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Adsorption Of 2,6-Dichlorophenol-Indophenol Sodium Dihydrate Salt From Aqueous Solutions Using Nano Magnesium Oxide; A Thermodynamic Study

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Abstract

The objectives of this study is to adsorb 2, 6-dichloro phenol indophenol sodium salt using nano magnesium oxide as a nano surface. The adsorption of dyes by using the nanoparticles is a modern and effective way to remove contaminants from their solutions. The UV spectrophotometer was used to follow the dye concentrations in the water solution after mixing them with 0.1 g of MgO and different concentrations of the dye solution were used to obtain the isotherm adsorption. The application of the Langmuir and Freundlich isotherms adsorption was investigated. The isotherm estimate shows that the Freundlich model obtain better fits to the experimental equilibrium data than the Langmuir model. The effect of temperature was investigated, the best temperature was 298 K. The adsorption decreases by increasing the temperature. The values of ΔG revealed that the process of adsorption was spontaneous within the experimental conditions. The effect of the acidic function was also studied. The adsorption value changed with the changing acidic function. The results showed that nano magnesium oxide can adsorb 2, 6-dichloro phenol indophenol sodium salt efficiently.

Keywords: 2,6-dichloro phenol indophenol , Nano magnesium oxide, Adsorption, Thermodynamic.

1. Introduction

There are many unique properties of hybrid nanoparticles including high ability of ionic exchange [1-3] large surface area [4], efficiency and effectiveness to adsorb big particles [5, 6], high absorption, and without toxicity[7- 9]. In this study, the nano surface of MgO was used to adsorb dye 2,6-dichloro phenol indophenol sodium salt dehydrate (DCPIP) from aqueous solutions the nano surface of MgO is an important inorganic material with a wide band-gap [10]. It has been used in many applications such as catalysis, catalyst supports, toxic waste remediation [11-13], refractory materials and adsorbents. The chemical formula for pigment $C_{12}H_6ClNNaO_2.2\ H_2O$, the molar mass (326.11 g / mol) and its structural formula is as in Fig.1.

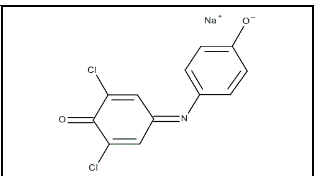

Fig.1 structural formula of DCPIP.

This dye is used to estimate vitamin C [14]. It also used in oxidation-reduction reactions to verification of the efficiency of nanoparticles in influencing enzyme activity [15].

Materials (chemicals)

All Analytical reagents grade chemicals and distilled water were used throughout

1- 2,6-Dichloro phenol indophenol sodium salt: CDH(P),Lid., INDIA.
2- Nano Magnesium oxide: Mknano, Mississauga, Canada.

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3- Hydrochloric acid: BHD Chemical, ltd. poole, England.
4- Sodium chloride: Fluka-Garantie, Switzerland.

Apparatus

1- Apple (PD-303 U.v.) Spectrophotometer Germany in Kerbala University
2- pH-Meter –WTW-720-ionlab Germany
3- Thermostatic Shaker Bath, GFL (D-3006) Germany.
4- Centrifuge, Megafuge 1.0, Herouse Sepatech , Germany.
5- Denver sensitive balance instrument ISO 9001.

Experimental Methods

Study the Uv-visible spectrum and calibration curve of DCPIP.

The UV-visible spectrum of DCPIP was studied in the range (200-800) nm to determine the maximum wavelength which was 620 nm, as shown in Fig. 2.

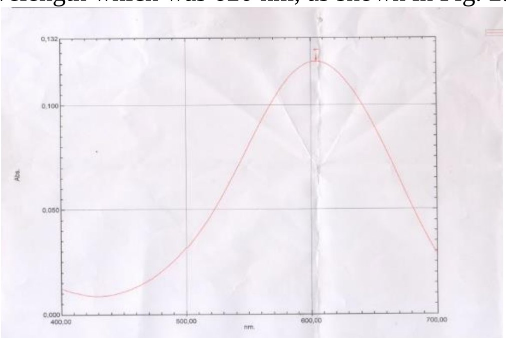

Fig.2 UV-visible spectrum of DCPIP versus the reagent blank.

The calibration curve of DCPIP was obtained after preparing 10 different solution within the range (2-12) ppm as shown in Fig 3. Then the absorption record for each concentration and then the standard curve plotting between the concentration and absorption.

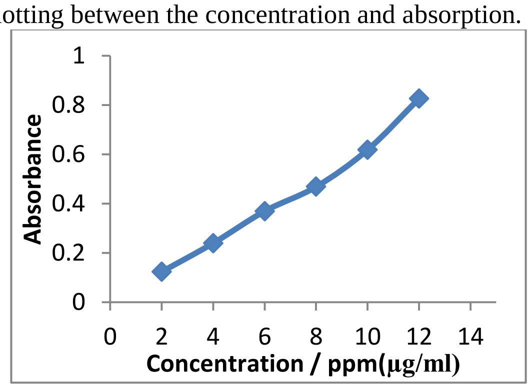

Fig. 3 Calibration curve of DCPIP.

The general procedure:

Five solutions of DCPIP were prepared in the range 10-50 µg /ml in100 ml volumetric flask, then a 25 mL of each solution was taken and placed in contact with 0.1g of nano particle of MgO. The mixture was placed for 30 minutes in a water bath at temperature of 298K. The solutions were placed in test tubes and left in the centrifuge at a speed of 3000 rpm. The absorbance of the different concentration was measured. The quantity of the adsorbent substance Qe (mg / g) was calculated according to the following equation [16].

Qe=V(Co-Ce)/m (1)

Qe= The amount of adsorbent (mg / g), Co = concentration of the primary adsorbent material (mg / L)

Ce = Concentration at the equilibrium of the adsorbent solution (mg / L) V = The total volume of the adsorbent substance solution (L), m= weight of adsorbent (g).

Results and Discussion

The equilibrium time has an effect on the adsorption of DCPIP on the surface of the magnesium oxide to reach the equilibrium state. Amount of 0.1 g of the surface is placed with 25 mL of the DCPIP in a concentration of 50 µg/mL. Ten flasks were taken and placed in a water bath and the temperature was stabilized at 298 K. The first flask was then withdrawn after five minutes. It was placed in the centrifuge and its absorbent was measured. This was done for the rest flasks after every five minutes for a period of 40 minutes. It was noted that the time required for equilibrium is 30 minutes. The mechanism of the reaction is due to the migration and transport of the molecules dye from the solution to the adsorption surface [17]. The results are shown in Fig.4.

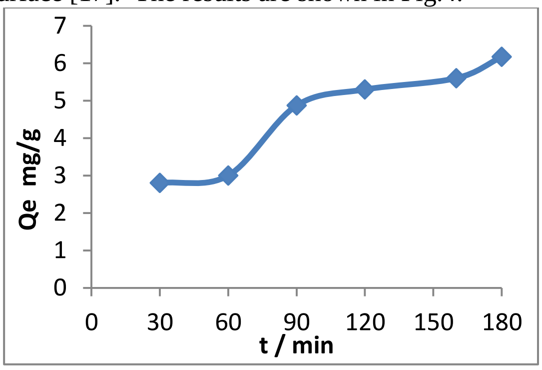

Fig.4 The effect of time on adsorption of DCPIP on the nano surface of MgO

The effect of pH on adsorption

In this study the highest adsorption was found at pH = 3. The reason for this is that the concentration of 2, 6-dichloro phenol indophenol for sodium salt in the solution decreased, resulting to decreased adsorption [18], according to Fig.5.

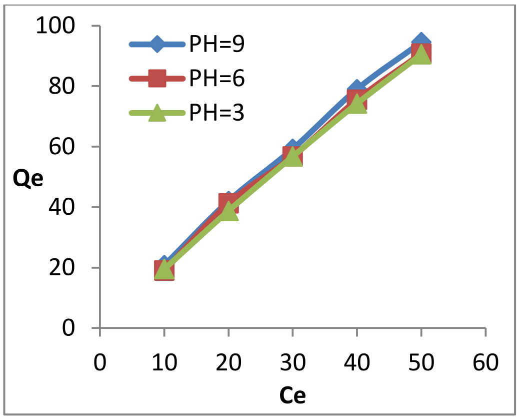

Fig.5 The effect of different acidic functions at 298 K

Determination of adsorption isotherms

A temperature effect was studied to determine isotherm adsorption, the results are illustrated in the Fig.6.

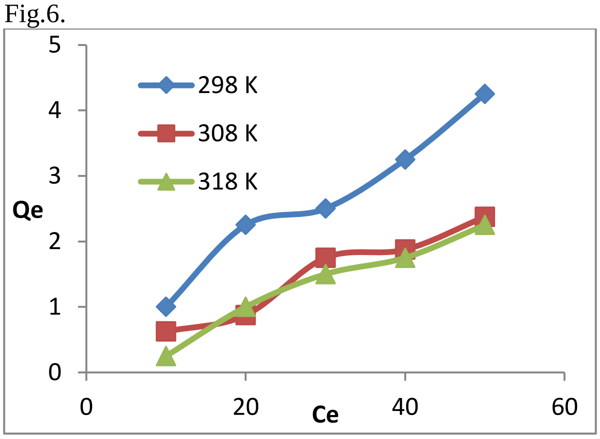

Fig.6 The adsorption isotherms of DCPIP on the nano surface of MgO in the temperature range (298-318) K

The general shape of isotherms in Fig.6 corresponds with S type according to Giles's classification [19]. The type(S) where the DCPIP particles are oriented on the nanosurface of the MgO in a diagonal or vertical manner.

Langmuir equation [20] was used to explicate the adsorption of the DCPIP on the nano surface of MgO according to equation (2)

Qe=abCe/1+bCe (2)

The Frandlish equation [21] is used to describe the adsorption properties of the non-homogeneous surfaces according to equation (3)

$$\log C_e \frac{1}{n} = \log K_F + \log Q_e \qquad (3)$$

The result showed in Fig.7 and 8 for Langmuir and Frandlich equations respectively.

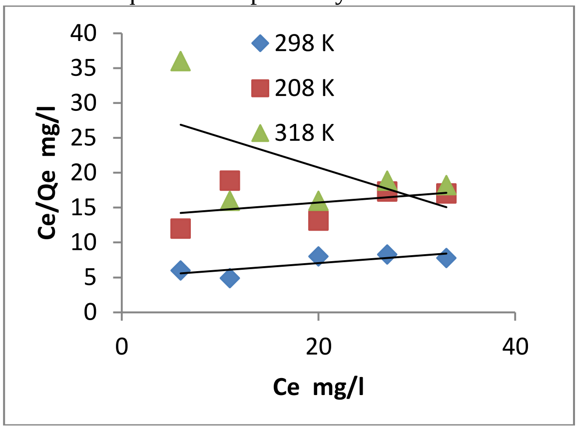

Fig. 7 Langmuir adsorption isotherm for the DCPIP at 298-318 K on nanosurface of MgO and pH=3

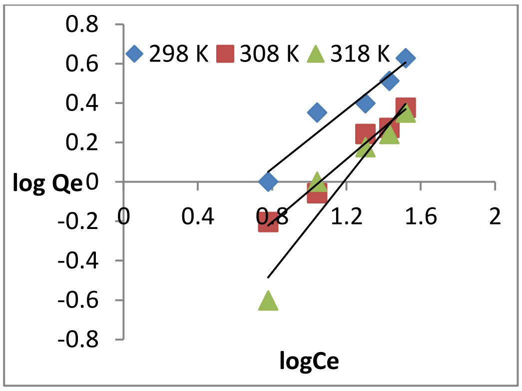

Fig. 8 Frandlich adsorption isotherm for the DCPIP on nanosurface of MgO at 298-318K and pH=3

RL is an essential characteristic of Langmuir isotherm, it is the measure of the adsorbent capacity used given by the equation:

RL=1/[1+b Co] (5)

The values of RL are in the range of 0.1-0.99 means 0< RL> 1 representing extremely favorable adsorption process [22].

The values of the isotherm constants of the (a, b, RL) for Langmuir model and (n, kf) Frandlich model were calculated with the correlation coefficients (r^2) are shown in TABLE 1.

The results show that the Freundlich model, obtain better fits to the experimental equilibrium data than the Langmuir model [9].

TABLE 1. The values of Langmuir and Frandlich constant with the correlation coefficients for adsorption of DCPIP on nanosurface of MgO at 298-318K and pH=3

Temp.	Langmuir isotherm				Freundlich isotherm		
K	a(mg/g)	b(mg/l)	R^2	RL	Kf	n	R^2
298	0.521257	9.48024	0.6263	1.21	0.291631	1.329423	0.9255
308	0.008711	0.000672	0.2481	1	0.111252	1.217776	0.9241
318	-0.01258	-0.00041	0.3353	1	0.015538	0.724018	0.9189

Effect of ionic strength on adsorption

A study of the effect of ionic strength for adsorption on the surface of MgO at 298 K for DCPIP and pH = 3. Table 6. and Fig. 9 show that the effect of adding NaCl as a catalyst is that adsorption is more effective than if it were without salt. Stimulation gives extra stability to the effective site versus electrostatic interference [23,24].

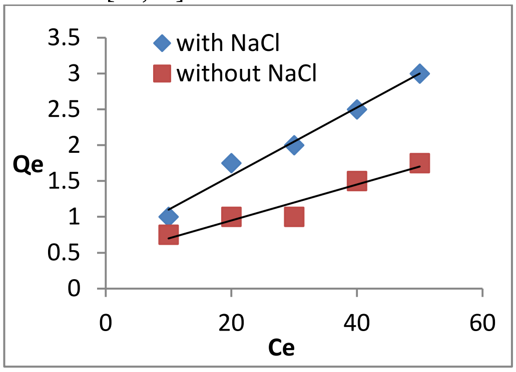

Fig.9 The effect of ionic strength for adsorption of DCPIP on the nanosurface MgO at 298 K and pH 3

Thermodynamic study

The highest adsorption was found at 298K the diffusion speed of adsorption molecular on the surface decrease resulting in reduced interaction between the surface and the adsorption molecule and when the temperature increase, the bonds will separate. The ΔH is calculated by plotting Log Xm vs. 1 / T K according to the equation (4) [25].

$$\text{Log Xm} = - \Delta H / (2.303\ RT) + \text{conc.} \quad (4)$$

A linear relationship was obtained as in Figure 10 according to the results in TABLE 2.

TABLE 2. The values 1 / T K and Log Xm for adsorption of DCPIP on nanosurface of MgO in the experimental range (298 – 318)

C°	TK	1/T K^{-1}	Xm	Log Xm
25	298	0.003356	4.25	0.628389
35	308	0.003247	2.37	0.375664
45	318	0.003145	2.25	0.352183

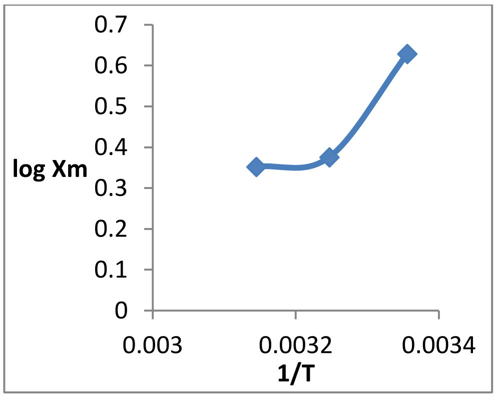

Fig.10 Log Xm vs. 1 / T K for adsorption of DCPIP on the nanosurface of MgO

$$\Delta G = -RT \ln[\ Qe / Ce\ ] \quad (5)$$

The entropy values were obtained by the following equation

$$\Delta G = \Delta H - \Delta T \Delta S \quad (6)$$

The results are illustrated in TABLE 3.

TABLE 3. The values of ΔH, ΔG and ΔS for adsorption of DCPIP on nanosurface of MgO at 298K

ΔH (KJ.mol^{-1})	ΔG (KJ.mol^{-1})	ΔS (kJ. mol^{-1})
-25.28	-5.076	6.77

The negative value of ΔH refers to the exothermic process, this indicates that the process is only adsorption [26]. The ΔG value refer to the spontaneously of the adsorption process for the DCPIP on the nano surface of MgO. The positive value of ΔS indicates the increased entropy.

Conclusion

The adsorption of 2, 6-dichlorophenol-indophenol sodium salt dihydrate from aqueous solutions by using the nanoparticles of surface magnesium oxide is a modern and effective way to remove contaminants from their solutions.

Conflicts of interest

"There are no conflicts to declare".

References

1- Patnaik, S., Mishra PC., Nayak RN., and Giri AK. "Removal of Fluoride from Aqueous Solution Using Chitosan-Iron Complex." *Journal of Analytical & Bioanalytical Techniques* 7(4) 2016.
2- eldamarawy, Y., assaad, F., Youssef, R., Mubarak, D. Adsorption Thermodynamics of Cu- Ca Ion Exchange on Nano-montmorillonite Clay System. Egyptian Journal of Chemistry, 62(Special Issue (Part 1) Innovation in Chemistry): 293-300(2019).
3- Guo Q., Tain J., Removal of fluoride and arsenate from aqueous solution by hydrocalumite via precipitation and ion exchange, *Chem. Eng. J.* (231) 121- 131(2013).
4- Mourabet M., EI Rhilassi A., EI Boujaady H., Bennani- Ziatni M., EI Hamri R., Taitai A., Removal of fluoride from aqueous solution by adsorption on hydroxyapatite(Hap) using response surface methodology, *J. Saudi Chem. Soc.* 19(6)603- 615(2015).
5- Ghaedi M., GolestaniNasab A., Khodadoust S., Sahraei R., Daneshfar A., Characterization of zinc oxide nanorods loaded on activated carbon as cheap and efficient adsorbent for removal of methylene blue, *J. Ind. Eng. Chem.* (21)986-993(2015).
6- Doma, A., Hassan, N., Abd-Elhamid, A., Soliman, H. Adsorption of Methylene Blue Dye on

Hydrothermally Prepared Tungsten Oxide Nanosheets. Egyptian Journal of Chemistry, 63(2): 2-3(2020).

7- Bhatnagar A., Kumar E., Sillanpaa M., Fluoride removal from water by adsorption- a review, *J.Chem. Eng.* 171(3)811- 840(2011).

8- Ali, E., Ismail, M., Elsabee, M. Chitosan based polyelectrolyte complexes development for anionic and cationic dyes adsorption. Egyptian Journal of Chemistry, 63(2): 4-5(2020).

9- Mohammed, M., Rheima, A., Jaber, S., Hameed, S. The removal of zinc ions from their aqueous solutions by Cr2O3 nanoparticles synthesized via the UV-irradiation method. Egyptian Journal of Chemistry, 2020; 63(2): 5-6.

10- Al-Gaashani, R., Radiman, S., Al-Douri, Y., Tabet. and Daud, A. R., Investigation of the opticalproperties of $Mg(OH)_2$ and MgO nanostructures obtained by microwave-assisted methods. *Journal of Alloys and Compounds*, (521) 71-76 (2012).

11- Daizy Philip Honey Mediated Green Synthesis of Silver Nanoparticles. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 75(3)1078-1081(2010).

12- Jintakosol T., Singjai P., Effect of annealing treatment on luminescence property of MgO nanowires, *Current Applied Physics.* 9(6)1288-1292(2009).

13- Duan G., Yang X., Chen J., Huang G., Lu L., Wang X., The catalytic effect of nanosized MgO on the decomposition of ammonium perchlorate, *Powder Technol*. 172(1)27-29(2007).

14- Mills A.and Grosshans P., UV dosimeter based on dichloroindophenol and tin (IV) oxide *the Analyst*, 134(5)845(2009).

15- Ramanaviciene A., Nastajute G., Snitka V., Kausaite A. German N., D.Barauskas, Ramanavicius A., Spectrophotometric evaluation of gold nanoparticles as red-ox mediator for glucose oxidase chemical, *Sensors and Actuators B: Chemical,* 137(2)483-489(2009).

16- Awwad A M., Farhan A M., Equilibrium, Kinetic and Thermodynamics of Biosorption of Lead (II) Copper (II) and Cadmium (II) Ions from Aqueous Solutions onto Olive Leaves Powder, *American Journal of Chemistry,* 2(4)238-244(2012).

17- Ali D., Al-Bayati R., and Alani R., Adsorption – Desorption and Theoretical Study of Propranolol Hydrochloride Drug on Chitosan and Cellulose Acetate Surfaces." *British Journal of Pharmaceutical Research* 10(4)1-8(2016).

18- Reyhanitabar A., Karimian N., M.Ardalan, Savaghebi G. and Ghannadha M., Comparison of five adsorption isotherms for predication of zinc retention in calcareous soils and the relationship of their coefficient with soil characteristics. *Communication in Soil Science and Plant Analysis*, 38: 147-158(2007).

19- Rani S., Sud D., Effect of temperature on adsorption-desorption behaviourof triazophos in Indian soils *Plant Soil Environment*, 61(1)36-42(2015).

20- Alka T. and Anita B. Effective Removal of Pesticide (Dichlorvos) by Adsorption onto Super Paramagnetic Poly (styrene-co-acrylic acid) Hydrogel from Water, *Int. Res. J. Environment Sci.* 3(11)41-46(2014).

21- Dave P. and Patel S., Adsorption studies for removal of organochlorine pesticides using modified unsaturated polyester resin *Advances in Applied Science Research*, 7(4)185-189(2016).

22- Zuhra G., Moghala M., Jamil R., Nusrat N., Bhangerb M., Adsorption of Selected Pesticides from Aqueous Solutions Using Cost effective Walnut Shells *IOSR Journal of Engineering* 4(10)43-56(2014).

23- Abdul Rahman E. and Umran M., Kinetic and thermodynamic studies of adsorption Pb (II) Ion on the micelles on anionic and nonionic surfactant, Journal of Chemical and Pharmaceutical Research, 7(10): 964-971(2015).

24- Girija, V.V., R. K. Rattan, and S. P. Datta. "Adsorption Study : A Systematic Approach to Determine Zinc Availability in Soils of Divergent Characteristics." *International Journal of Agricultural sciences* 4(2): 102–5(2013).

25- P.W. Atkins, Physical chemistry, Oxford university press, Ox Ford, 9th ed. , 2010.

26- Vasu, A., Adsorption of Ni(II), Cu(II) and Fe(III) from Aqueous Solutions Using Activated Carbon, *Journal of Chemistry*, (5)1-9(2008).