. Soc Faraday Trans.* 73 (1977) 456–464. <https://doi.org/10.1039/F19777300456>
- [14] Hu, Q., Zhang, Z. Application of Dubinin–Radushkevich isotherm model at the solid/solution interface: A theoretical analysis. *Journal of Molecular Liquids* Volume 277, 1 March 2019, Pages 646-648. <https://doi.org/10.1016/j.molliq.2019.01.005>.