Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

The uptake of Eriochrome Black T dye from Wastewater utilizing synthesized Cadmium Sulfide Nanoparticles

Rasha Shakir Mahmood

[1] *Department of Chemistry, College of Science, Mustansiriyah University, Baghdad, Iraq.*

Abstract

Eriochrome Black T dye is an indicator of complex titration as water hardness, as an azo dye, blue in its deprotonated form, and turns red when it forms a complex with metal ions such as Ca, Mg, Cd . .etc. Water contamination is considered one of the most important problems that threaten human life on earth. An efficient method is done to remove EBT from wastewater via using cadmium sulfide Nanoparticles (CdS NPS) that was prepared by using an inexpensive and simple method (chemical precipitation) and was diagnosed this nanomaterial using an X-ray diffractometer (XRD), Transmission electron microscope (TEM), Scanning electron microscope (SEM) and Energy Dispersive X-Ray Analyzer (EDX). TEM characterization results for CdS nanoparticles illustrated that the nanoparticles have a pointy shape-like needles morphology and with miscellaneous sizes, the statistical calculation gives (32) nm as the rate particle size.

Through this study, the CdS nanomaterial proved that it has a high ability to adsorb Eriochrome Black-T (EBT) dye under certain conditions where we noticed that the maximum adsorption capacity of this dye by CdS nanoparticles was at Temperature (293) K, (pH = 6) and at a concentration (0.01 g) of the CdS nanomaterial with contact time up to (40) minutes and CdS. Also calculated the thermodynamic functions, (ΔS, ΔH, ΔG), we found that the process was spontaneous and exothermic under the specific condition through The thermodynamic parameters.

Keywords: CdS NPs, Eriochrome black-T Dye, Adsorption, Wastewater

Introduction

The presence of several types of toxic dyes in wastewater due to industrial activities such as rubber, textile, paper, leather and plastic industries represents one of the major challenges in environment[1].Harmful dyes affect the ecosystem although they have wide applications such as coloring paper, dying cotton, and wool [1]. Eriochrome Black T dye is and indicator of complex titration as water hardness, as azo dye, blue in its deporotonated form, and turns red when it forms a complex with metal ions such as Ca, Mg, Cd …..etc [2] (Figure 1.a).The wavelength of EBT dye is (530) nm and EBT is difficult to remove from water because to its chemical stability and high water solubility[3].

*Corresponding author e-mail: rashashakir.m@uomustansiriyah.edu.iq.; (Rasha Shakir Mahmood).
Receive Date: 25 December 2021, Revise Date: 31 December 2021, Accept Date: 31 December 2021
DOI: 10.21608/EJCHEM.2021.112946.5131

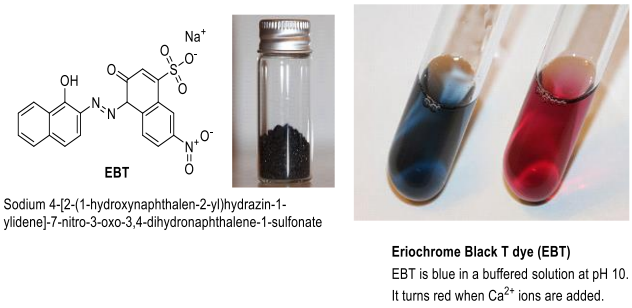


Figure 1.a) Chemical Structure and color of EBT

Pollution is introducing a harmful substance to environmental sphere, it is one of the biggest problem to universe with many form of pollutant such as chemical, biological, or naturally fixed pollutants [4-6]. Besides, Water pollution is one of pollution forms that has great effect on the environment, human and animals [7, 8]. It is subjected to the effects of various drivers and exhibits significant spatiotemporal effects[8]. Now, there are many tries to control all types of pollutions [9].

Water contamination is considered one of the most important problem that threatens human life on earth, especially since water is the basis for the existence of life on this planet, and perhaps dyes are the most important origins of pollution to which water is greatly exposed.[10-13].

Conventional methods such as photodegradation, biosorption, reverse osmosis, coagulation, ozonation, electrochemical oxidation, and adsorption had been used to remove the hazardous pollutants [14-16]. However, adsorption process found particular interest because of its high efficiency and economic consideration [14, 17-19]. Many types of adsorbents such as carbon materials, clay material, biomaterials, nanoparticles, nanocomposites, leaves and fly ash have been extensively used for the removal of dye from aqueous solution [20-22]. Double hydroxide (LDH) [23], Rutile TiO_2 [24], layered graphene and acid-modified graphene [25], and maize stem tissue [26] were used to extract EBT.

Freundlich equation (Freundlich adsorption isotherm) is an empirical relationship between adsorbed gas quantity in solid surface and gas pressure. Also, this equation is applicable for solute concentration that adsorbed onto solid surface and solute concentration of solute in liquid phase [27]. However, Langmuir adsorption model is designed to explain adsorption depending on assume adsorbate behaves as an ideal gas at isotherm conditions and adsorption with desorption in reversible relationship [28, 29].

So, according to this survey, our work aims to get efficient method to remove EBT from waste water via using cadmium sulfide Nanoparticles (CdS NPs) from their aqueous solutions via using adsorption technology.

Experimental:

Synthesis of Cadmium Sulfide Nanoparticles (CdS NPs)[30]

Equimolar Cadmium carbonate and sodium sulfide were added to each other under constant stirring (10min), then, propylene glycol (5 drops as drop by drop as a capping agent). The reaction was kept under constant stirring for 5h to get a yellow precipitate of CdS, filtered out, washed with distilled water and dried at room temperature (Figure 1.b).

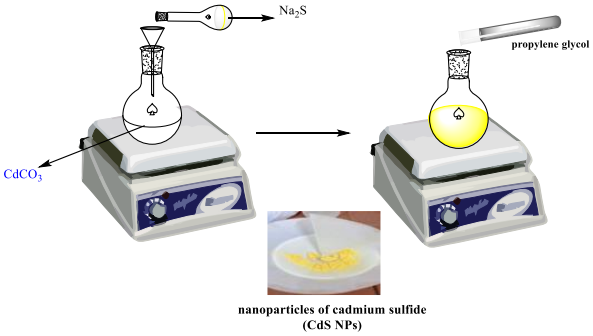


Fig. 1.b Synthesis of Cadmium Sulfide Nanoparticles.

The size and morphology of CdS NPs were studied by XRD-6000 that was operated at 30 mA and 40 kV to generate radiation at λ = 1.5406 Å, SEM and JEOL JEM-2100 TEM.

Adsorption experiment

To study the adsorption of Eriochrome Black T dye (EBT) on CdS NPs; 5-25 mg/L EBT dissolved in deionized water (0.01g of CdS NPs were added to 50 ml of EBT solution at each concentration). The mixture was shaken for 60 min at (293, 298, 303, 308 and 313) K.

Results and Discussion

XRD of CdS NPs showed characteristic peak at a high degree of pureness and with absence of peaks of other materials. So, this sharp peaks indicate high crystallinity nanoparticles of CdS. according to the Scherrer equation [31, 32] (Figure 2, Table 1).

$$D = k\,\lambda \setminus \beta\, cos\,\theta \ldots [1]$$

Where D, is a crystallized size, K is a Scherrer constant and equal to 0.9, λ is the X-ray wavelength 0.15406 nm by Cu-Kα radiations, θ is the angle of Bragg diffraction, and β is the full width at a maximum of half (FWHM) of an integral peak of

diffraction, the average particle size was calculated to be (32) nm.

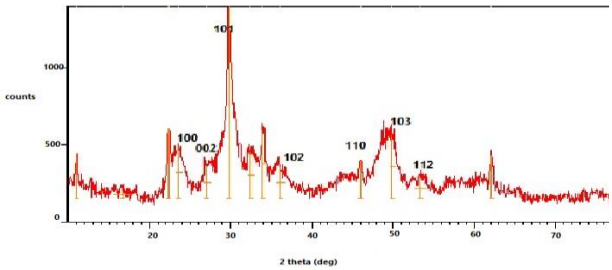


Figure 2: XRD pattern of the CdS nanoparticles.

Table. 1: shows the X-ray diffraction data for CdS nanoparticles.

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip Width
11.0374	290.60	0.2952	8.01638	22.71	0.3542
16.7576	47.64	2.3616	5.29065	3.72	2.8339
22.3771	456.95	0.3444	3.97312	35.72	0.4133
23.5321	329.29	0.7872	3.78065	25.74	0.9446
26.9965	206.44	0.9840	3.30285	16.14	1.1808
29.7229	1279.37	0.2460	3.00581	100.00	0.2952
32.4358	300.84	0.7872	2.76034	23.51	0.9446
33.9669	447.68	0.3936	2.63934	34.99	0.4723
36.1184	201.06	1.1808	2.48690	15.72	1.4170
46.0346	242.22	0.3936	1.97166	18.93	0.4723
49.9233	409.08	0.7872	1.82682	31.98	0.9446
53.3493	130.74	1.5744	1.71730	10.22	1.8893
62.1536	277.71	0.3936	1.49352	21.71	0.4723

While Figure 3 reveals distinct peaks of Cadmium (Cd) and Sulphur (S), and EDAX compositional analysis verifies that the sample is close to the nominal composition. Table (2) shows EDAX data that shows the components of prepared samples in weight percentages.

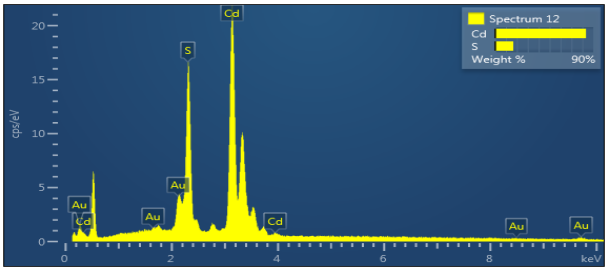


Figure 3: EDAX of CdS nanoparticles.

Table 2: EDAX data for CdS nanoparticles.

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard
S	K series	2.61	0.02252	16.70	0.18	41.27	FeS2	Yes
Cd	L series	10.35	0.10352	83.30	0.18	58.73	Cd	Yes
Total:				100.00		100.00		

Actually, picked area electron diffraction (SAED) patterns to evaluate the structure of the synthesized sample, and diffraction contrast images were taken. Figure 4 depicts a typical SAED from a sample of agent CdS nanoparticles this figure illustrated over all the rods, indicating the single-crystalline nature of the CdS nanorods. It is also interesting to note that the tip of the nanorods had a dark spot, which might have been CdS nanoparticles.

.

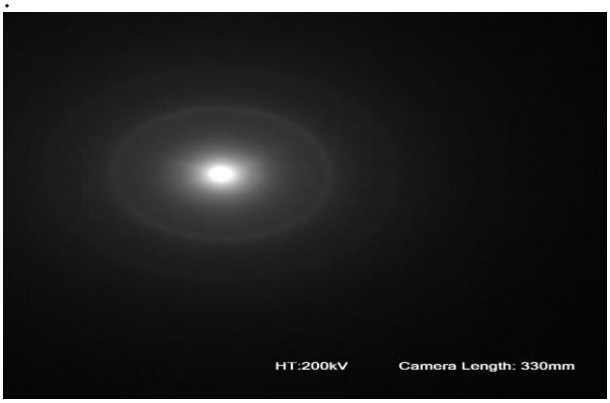


Figure 4: shows the selected area electron diffraction (SAED) pattern for CdS nanoparticles.

Figure.5 shows the TEM characterization that was obtained for CdS nanoparticles, as shown the nanoparticles have pointy shape like needle morphological (nanorode) with different sizes that conset with the XRD calculation, while Figure.6 illustrated the SEM for CdS nanoparticles with different scales which are 200 nm and 1μm, When preparing (CdS) nanoparticles, the covering factor propylene glycol (PG) was added, and when adding it, it was noted that the length of the nanoparticles (CdS) increased by 1 μm.

The reason for this is that (PG) has a strong interaction with the sides of nanoparticles more than with its ends, as it inhibited the growth of the side faces by covering them significantly compared to the other faces that continue to grow.

It was also noted that when the reaction continues for (5) hours, the length of the nano-needles will increase, or we can call them nano-rods, to several micro meters, but at the same time the diameter showed a very small change and this means that both the covering factor (PG) and the preparation time affect the growth of nanoparticles for (CdS).

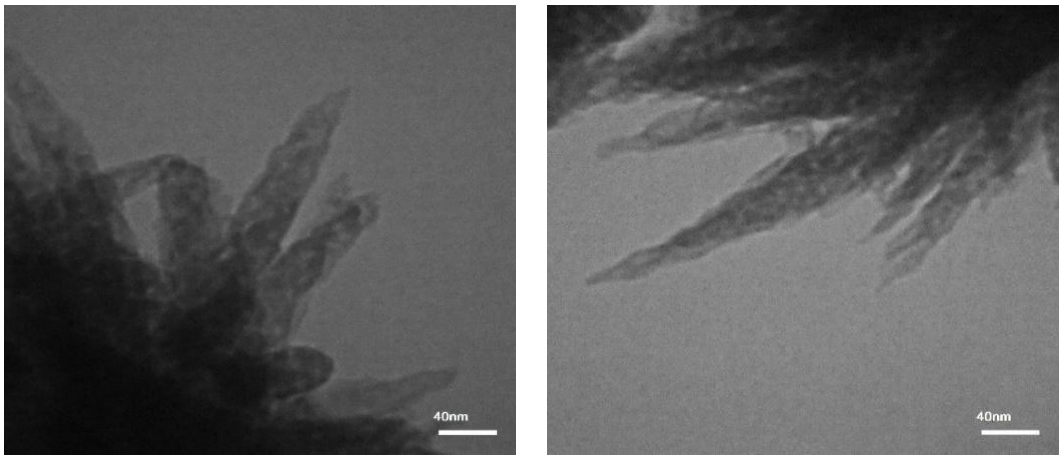
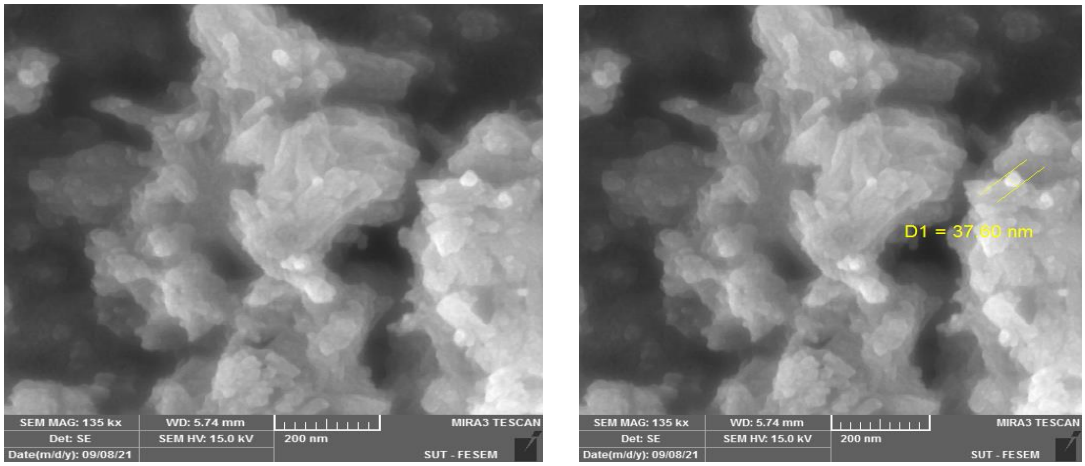


Figure 5: Transition electron microscope (TEM) images of the CdS nanoparticles



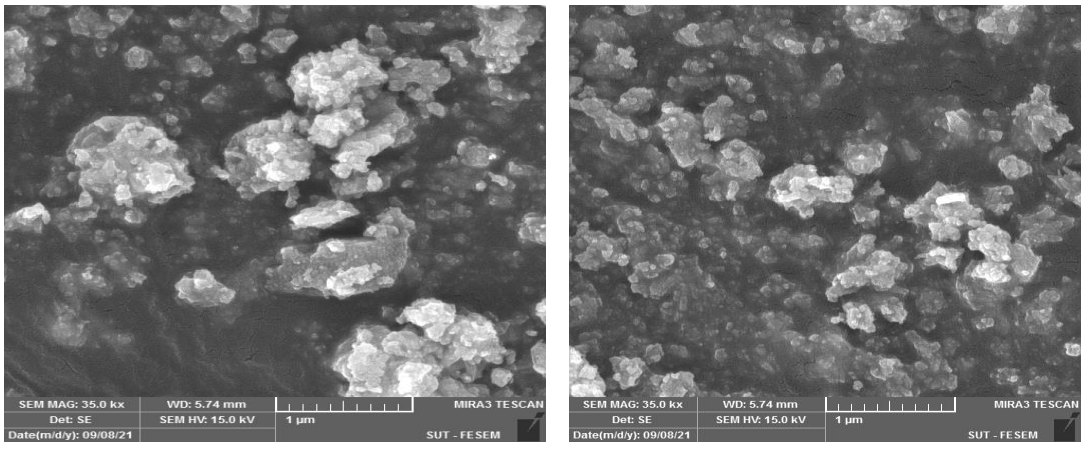


Fig.6. SEM images of the CdS nanoparticles with different enlargements

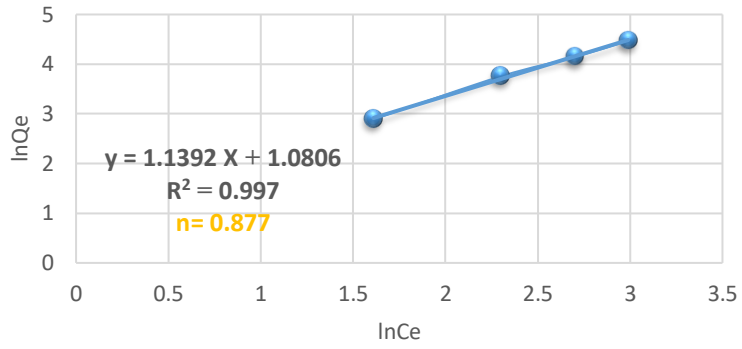


Figure 7: Adsorption equation of Freundlich isothermal at 293 K.

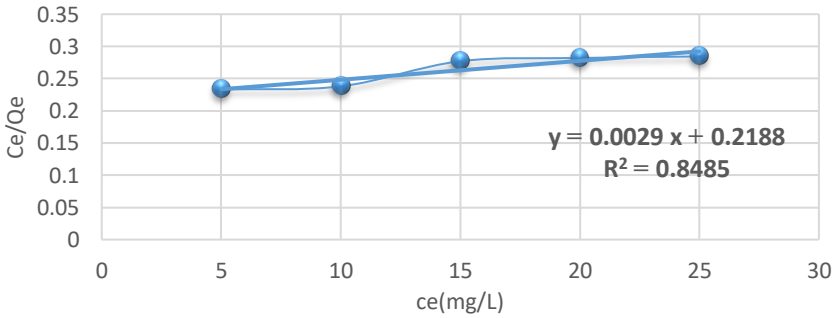


Figure 8: Adsorption equation of Langmuir isotherm at 293 K

. **Adsorption isotherm**

set The adsorbent phase of the retained concentration of (EBT) was set according to the equation:

$$Qe = (Ce - Co)V\ sol\ /\ M \ldots\ldots \quad [2]$$

Where, equilibrium ion concentration (mg/L), is equilibrium capacity (mg/g), is concentration of initial ion solution (mg/L), is solution volume (L) and is mass adsorbent (g).

The isotherm of (EBT) adsorption is in accord with the linearized Freundlich isotherm [33, 34]as seen in Figure.7. The relationship between the (EBT) concentration at equilibrium and CdS NPs is given by this equation

$$Log\ Qe = log\ kF + 1/n\ log\ Ce \quad \ldots\ldots. [3]$$

Langmuir isotherm equation:

$$Ce/Qe = (Ce/Qm) + (1/Qm\ kL) \quad \ldots\ldots.[4]$$

Throw Figure 8 noticed that the linear fitting of Langmuir isotherm data for EBT adsorption in its solution did not undergo the Langmuir isotherm according to the low value of R2 which is 0.8485. So It is not formed single-layer adsorption because CdS is a nanomaterial so we can say is dealing with Freundlich isotherm and not dealing with Langmuir isotherm. [35]

The Influence of Contact Time

Also in this paper, treatise the effect of the contact time between the adsorbent surface represented by cadmium sulfide nanoparticles with the adsorbent material, which represents the EBT dye, by changing the contact time, which ranges between (10-100) minutes, where we took the measurement every (10) min while maintaining the concentration The nanomaterial at (0.01) gm and the dye at (10) mg/Lat a temperature (293) K and as shown in Figure. 9, where we notice the occurrence of severe adsorption at the first ten minutes, and then the adsorption gradually decreases until the equilibrium point is reached at a time (40) minutes and the reason for this is due to the presence of many of the vacant sites on the surface of the adsorbent material, which gradually fills up over time, which leads to a decrease in the rate of adsorption.

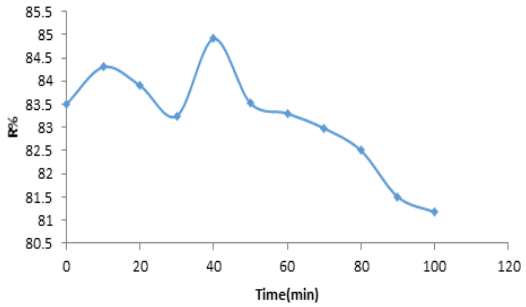


Fig .9. Effect of contact time

The influence of Temperature

Also studied the effect of the change in temperature on the process of removing EBT dye using nanoparticles CdS by using a temperature range of (293, 298, 303, 308, 313) K. observed that the adsorption process decreased when temperature increased and that case did according to the type of adsorption so the Our adsorption is physical adsorption and its exothermic, this effect illustrated by Figure.10.

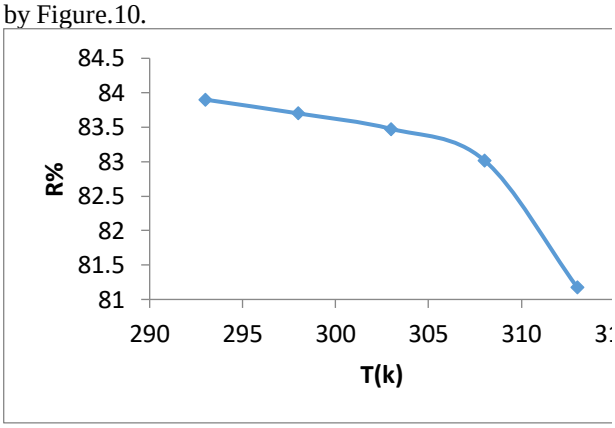


Fig .10. Effect of Temperature

The influence of PH

The PH is considered one of the most important measurements that must be taken into significance when studying adsorption because of its high sensitivity and for the purpose of determining the optimum pH at which the highest amount of EBT dye adsorption can occur by using CdS nanoparticles.

carried out the adsorption with different acidic degrees ranging in values (2, 4, 6, 8, 10, 12), and all experiments were carried out using an initial concentration of (EBT) dye of (10) ppm versus a concentration of (0.01) g of CdS nanomaterial, At a temperature of (293) K, all the results are shown in Figure.11, where it appears to us that the highest absorption rate of the (EBT) dye appeared from PH = 6 where the color of dye changes with constant the wavelength at (530)nm. It was also shown that the greater the PH value, the lower the absorption rate. This is due to the OH group combining with the anionic ion in the dye, which results in a reduction in the positive charge, and therefore the adsorption capacity drops. [13]

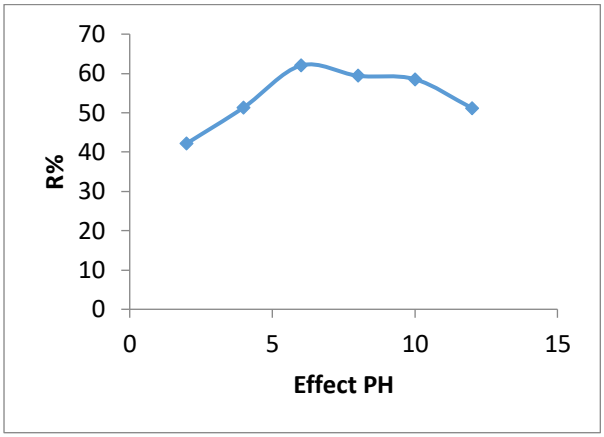


Fig .11. Influence of PH

The Influence of CdS nanoparticles dose

to study the influence of the adsorbent dose of CdS nanoparticles on the amount of adsorption of EBT dye in the solutions, we used different concentrations of the adsorbent surface that ranged (0.001, 0.003,0.005, 0.007, 0.009, 0.01g) taking into account the pH constancy at (6), the temperature at (293 K) and the contact time between the adsorbent surface and the adsorbate at (40min) Note that the initial concentration used for the dye is (10 mg/L).

from the Figure.12 noticed an increase in the absorption rate of the dye with an increase in the adsorbent concentration, where noticed that when the concentration of CdS particles (0.001g) the removal rate was reached (84.634 %), while noticed that the highest absorption rate occurs when reaching Concentration (0.01g) of CdS nanoparticles, and this is due to the rising in the number of active sites that be on the surface of CdS adsorbent, and thus the removal rate for EBT dye becomes higher reached to (86.72 %).

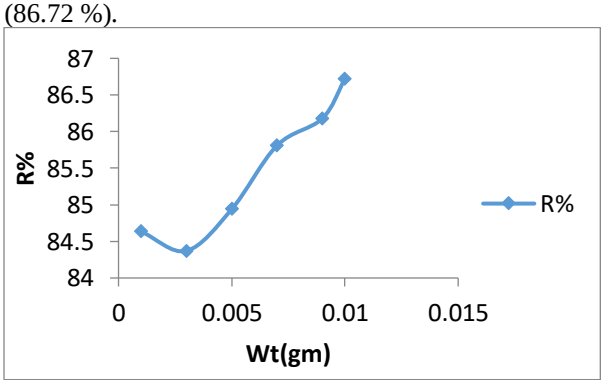


Fig.12. Effect of CdS nanoparticles dose.

Thermodynamic parameter

Usually, calculate the thermodynamic functions by using the following equations [36]:

$$\Delta G = \Delta H - T\Delta S \quad \ldots [5]$$

$$log\ X/m = -\Delta H/\ 2.303R + \Delta S/\ R \quad \ldots [6]$$

Where X/m is the utmost Adsorbate concentration (mg/g), R is considered the gas constant (8.314 J/mol K), and T is the temperature (K). ΔH was taken by the slope of the van Hoff plots of log (X/m) versus 1/T, as shown in Figure. 13, and (ΔS) was taken from the y-intercept.

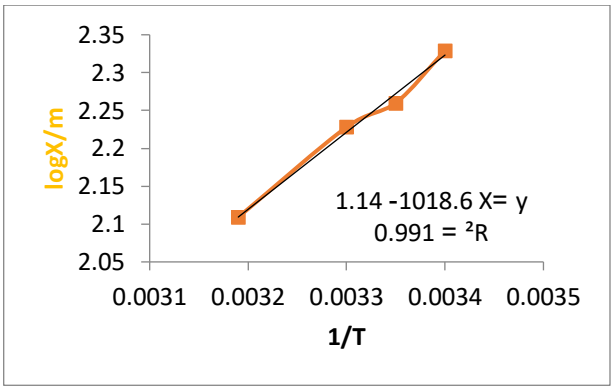


Fig. 13. The relation between log X/m and 1/T for the adsorption of EBT dye.

The slope showed value of ΔH (- 8468.6) kJ/mol and ΔS value from the y-intercept was (-9.47796) J/(mol·K), from The value of ΔH shows that the adsorption process of EBT dye by CdS nanoparticles is exothermic. While ΔG for the adsorption was (-5690.97) kJ/mol at 293 K and this refers that the adsorption was spontaneous.

Conclusion

Through all of the above, we concluded that the cadmium sulfide nanomaterial that was prepared by using a simple method (chemical precipitation) can be considered as one of the nanomaterials that have a high ability to adsorb EBT dye in aqueous solutions because their hexagonal structure of cadmium sulfide (CdS) that was gave it a range of physical, chemical, and biological applications and the nanosize made CdS have a higher surface area and that made it a good adsorbent under certain experimental conditions and from results were noticed that the maximum adsorption capacity of this dye by CdS nanoparticles was at Temperature (293) K, pH = 6 and at a concentration (0.01 g) of the CdS nanomaterial with contact time up to (40) minutes and CdS nanomaterial is considered a low-cost material so it's very useful in pollutants removal applications.

References

1. AGARWAL, Shilpi, et al. Efficient removal of toxic bromothymol blue and methylene blue from wastewater by polyvinyl alcohol. *Journal of Molecular Liquids*, 2016, 218: 191-197.
2. DUBENSKAYA, L. O.; LEVITSKAYA, G. D. Use of Eriochrome Black T for the polarographic determination of rare earth metals. *Zhurnal Analiticheskoj Khimii*, 1999, 54.7: 742-744.
3. ABU-NADA, Abdulrahman; ABDALA, Ahmed; MCKAY, Gordon. Removal of phenols and dyes from aqueous solutions using graphene and graphene composite adsorption: A review. *Journal of Environmental Chemical Engineering*, 2021, 9.5: 105858.
4. DUFOUR, Philippe; KOUASSI, A. M.; LANUSSE, Alain. Les pollutions. *Environnement et ressources aquatiques de Côte d'Ivoire*, 1994, 2: 320-331.
5. MACLEOD, Matthew, et al. The global threat from plastic pollution. *Science*, 2021, 373.6550: 61-65.
6. DOUGLAS, Mary. Pollution. *International encyclopedia of the social sciences*, 1968, 12: 336-342.
7. KAMIL, Amal Fadhil, et al. Cibacron red dye removal in aqueous solution using synthesized CuNiFe2O5 Nanocomposite: thermodynamic and kinetic studies. *Egyptian Journal of Chemistry*, 2021, 64.11: 5-6.
8. SHENG, Jichuan; TANG, Weizong. Spatiotemporal variation patterns of water pollution drivers: The case of China's south-north water transfer project. *Science of the Total Environment*, 2021, 761: 143190.
9. GONZALEZ-MARTIN, Javier, et al. A state–of–the-art review on indoor air pollution and strategies for indoor air pollution control. *Chemosphere*, 2021, 262: 128376.
10. SCHWEITZER, Linda; NOBLET, James. Water contamination and pollution. In: *Green chemistry*. Elsevier, 2018. p. 261-290.
11. TEO, Siow Hwa, et al. Sustainabletoxic dyes removal with advanced materials for clean water production: A comprehensive review. *Journal of Cleaner Production*, 2021, 130039.
12. ABDEL-FATAH, Mona A.; ALABD, H.; ELSAYED, Marwa M. Efficient Water Treatment of Swimming Pools Using Ozone. *Egyptian Journal of Chemistry*, 2021, 64.9: 1-2.
13. ABDEL-FATAH, Mona A.; AMIN, Ashraf; AL BAZEDI, Ghada A. Model and protected design of water piping system to minimize the water hammer effect. *Egyptian Journal of Chemistry*, 2022, 65.1: 1-2.
14. MOHAMMED, Mahdi Ahmed, et al. 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: 425-431.

15. BHAWANA, Jain, et al. Degradation of naphthylazo anionic dye by Fenton and Fenton-like processes: a comparative study with Fast sulphon black-F. *Desalination and Water Treatment*, 2017, 62: 252-256.
16. HUSSAIN, Dhia Hadi, et al. Cadmium ions pollution treatments in aqueous solution using electrochemically synthesized gamma aluminum oxide nanoparticles with DFT study. *Egyptian Journal of Chemistry*, 2020, 63.2: 417-424.
17. SHINDE, P. S., et al. Synthesis and Characteristics of CdS Nanoparticles in Normal (1 g) and Simulated Microgravity (SMG). *Buletin Fisika Vol*, 2021, 22.1: 7-11.
18. DABHANE, Harshal, et al. A review on environmentally benevolent synthesis of CdS nanoparticle and their applications. *Environmental Chemistry and Ecotoxicology*, 2021.
19. KAMIL, Amal Fadhil, et al. Cibacron red dye removal in aqueous solution using synthesized CuNiFe2O5 Nanocomposite: thermodynamic and kinetic studies. *Egyptian Journal of Chemistry*, 2021, 64.11: 5-6.
20. PHAM, Xuan-Hung, et al. Synthesis and Application of Silica-Coated Quantum Dots in Biomedicine. *International Journal of Molecular Sciences*, 2021, 22.18: 10116.
21. GHAEDI, Mehrorang, et al. Oxidized multiwalled carbon nanotubes as efficient adsorbent for bromothymol blue. *Toxicological & Environmental Chemistry*, 2012, 94.5: 873-883.
22. KONG, Lingying; GONG, Lei; WANG, Jiaoqin. Removal of methylene blue from wastewater using fallen leaves as an adsorbent. *Desalination and Water Treatment*, 2015, 53.9: 2489-2500.
23. MU'AZU, Nuhu Dalhat, et al. Bentonite-layered double hydroxide composite for enhanced aqueous adsorption of Eriochrome Black T. *Applied Clay Science*, 2018, 161: 23-34.
24. B. Priyadarshini, P. Rath, S. Behera, S. Panda, T. Sahoo, P. Parhi, Kinetics, Thermodynamics and Isotherm studies on Adsorption of Eriochrome Black-T from aqueous solution using Rutile TiO2, IOP Conference Series: Materials Science and Engineering, IOP Publishing, 2018, p. 012051.
25. KHALID, Arsalan, et al. A comparative study on the adsorption of Eriochrome Black T dye from aqueous solution on graphene and acid-modified graphene. *Arabian Journal for Science and Engineering*, 2018, 43.5: 2167-2179.
26. SALIMI, Farhad; VALIEI, Vahid; KARAMI, Changiz. Removal of EBT dye from aqueous solution by modified MoNiO4 adsorbent. *Desalination Water Treat*, 2020, 190: 340-352.
27. ABBAS, Ruba Fahmi, et al. Removal of Eriochrome Black T Dye by Using Al 2 O 3 Nanoparticles: Central Composite Design, Isotherm and Error Analysis. *Iranian Journal of Science and Technology, Transactions A: Science*, 2020, 44.4: 993-1000.
28. HANAOR, Dorian AH, et al. Scalable surface area characterization by electrokinetic analysis of complex anion adsorption. *Langmuir*, 2014, 30.50: 15143-15152.
29. LANGMUIR, Irving. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical society*, 1918, 40.9: 1361-1403.
30. RAHMAN, MOHAMMAD MAHBUBUR. SYNTHESIS AND CHARACTERIZATION OF ZINC SELENIDE THIN FILM SEMICONDUCTOR BY THERMAL EVAPORATION TECHNIQUE. 2018.
31. MONGKOLSUTTIRAT, K.; BUAJARERN, J. Uncertainty evaluation of crystallite size measurements of nanoparticle using X-Ray Diffraction analysis (XRD). In: *Journal of Physics: Conference Series*. IOP Publishing, 2021. p. 012054.
32. RHEIMA, A. M., et al. Study the adsorption ability of alizarin red dye from their aqueous solution on synthesized carbon nanotubes. *Digest Journal of Nanomaterials and Biostructures*, 2020, 15.4.
33. LIN, Kun-Yi Andrew; CHEN, Yu-Chien; PHATTARAPATTAMAWONG, Songkeart. Efficient demulsification of oil-in-water emulsions using a zeolitic imidazolate framework: adsorptive removal of oil droplets from water. *Journal of colloid and interface science*, 2016, 478: 97-106.
34. UMPLEBY, Robert J., et al. Characterization of molecularly imprinted polymers with the Langmuir–Freundlich isotherm. *Analytical chemistry*, 2001, 73.19: 4584-4591.
35. RHEIMA, Ahmed Mahdi; HUSSAIN, Dhia Hadi; ALMIJBILEE, Muntadher M. Alwan. Graphene-silver nanocomposite: Synthesis, and adsorption study of cibacron blue dye from their aqueous solution. *Journal of Southwest Jiaotong University*, 2019, 54.6.
36. ABOUDA, N. A.; JASIMA, B. E.; RHEIMAB, A. M. Methylene Orange dye removal in aqueous solution using synthesized CdO-MnO2 nanocomposite: kinetic and thermodynamic studies. *Chalcogenide Letters*, 2021, 18.5: 237-43.