Marine Science Center-University of Basrah

Mesopotamian Journal of Marine Sciences
Print ISSN: 2073-6428
E- ISSN: 2708-6097
www.mjms.uobasrah.edu.iq/index.php/mms

The possibility of using TiO2 Nanotube Arrays as an adsorbent for removing lead ions from aqueous solutions

Methaq I. Abood[1] *and iD Zainab T. Y. Al-Abdullah[2]
1-Department of Marine chemistry , Marine Science Centre, University of Basrah, Iraq
2-Department of Chemistry ,College of Education for pure science University of Basrah, Iraq
*Corresponding Author: e-mail: alshrhanm@yahoo.com

Article info.
✓ *Received: 4 September2022*
✓ *Accepted:14February 2023*
✓ *Published: 29 June2023*

Key Words:
Adsorption,
Freundlich ,
Lead ,
Titanium Nanotubes.

Abstract - This work focused on the elimination of lead ions from aqueous solutions using titanium dioxide nanotubes synthesised by anodization method as an adsorbent material using the batch system. The prepared titanium dioxide tubes(TNTs) were characterized using a scanning electron microscope device(SEM). The prepared tubes were within the nanoscale. Various conditions affected the adsorption process were studied, such as equilibrium time, temperature, acidity function and initial concentration of lead ions. It was found that the highest removal percentage occurred at the pH = 8 and that the time required for system equilibrium was 60 minutes. It was also found that the removal percentage increases with increasing temperature, which indicates the adsorption reaction as an endothermic. The Langmuir and Freundlich adsorption isotherms were also studied. The Freundlich equation was the most appropriate to the studied system. The thermodynamic studies also exhibited that the removal process was spontaneous, and the ΔS positive values indicated randomness increasing.

امكانية استخدام انابيب ثنائي اوكسيد التيتانيوم النانوية كمادة مازة لإزالة ايونات الرصاص من المحاليل المائية

ميثاق ابراهيم عبود[1] ، زينب طه ياسين العبدالله[2]
1- قسم الكيمياء البحرية، مركز علوم البحار، جامعة البصرة – العراق
2- قسم الكيمياء ، كلية التربية للعلوم الصرفة جامعة البصرة – العراق

المستخلص- ركزت هذه الدراسة على إزالة أيون الرصاص من المحاليل المائية باستخدام الأنابيب النانوية لثاني أوكسيد التيتانيوم المُصنَّعة بطريقة الأنودة كمواد مازة باستخدام نظام الدُفعات. تم تشخيص أنابيب ثاني أوكسيد التيتانيوم المحضرة باستخدام المجهر الإلكتروني الماسح (SEM). ووجد ان الأنابيب المحضرة هي ضمن المقياس النانوي ، كذلك درست الظروف المختلفة التي تؤثر على عملية الامتزاز ، مثل زمن الاتزان ، درجة الحرارة pH، والتركيز الأولي لأيون الرصاص. وجد أن أعلى نسبة إزالة حدثت عند الأس الهيدروجيني =8 وأن الوقت المطلوب لتوازن النظام كان 60 دقيقة. كما وجد أن نسبة الإزالة تزداد مع زيادة درجة الحرارة مما يعني أن تفاعل الامتزاز هو ماص للحرارة. ايضا درست ايزوثيرمات الامتزاز في لانكماير وفريندلش. وكانت معادلة لانكماير هي الأكثر قابلية للتطبيق على النظام المدروس. أظهرت الدراسات الثرموديناميكية أيضًا أن عملية الإزالة كانت تلقائية، وأن القيم الإيجابية لـ ΔS تشير إلى زيادة العشوائية.

الكلمات المفتاحية: الامتزاز، فريندليش ، الرصاص ، انابيب التيتانيوم النانوية

DOI: https://doi.org/10.58629/mjms.v38i1.224., ©Authors, Marine Science Centre, University of Basrah.

Introduction

Titanium dioxide (TiO_2) is one of the most common and used compounds because of its properties, and it has been widely used in paints (Haider *et al*., 2019) cosmetics (SCCS, 2020), toothpastes, sunscreens and foods (Musial *et al*., 2020). Its many uses are due to its abundance as titanium which is the ninth element abundant in the crust's of the earth, its moderate cost, non-toxicity (Kumar and Pandey, 2018), and high biocompatibility and stability (Sivaprakash and Narayanan , 2021). TNTs is a corrosion-resistant chemical with typical dimensions of less than 100 nm (Indira *et al.*, 2015) .They are one-dimensional and offer unique bending properties such as high electron mobility and very high mechanical forces (Kafshgari *et al*., 2019 ; Albu , 2012). TNTs are one of the important materials in the organic matter removal, the most promising properties of TiO_2 lie in its photochemical properties such as high photo catalytic activity (Rojviroon *et al.,* 2021 ; Tekin, 2014) . Also TNTs showed high adsorption efficiency of heavy metal because of strengthening the (O – H) bond and the insertion of H into the TNTs structure (Khan *et al*., 2019). The ions of heavy metal such as lead, zinc, cobalt, copper and nickel are found in fluidity waste from operations of mining, microchip technology, leather tanning industry of petrochemical and batteries as well as the industries of textile. The contamination of lead comes mainly through battery and car industrialists, the heavy metals damage comes on the human occurs from its effect on physiology and functions of organ and other ecosystems when above allowed levels (Esmaeili and Foroutan, 2015; Velusamy *et al*., 2021). Therefore, great efforts have been made by many researchers to remove ions dissolved and suspended heavy metals from industrial wastewater, different types of techniques have been used to accomplish this objective, like ion exchange (Koliehova *et al*., 2019), solvent extraction , chemical precipitation(Wang *et al*., 2020), reverse osmosis (Mehdipour *et al*., 2015), and adsorption. But adsorption has become the preferred method for eliminating toxic heavy metals and recovering them from waste water.

Materials and Methods

Preparation of the electrolyte solution

The electrolyte solution had been prepared by weight formula (W/W) from mixing materials (ethylene glycol + ammonium fluoride + ionic water) with weights 2 ,0.6 , 97.4 g respectively.

Preparation of titanium dioxide nanotubes

Titanium dioxide nanotube (TiO_2) had been synthesied by Anodization method. In this work we use Polished titanium plate of purity 99.5% , dimensions of 2.5 cm length, 2 cm width and 1 mm thickness using diamond paste. Then wash the plate with ethanol, then with deionized water and leave it to air dry. After the plate was polished, washed and dried, the anodization process was carried out using an anodizing device, where the titanium plates were installed as a cathode electrode and anode electrode with a depth of 1 cm inside the electrolyte, the anodization process was carried out at a voltage of 65 V for a period of one hour and a half, after completion the electrodes were removed from the solution and the anode has been washed many times with distilled water. After the formation of the thin film of titanium dioxide nanotubes, the film was washed with an ultrasonic device for 10-15 min to clean the film from residual materials and impurities.

Lead stock solution preparation

A standard lead solution was prepared at a concentration of 1000 mg L^{-1}, then a series of standard solutions have been prepared by diluting with deionized distilled water within the range 1-20 mg L^{-1}

Adsorption studies

The isotherms of adsorption for lead ions were studied using titanium nanotubes as an adsorbent surface using a series of lead ions concentrations within the range of 50-100 mg/l. A volume (25 ml) of these concentrations was taken and placed in beakers with TiO2 nanotube film. The beakers were placed in a vibrating incubator at a speed of 110 rpm at different temperatures (15,25,35 and45ºC). It was shaken until equilibrium was reached. The lead concentration was estimated by atomic absorption device. The efficiency of adsorption and the adsorption equilibrium of lead were calculated by the equations:

Removal % $\frac{C0-Ce}{C0}$ 100 …..1

Qe = $Vsol.\frac{(C0-Ce)}{m}$ …….2 ,where

Ce Is the lead ion concentration at equilibrium (mg. L^{-1})

C_0: Initial concentration of lead ions (mg. L^{-1})

V: Volume of solution in liters

Qe: Is the adsorption capacity (mg.g^{-1}).

Results and Discussion

TiO2NTs characterization

The microstructure of titanium dioxide nanotubes was examed by a scanning electron microscope (SEM), where the prepared film was photographed after washing with an ultrasonic device to get rid of residual materials or suspended impurities.

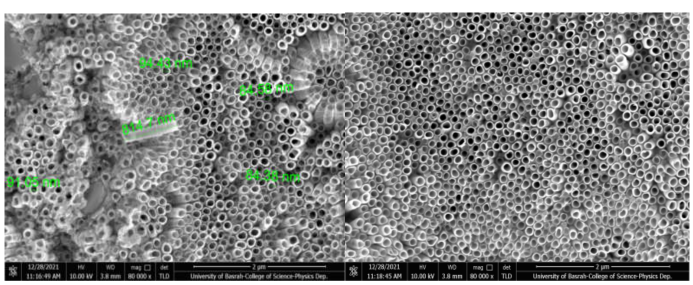

Figure1: FE-SEM image of TiO2 nanotubes

Through the scanning electron microscope images, we notice the regular and ordered shape of the prepared nanotube arrays, whose diameters range from 80-94 nm which were prepared using an applied voltage (65 V) and anodizing time (90 min). Changed anodizing conditions cause diverse structures of titanium surface, and the fluoride ion-containing electrolyte is the most effective electrolyte for the synthesis of titanium nanotube arrays (Xie and Blackwood, 2010). The applied electric field causes the formed oxide layer to dissolve and the chemical melting of TiO2 by fluorine ions present in the electrolyte. Therefore, both dissolving processes form titanium nanotubes by anodization process (Neupane *et al*., 2011)

Equilibrium Time of Adsorption Systems

The time effect on lead ions elimination process on the surface of the studied titanium dioxide tubes was studied in different time periods ranging from 15-210 min and at a temperature of 25ºC and a constant concentration and fixed volume of lead ions ($50mg^{-1}L^{-1}$/50ml). The incubator speed is rpm (110). The results of the study indicated that the rate of removal of lead ions increases in general with the increase of time, and the required equilibrium time on the surface of titanium dioxide is 60 min, as shown in Fig.(2).

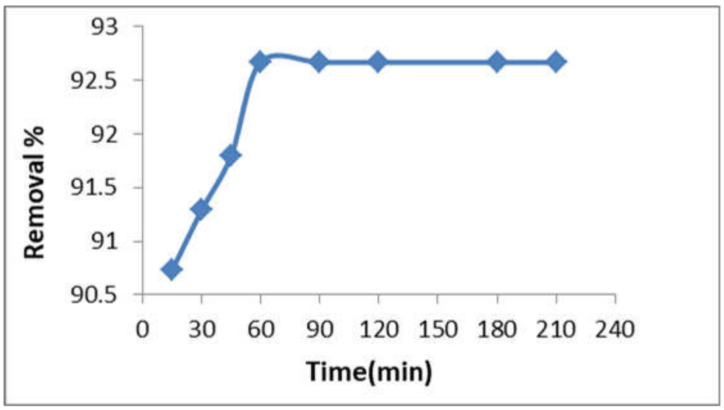

Figure 2. The effect of contact time on lead removal by TiO2NTs

The pH effect on lead adsorption

The influence of the acidity function on the lead ions adsorption on the titanium dioxide nanotubes surface in different acidity functions within the range of 4-8 at constant concentrations and temperature 25°C was studied, as shown in Fig.(3)

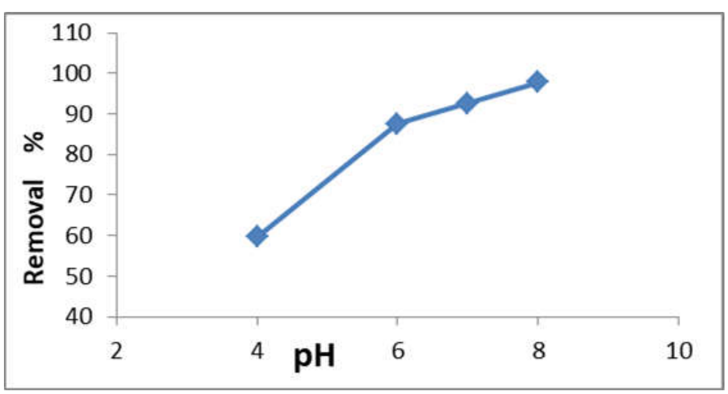

Figure 3. The effect of pH on the lead removal by TiO2NTs

The acidity function is an important and influential factor that regulate the removal process, especially the capacity of adsorption, as the adsorption efficiency depends on the acidity function of the solution because the modification in the pH of the solution causes a change in the ionization degree of the adsorbed molecule and the characteristics of the adsorbing surface (Banerjee and Chattopadhyaya, 2017). We note through the obtained results that the percentage of adsorption and adsorption capacity of the lead ions on the titanium dioxide nanotubes surface increases by increasing the acidity function, when moving from acidic media to the base medium, where the adsorption ratio was highest at pH = 8. In the acidic media, there is an increase in the hydrogen ions concentration (H+) in the system, and then the surface is charged with a positive charge resulting from the adsorption of positive hydrogen ions, which contest with the lead ions of the vacant sites on the materials surface of the adsorbent (Poursani *et al*., 2016; Ali *et al*., 2022).

Effect of initial metal concentration

The adsorption of lead (II) on the surface of the prepared titanium dioxide nanotubes has been studied, using different primary concentrations from lead solution 10,20,30 and40 mg/l at a temperature of 25°C and at pH=8 as shown in Fig. (4)

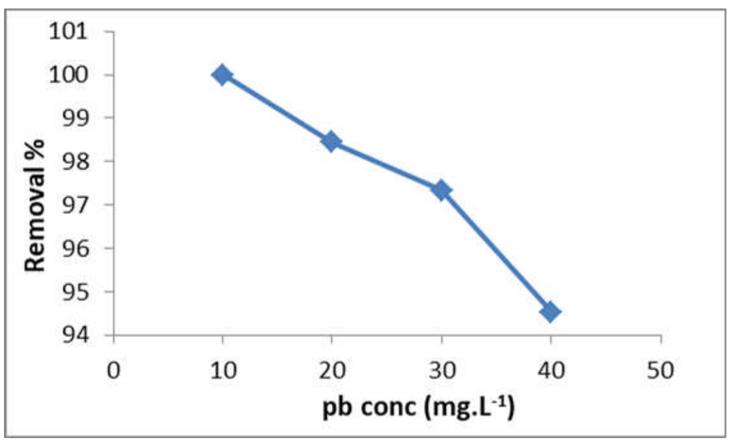

Figure 4. The effect of lead concentrations on the adsorption process by TiO2NTs

We note through the results below that the removal percentage of the lead ions decreased with the initial concentration of lead increasing, and the main reason for this is that with the increase in the lead ions concentration the present of ions number in the solution increases, and therefore it works on occupying the largest number of effective places on the surface of the adsorbent ,so the ratio of ions that experience adsorption is less than the ratio of free ions in the solution (Shojaei *et al*., 2020), while in solutions with low concentrations, the percentage of free ions in the solution is less than or equal to the effective sites number on the adsorbing surface (Vardhan *et al*., 2020; Hmood and Jassim, 2015).

Adsorption Isotherms

Adsorption isotherms are defined as describing the process of adsorption when there is an equilibrium between the solid phase of the surface of adsorbent and the solution , or as the relationship between the amount of an adsorbent on a surface and the concentration of an adsorbent at constant temperatures. The lead ion adsorption study on titanium dioxide nanotubes surface was conducted at diverse temperatures.

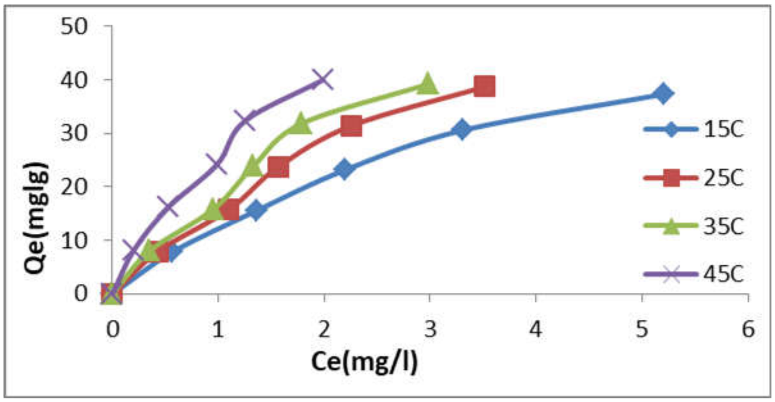

Figure (5) Adsorption isotherm of pb(II) onto TiO2NTs at different temperatures

It is clear from Fig .(5) that the form of adsorption for lead ions on the surface of titanium dioxide nanotubes (TiO2NTs) follows class S (group 4) according to the classification of Giles for adsorption isotherms. vertically, as indicated by a high affinity for the adsorbed molecules towards the adsorption layer Giles *et al*., 1960.

The Langmuir (eq.3) and Freundlich (eq.4). Isotherms were obtained by applying experimental adsorption data.

$$\frac{Ce}{Qe} = \frac{Ce}{Qmb} + \frac{Ce}{Qe} \quad \dots\dots..3$$

Whereas Qm is the maximum capacity of adsorption (mg/g) and b Langmuir constant value

$logQe = logKf + \frac{1}{n} logCe \dots\dots 4$,where

Kf is the Freundlich constant and n is the Freundlich indicator.

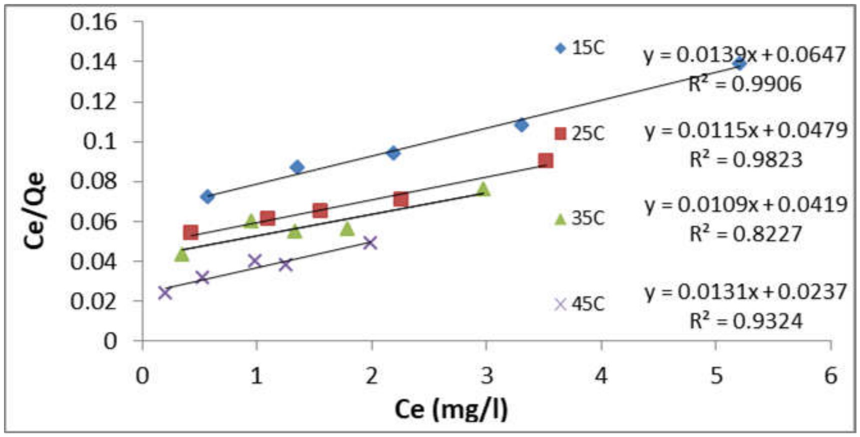

Figure (6): Linear form of Langmuir isotherms of pb(II) on TiO2NT

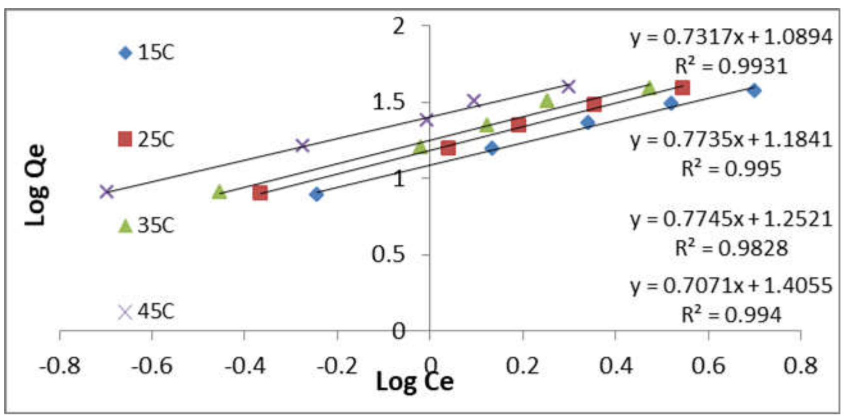

Figure (7): Linear form of Freundlich isotherms of pb(II) on TiO2NTs

Table (1) Results of Langmuir and Freundlich isotherms application for lead ion adsorption on TiO2NTs

	Temp° C	Langmuir			Freundlich		
		Q_m mg/g	b l/g	R^2	Kf	n	R^2
Pb(II)	15	71.942	0.215	0.990	12.28	1.366	0.993
	25	86.956	0.240	0.982	15.27	1.292	0.992
	35	91.743	0.260	0.822	17.86	1.291	0.985
	45	76.335	0.552	0.932	25.43	1.414	0.994

Through the results shown in Table 1, it was found that the R^2 value of the Freundlich equation is greater than the R^2 value of the Langmuir equation, and thus the Freundlich equation is the most appropriate to the lead ion adsorption process on the studied surface.(Kadhim and Saleh,2022; Cherono *et al*.,2021).

Thermodynamic Study

The removal of the lead ions onto titanium dioxide nanotubes was checked out as a temperature function . The temperature effects on the lead ions adsorption on the surface of titanium dioxide nanotubes was carried out at different temperatures (15, 25,35 and45C°) and at different concentrations. The study of the temperature effect on the removal process helps in estimating the values of thermodynamic functions ΔG (Free Energy) ΔH (Enthalpy) and ΔS (Entropy). Due to the importance of thermodynamic functions in the study of the adsorption process

$$\Delta G = -RT\, lnK \dots\dots\dots 5$$

$$K = \frac{C\ soild}{C\ liquid} \dots\dots\dots\dots 6$$

$$\Delta G = \Delta H - T\,\Delta S \dots\dots\dots 7$$

$$lnK = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots 8$$

Whereas ΔG is the change in free energy ($KJ.mol^{-1}$), K is the thermodynamic equilibrium constant for the adsorption process, C_{solid} is the concentration at equilibrium for the solid phase (mg/l), C_{liquid} is the concentration at equilibrium for the liquid phase (mg/l), R is the gas constant (0.008314 KJ. mol-1. K-1). and T is the temperature in Kelvin.

Table (2): Thermodynamic function for adsorption of pb(II) on TiO2NTs

C_o mg/l	G ($KJ.mol^{-1}$)-Δ				HΔ $KJ.mol^{-1}$	SΔ $J.mol^{-1}.k^{-1}$
	15°C	25 °C	35 °C	45 °C		
10	6.564	7.714	8.864	10.01	26.556	0.115
20	5.974	7.044	8.114	9.184	24.842	0.107
30	6.086	7.006	7.926	8.846	20.410	0.092
40	5.539	6.609	7.679	8.749	25.277	0.107
50	5.097	6.127	7.157	8.187	24.567	0.103

The values of thermodynamic functions were calculated through equation (8), as the values listed in Table (2) were calculated according to the van't Hoff - Arinos equation, depending on Fig. (8) where the slope (-H / R) and the cut-off is (ΔS/R) (Munagapati *et al*., 2018).

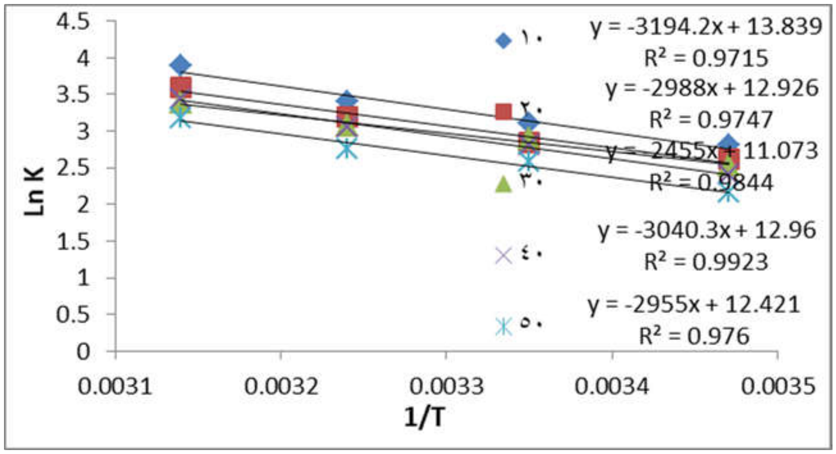

Figure (8) Plots of van't Hoff relationship between lnK and 1/T.

The results shown in Table (2) indicated that the values of the heat of adsorption (ΔH) for adsorption of lead ions on the titanium dioxide nanotubes surface were positive values, meaning that the type of adsorption reaction is an endothermic reaction (where the amount of adsorbed substance increases with increasing temperature). We also note that the values of ΔH ranged between 20.410-26.556. The removal process was all less than 40kJ. mol^{-1} , that is physical adsorption on the prepared titanium dioxide nanotubes surface (Wang *et al*., 2020 ; Abbou *et al*., 2021). Also, the positive values of (ΔS) on the titanium dioxide nanotubes surface indicate that the adsorbed molecules are less regular, because it constantly moving on the adsorbing surface than their shape in the solution (Khan *et al*. 2019 ; Húmpola *et al*., 2013). While the (ΔG) values were all negative, which means that the adsorption of Pb(II) on the surface of the studied titanium dioxide nanotubes is a spontaneous process. We also note that the negative value of (ΔG) increases with temperature increasing, meaning that the adsorption process becomes more automatic with increasing temperature (Kefi *et al*., 2017 ; Abood and Jassim, 2017).

Conclusions

In this study , titanium dioxide nanotubes were used as an adsorbents for removal lead ions from polluted solution. titanium dioxide nanotubes were synthesized using electrochemical method (Anodization method). Titanium dioxide nanotubes have been distinguished with Scanning electron microscope (SEM). Electron microscopy images showed that titanium nanotubes at the nanoscale. Various factors affecting the lead ion adsorption process on the titanium dioxide nanotubes surface were studied, such as temperature, acidity function and initial concentrations. The results showed that the removal percentage increases with acidity function increasing. Where the highest adsorption ratio was at pH = 8.

The results also showed that the process of removing lead ions from water was of the endothermic type, and spontaneous through negative ΔG, ΔH values. Also through the results, we note that the Freundlich equation is the most appropriate to the lead ions removal process on the surface of TiO_2 nanotube because of the best linear relationship between Log Ce and Log Qe.

That is, the adsorption process in the solution in the case of heterogeneous surfaces is more responsive to the Freundlich equation than to the Langmuir equation, and in this case the adsorption is more than one layer .

References:

Abbou, B., Lebkiri, I., Ouaddari, H. and Kadiri, L. .2021. Removal of Cd (II), Cu (II), and Pb (II) by adsorption onto natural clay : a kinetic and thermodynamic study, Turkish Journal of Chemistry, Vol. 45: No. 2, Article 9 : 362–376. https://doi.org/10.3906/kim-2004-82.

Abood, M I, and Jassim T E. 2017. Adsorption Equilibrium , Kinetics and Thermodynamics of Rhodamine B Dye from Aqueous Solution Using Iraqi Porcellanite Rocks . Mesopotamian Journal of Marine Sciences,32 (2): 88–103. https://doi.org/10.58629/mjms.v32i2.64.

Albu, S. P. 2012. Morphology and Growth of Titania Nanotubes: Nanostructuring and Applications. Friedrich-Alexander-Universitaet Erlangen-Nuernberg (Germany). https://opus4.kobv.de/opus4-fau/files/2676/Sergiu_P_Albu_Dissertation.pdf.

Ali, R.T., Saeed, N.H.M. and Al-niemi, K.I. .2022. Study of Isothermal , Kinetic and Thermodynamic Parameters of Adsorption of Glycolic Acid by a Mixture of Adsorbent Substance with ab- Initio Calculations. Egyptian Journal of Chemistry, 65(6), 489–504. https://doi.org/10.21608/ejchem.2022.118101.5321.

Banerjee, S. and Chattopadhyaya, M.C. 2017. Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. Arabian Journal of Chemistry, 10, 629–638. https://doi.org/10.1016/j.arabjc.2013.06.005.

Cherono, F., Mburu, N. and Kakoi, B. 2021. Adsorption of lead, copper and zinc in a multi-metal aqueous solution by waste rubber tires for the design of single batch adsorber. Heliyon, 7(11), p. e08254. https://doi.org/10.1016/j.heliyon.2021.e08254.

Esmaeili, H. and Foroutan, R. 2015. Investigation into ion exchange and adsorption methods for removing heavy metals from aqueous solutions. International Journal of Biology, Pharmacy and Allied Sciences, , 4(12), 620-629. https://ijbpas.com/pdf/2015/December/1448178944MS IJBPAS 2015 DEC SPCL 1053.pdf.

Giles, C.H., MacEwan, T.H., Nakhwa, S.N. and Smith, D. (1960) Studies in Adsorption: Part XI. A System of Classification of Solution Adsorption Isotherms and Its Use in Diagnosis of Adsorption Mechanisms and in Measurement of Specific Surface Area Solids. Journal of the Chemical Society, 14, 3973-3993. http://dx.doi.org/10.1039/jr9600003973.

Haider, A.J., Jameel, Z.N. and Al-Hussaini, I.H.M. 2019. Review on: Titanium dioxide applications. Energy Procedia, 157, 17–29. https://doi.org/10.1016/j.egypro.2018.11.159.

Hmood, A.Y., and T.E. Jassim. 2015. Adsorption of Copper(II) and Lead(II) Ions from Aqueous Solutions by Porcellanite. International Journal of Marine Science 28 (2): 109–20. doi: 10.5376/ijms.2015.05.0029

Húmpola, P. D., Odetti, H. S., Fertitta, A. E., and Vicente, J. L. 2013. “therodynamic analysis of adsorption models of phenol in liquid phase on different activated carbons. Journal of the Chilean Chemical Society, 58 (1),1541–44. http://dx.doi.org/10.4067/S0717-97072013000100009.

Indira, K., Mudali, U.K. and Rajendran, N. 2015. In-vitro biocompatibility and corrosion resistance of strontium incorporated TiO2 nanotube arrays for orthopaedic applications.

Journal of Biomaterials Applications, 29(1), 113–129. https://doi.org/10.1177/0885328213516821.

Kadhim, H.H. and Saleh, K.A. 2022. Removing of Copper ions from Industrial Wastewater Using Graphene oxide/Chitosan Nanocomposite. Iraqi Journal of Science, 63(5), pp. 1894–1908. https://doi.org/10.24996/ijs.2022.63.5.4.

Kafshgari, M.H. , Kah,D.; Mazare,A., Nguyen, N.T., Distaso, M.; Peukert,W., Goldmann,W.H., Patrik Schmuki,P and Fabry,B. . 2019. Anodic Titanium Dioxide Nanotubes for Magnetically Guided Therapeutic Delivery. Scientific Reports volume 9, Article number: 13439. https://doi.org/10.1038/s41598-019-49513-2.

Khan, S., Dan, Z. and Haiyan, H. 2019. Adsorption mechanism of Pb (II) and Ni (II) from aqueous solution by TiO2 nanoparticles : kinetics , isotherms and thermodynamic studies. Desalination and Water Treatment Vol.155 pp.237-249. https://doi.org/10.5004/dwt.2019.23933.

Koliehova, A., Trokhymenko ,H., Melnychuk,S. and Gomelya, M. 2019. Treatment of wastewater containing a mixture of heavy metal ions (copper-zinc, copper-nickel) using ion-exchange methods, Journal of Ecological Engineering, 20(11), pp. 146–151. https://doi.org/10.12911/22998993/112746.

Koliehova,A., Trokhymenko ,H., Melnychuk,S. and Gomelya,M. 2020. Titanium Dioxide Nanoparticles in Food and Personal Care Products — What Do We Know about Their Safety ? Nanomaterials 10 (6): 1–23. https://doi.org/10.3390%2Fnano10061110.

Kumar, A. and Pandey, G. 2018. Different Methods Used for the Synthesis of TiO2 Based Nanomaterials : A Review. American Journal of Nano Research and Applications, 6(1), 1. https://doi.org/10.11648/j.nano.20180601.11.

Mehdipour, S., Vatanpour, V. and Kariminia, H.R. 2015. Influence of ion interaction on lead removal by a polyamide nanofiltration membrane, Desalination, Volume 362, 15, pp. 84–92. https://doi.org/10.1016/j.desal.2015.01.030.

Munagapati,V.S., Yarramuthi,V., Kim, Y., Lee, K.M. and Kim,D.2018. Removal of anionic dyes (Reactive Black 5 and Congo Red) from aqueous solutions using Banana Peel Powder as an adsorbent, Ecotoxicology and Environmental Safety. Vol.148, pp. 601–607. https://doi.org/10.1016/j.ecoenv.2017.10.075.

Neupane,M.P., Park,S., Bae,T.S., Yi,H.K., Watari,F. and Min Ho Lee,M.H.2011. Synthesis and Morphology of TiO2 Nanotubes by Anodic Oxidation Using Surfactant Based Fluorinated Electrolyte, Journal of The Electrochemical Society, 158(8), p. C242. http://dx.doi.org/10.1149/1.3598164.

Poursani, A. , Nilchi, A. , Hassani, A. , Shariat, S. and Nouri, J. 2016 The Synthesis of Nano TiO2 and Its Use for Removal of Lead Ions from Aqueous Solution. Journal of Water Resource and Protection, 8, 438-448. http://dx.doi.org/10.4236/jwarp.2016.84037.

Rojviroon, T., Rojviroon, O., Sirivithayapakorn, S. and Angthong,S. 2021. Application of TiO2 nanotubes as photocatalysts for decolorization of synthetic dye wastewater. Water Resources and Industry, 26(September), p. 100163. https://doi.org/10.1016/j.wri.2021.100163.

Scientific Committee on Consumer Safety (SCCS) .2020. Scientific Committee on Consumer Safety SCCS OPINION on Titanium dioxide (TiO2) used in cosmetic products that lead to exposure by inhalation. https://health.ec.europa.eu/system/files/2021-11/sccs_o_238.pdf.

Shojaei, Z., Iravani, E. , Moosavian, S.M. and Mostaedi, M. 2020. Lead adsorption onto surface modified nano titania: Kinetic and thermodynamic studies. Iranian Journal of Chemistry and Chemical Engineering, 39(6), pp. 105–119. https://doi.org/10.30492/ijcce.2019.36577.

Sivaprakash V. and Narayanan R . 2021. Surface Modification TiO2 Nanotubes on Titanium for Biomedical Application Materials Science Forum,. 1019 ,157-163. https://doi.org/10.4028/www.scientific.net/MSF.1019.157.

Tekin, D. 2014. Photocatalytic degradation kinetics of Congo Red dye in a sonophotoreactor with nanotube TiO2, 39(3), pp. 249–261. doi:10.3184/146867814X14043731662747.

Vardhan, K.H., Kumar, P.S. and Panda, R.C. 2022. Adsorption of copper ions from polluted water using biochar derived from waste renewable resources : static and dynamic analysis, International Journal of Environmental Analytical Chemistry, 102(16), 1–22. https://doi.org/10.1080/03067319.2020.1779245.

Velusamy, S., Roy, A., Sundaram, S. and Kumar, 2021. A Review on Heavy Metal Ions and Containing Dyes Removal Through Graphene Oxide-Based Adsorption Strategies for Textile Wastewater Treatment. The Chemical Record, 21(7), 1570– 1610. https://doi.org/10.1002/tcr.202000153.

Wang, C., Guo L., Yunhao X., Xiteng L. and Zhen H., 2020. Development of mercaptosuccinic anchored MOF through one-step preparation to enhance adsorption capacity and selectivity for Hg(II) and Pb(II). Journal of Molecular Liquids, Volume 317. https://doi.org/10.1016/j.molliq.2020.113896.

Wang, L., Gao, C., Feng, J., Xu, Y., Li, D., and Zhang, L. 2020. Adsorption properties of comb-shaped polycarboxylate dispersant onto different crystal pyraclostrobin particle surfaces. Molecules, 25(5637). https://doi.org/10.3390/molecules25235637.

Xie, Z.B. and Blackwood, D.J. 2010 .Effects of anodization parameters on the formation of titania nanotubes in ethylene glycol', Electrochimica Acta, 56(2), 905–912. https://doi.org/10.1016/j.electacta.2010.10.004.