International Journal of Chemical and Biochemical Sciences
(ISSN 2226-9614)

Journal Home page: www.iscientific.org/Journal.html

Doped (Ag) ZnO nanoparticles for removal of azo dyes from aqueous solutions

Mazen S. Hamada, Rami Abu Jabal

Chemistry Department, Al Azhar University, Gaza, Palestine.

Abstract

The color removal of azo dyes (E102, E110, E122 and E124) was carried out by using chemically synthesized disperse zinc oxide nanoparticles (ZnO $_{NPs}$) in aqueous solutions. Different factors and parameters that affect the degradation efficiency of azo dyes were studied including the initial concentration of pollutant, pH of solution, treatment time, concentration of ZnO $_{NPs}$ and temperature. The achieved optimal treatment conditions were: initial concentration of dye solution 5ppm, treatment time 80 min, concentration of ZnO $_{NPs}$ 0.08g, pH 7 and temperature of 40°C. In addition, the efficiency of ZnO $_{NPs}$ doped with Ag at different amounts (0.5 – 2%) was also investigated for the removal of azo dyes in aqueous solutions. The optimum dose of Ag doped on ZnO $_{NPs}$ was at 1% Ag which achieved a removal percent of 98.4, 93.6, 91.5 and 84.7 for E110, E124, E102 and E122 respectively.

Keywords: E102; E110; E122; E124 ; ZnO ; Nanoparticle ; Ag doped ; water treatment, azo dyes

Full length article **Corresponding Author*, e-mail: *dr.mazenhamada@gmail.com*

1. Introduction

Various feed additives contribute to the growth of human, society, science, and technology but there is a rapid growth in environmental pollution problem. One of the biggest risks is the water pollution which associated with release of many different pollutants [1]. One of the most menacing water pollutants are synthetic dyes and could be mutagenic or even lethal for the biosphere [2]. The release of these dyes into fresh and seawater reservoirs badly influences all sorts of living organisms. Dye is the most visible pollutant and obstructs the penetration of light and decelerates the photosynthesis, which stops or slows down the growth of aquatic plants [3]. This water containing dyes causes aesthetic problems due to the color. Also, these dyes damage the quality of the receiving water because many of dyes released, and their breakdown products are toxic, carcinogenic or mutagenic to life forms [4]. Azo dyes are the largest group of dyes used in the textile industry [5] constituting 20-40% of the dyes used for dyeing cotton, rayon, silk, wool, nylon, and leather [6,7]. They have one or more azo groups (R1-N=N-R2) having aromatic rings mostly substituted by sulfonate groups. These complex aromatic conjugated structures are responsible for their intense color, high water solubility and resistance to degradation under normal conditions [8,9]. It is estimated that the leather industry wastewater consists approximately 10 to 200 mg L^{-1} of the dye/constituents [10-11].

Removal of these contaminants down to safe levels is expensive, high energy and unsustainable by current approaches such as oxidation [12], biodegradation [13], adsorption [14], ultrafiltration [15] and Electrocoagulation [16], so the demand for the development of simple and efficient method for the removal of harmful chemicals from pollutant water is ever growing. Nanotechnology is currently being considered as a promising technique for water purification in comparison to other conventional methods. As it can break up complex long chained organic molecules (normally toxic) into simpler fragments. Nanotechnology offers lot of promise in the area of water purification owing to large surface to volume ratios offered by nanostructures [17-18]. Metal oxide like zinc oxide (ZnO), titania (TiO_2), tungsten oxide (WO_3), zinc stannate (Zn_2SnO_4), etc. can be an attractive way of water purification as it is capable of removing chemical as well as biological contaminants [19].

The purpose of this study is to conduct an experimental investigation on the removal of different azo dyes. The color removal of the E102, E110, E122 and E124 dye solution was carried out by using chemically synthesized disperse ZnO_{NPs} in aqueous solution. The various parameters such as time, nanoparticle concentration, initial dye concentration and pH were studied. Additionally, the effect of presence of Ag concentration to ZnO_{NPs} was investigated for the removal of azo dyes in aqueous solutions.

2. Materials and methods

The dyes used in the present work was E124, E122, E110 and E102. The chemical and physical properties of this dyes are given in figure 1 and table 1. Undoped and doped (Ag) ZnO_{NPs} were successfully synthesized and mediated by the combustion method [20]. Sodium hydroxide, hydrochloric acid was of analytical grade and purchased from Merck. Distilled water was used for the preparation of solutions. A stock solution of dye (100 mg/L) was prepared by dissolving an accurate quantity of the dye in distilled water and suitably diluted to the required initial concentrations. Different standard solutions of E124, E122, E110 and E102 with concentration from 5-20 ppm were prepared to measure its removal at different conditions. The pH of the working solution was adjusted to the desired values with 0.1N HCl or 0.1N NaOH.

2.1. Equipment's and Procedures

The dyes concentration was determined using a double - beam UV-Vis spectrophotometer, model UV 1601 is from Shimadzu (Japan). Hot Plate, model (HB502), BIBBY STERILIN LTD. (U.K.) was used while preparing the solutions. To adjust the pH of the solutions a pH meter model AC28, TOA electronics Ltd., (Japan) was used. Water bath model SB-650, Tokyo Kikakkai CO. Ltd., (Japan) was used for heating the solutions to the desired temperature.

2.2. Analysis

Stoke solutions of each dye (100 ppm) were prepared and suitable dilutions were examined as described below. To evaluate the removal efficiency, the remaining dyes (E124, E122, E110 and E102) concentration was measured with the double-beam UV-visible spectrophotometer at λ_{max} = 503 nm, 516.14 nm, 480 nm and 426 nm respectively using calibration curve with standard error ±0.5%. The equation used to calculate the color removal efficiency in the treatment experiments was

$$\%E = [(A_0 - A)/A_0] \times 100$$

Where A_0 and A are absorbance values of dyes solutions before and after treatment with respect to their λ_{max} [21].

3. Results and discussions

3.1. Effect of Contact Time

Equilibrium time is one of the important parameters to design a low-cost adsorbent for removal of organic wastes. The adsorption of E124, E122, E110 and E102 dyes onto ZnO_{NPs} were studied as a function of contact time to determine the necessary adsorption equilibrium time. The reaction duration was varied from 10-100 min. The results reveal that about 28%, 37.4, 26.6 and 33.8 of E124, E122, E110 and E102 dyes respectively were adsorbed in 80 minutes, Figure 2. By increasing the duration of treatment, more time is given for the reaction between dye and the nanoparticles. The dye particles were adsorbed chemophisically on the surface of the nanoparticle through electrostatic forces due the available lone pair electrons on the nitrogen and oxygen atoms of the investigated dyes and reached its maximum after 80 min contact time. Longer treatment duration will lead to a reverse reaction which enhance the release of the dye particles from the surface of nanopatricles.

3.2. Effect of ZnO_{NPs} Dose

The amount of solid nanoparticles is important parameter for detection of adsorption capacity of solid in removing organic wastes. A rapid uptake of pollutants and establishment of equilibrium in a short period signify the efficiency of the solid in removal of various organic pollutants. The effect of ZnO_{NPs} dose on adsorption of E124, E122, E110 and E102 dyes were investigated in range of 0.01 – 0.1mg at fixed amount of dye and contact time of 80 min. The removal of azo dyes increases with increase catalyst amount and the maximum removal of the investigated dyes was reached at ZnO_{NPs} dose of 0.08mg, Figure 3.

3.3. Effect of Dye Concentration

The initial concentration of adsorbate also plays an important role as a given mass of the adsorbent can adsorb only a fixed amount of the solute. Dye concentration in this step of the experiment varied from 5 to 20 ppm, ZnO_{NPs} dose 0.08 mg and contact time 80 min. The adsorption capacity of E124, E122, E110 and E102 dyes increased upon decreasing in dye concentration as indicated in Figure 4. The optimal initial concentration of dye solution was 5 ppm for all dyes. The maximum decolorization% obtained was 48.6, 50, 54.7, and 60 for E110, E124, E102 and E122 respectively. In dilute solutions the dye particles will have more opportunity for chemophysical adsorption on the surface of the nanoparticles and hence increasing the removal % of dye particles [22]. However, by increasing the dye concentration a reverse reaction will occur. This indicate that the dye decolorization rate is strongly dependent on the initial dye concentration.

3.4. Effect of pH solution

The initial pH has a considerable effect on the efficiency of the removal of organic pollutants. The influence of pH on removal of dyes was investigated from pH 2 to 11 while keeping the other parameters constant. The obtained results from the effect of pH on removal efficiency of E124, E122, E110 and E102 dyes are shown in Figure 5. The plots showed that the removal of E124, E122, E110 and E102 dyes increases up to 72% ,80.2%, 68.6% and 75.5% respectively at pH 7. This can be due to the electrostatic attraction between the adsorptive anion and the surface of the ZnO_{NPs} that gradually becomes more negatively charged [23]. The decrease in adsorption capacity at higher pH was due to competition between anionic dye molecules and OH^- ions [24]. The results show that below this pH, the ZnO_{NPs} acquire positive charge owing to the protonation of functional groups and above this pH the surface of ZnO_{NPs} has a negative charge [25].

Table 1: Chemical and physical properties of this dyes

Dyes	**E124**	**E122**	**E110**	**E102**
Molar mass g·mol^{-1}	604.46	502.44	452.36	534.36
Chemical formula	$C_{20}H_{11}N_2Na_3O_{10}S_3$	$C_{20}H_{12}N_2Na_2O_7S_2$	$C_{16}H_{10}N_2Na_2O_7S_2$	$C_{16}H_9N_4Na_3O_9S_2$
λmax nm	503	516.41	480	426

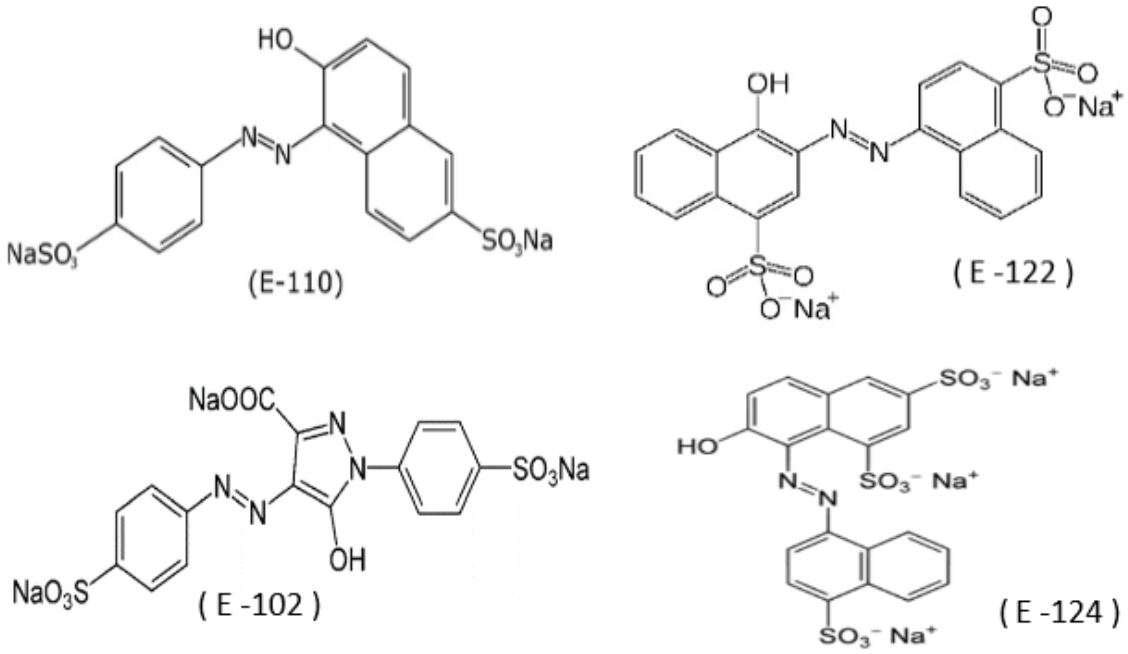

Figure 1. Chemical structure of azo dyes

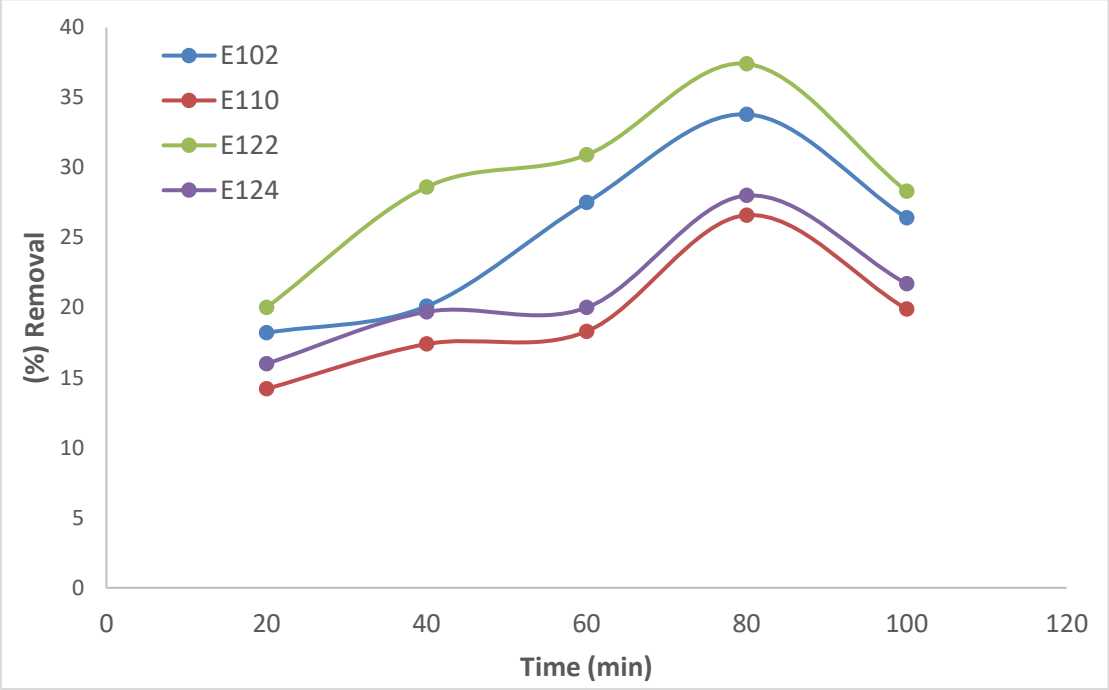

Figure 2. Effect of time on the removal of E124, E122, E110 and E102 dyes

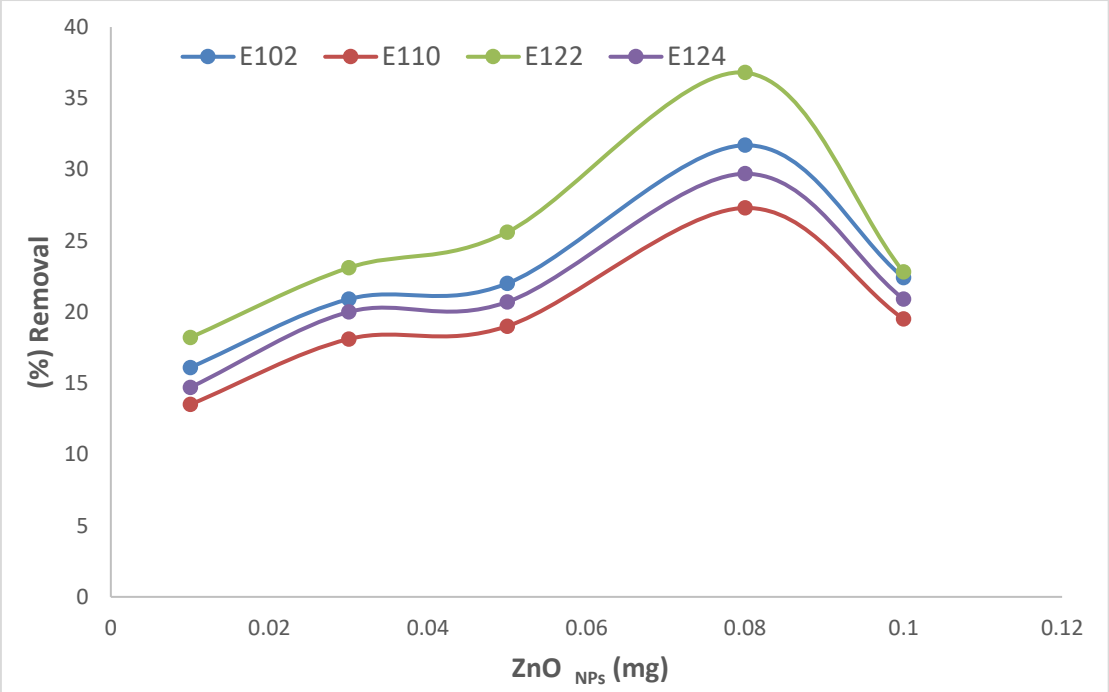

Figure 3. Effect of concentration of ZnO $_{NPs}$ on the removal of E124, E122, E110 and E102 dyes

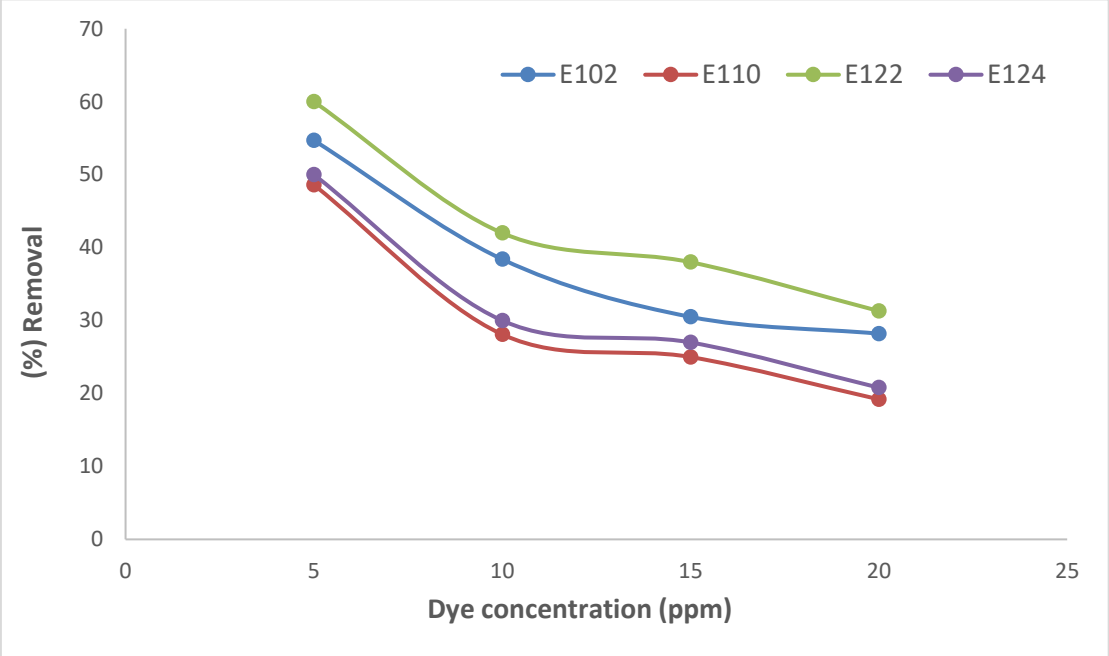

Figure 4. Effect of initial dye concentration on the removal of E124, E122, E110 and E102 dyes

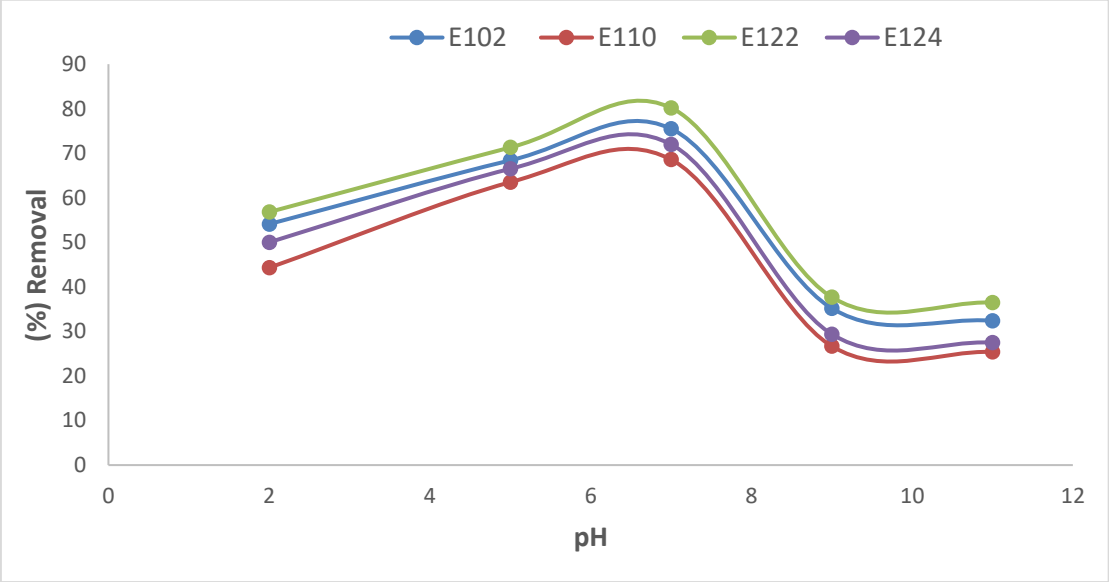

Figure 5. Effect of pH on the removal of E124, E122, E110 and E102 dyes

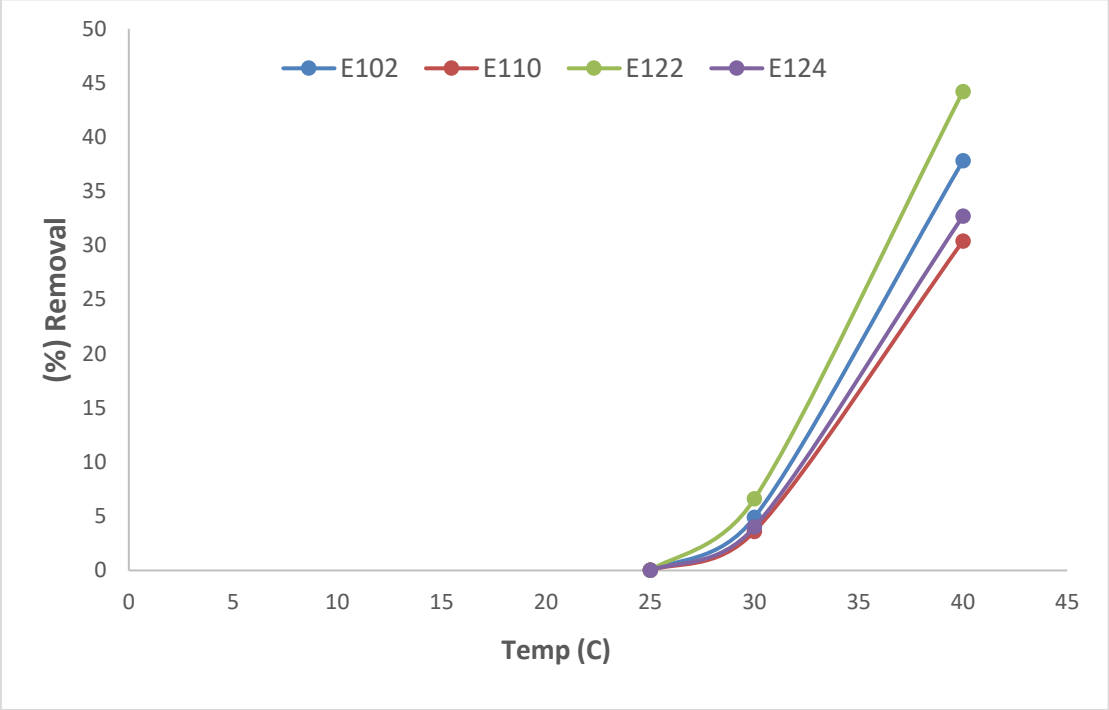

Figure 6. Effect of Temperature on the removal of E124, E122, E110 and E102 dyes

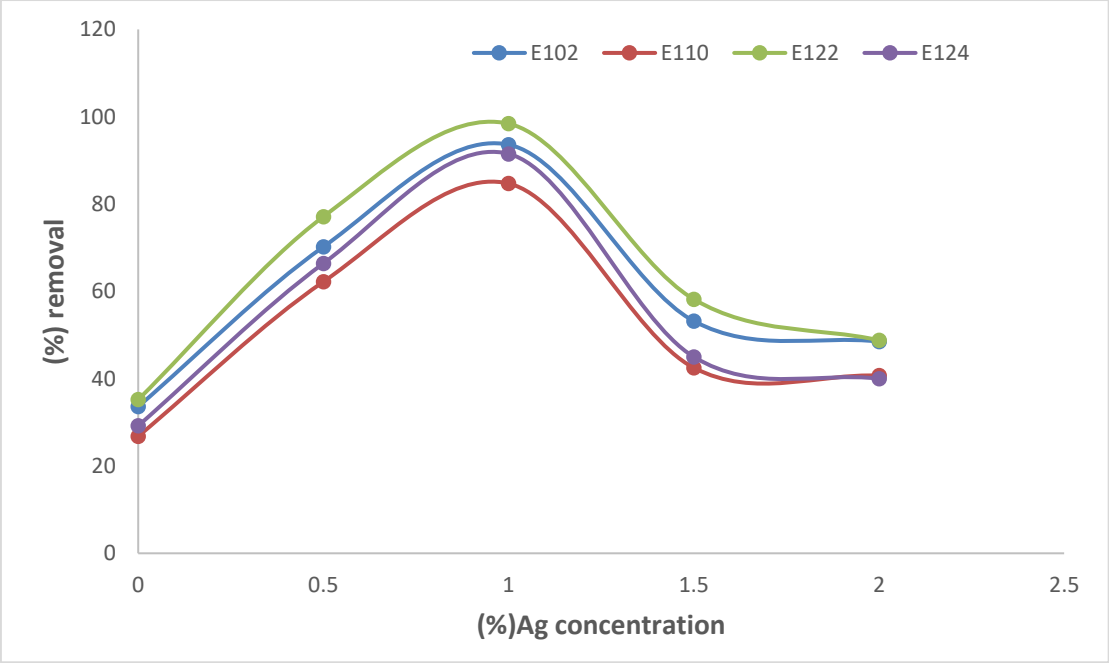

Figure 7. Effect of doped (Ag) ZnO $_{NPs}$ dose on removal of E124, E122 , E110 and E102 dyes

3.5. Effect of temperature

The percentage removal of E124, E122, E110 and E102 dyes onto ZnO_{NPs} were studies by varying the temperature from 25 to 40°C. The experiments were performed by adding 0.08 mg of ZnO_{NPs} into 100mL of 5 ppm solutions of dyes at pH 7, figure 6. The obtained results showed that the increase in the temperature of the solutions of dyes from 25 to 40°C leads to increase in the adsorption percentage removal of dyes onto the ZnO $_{NPs}$, which shows that the adsorption process is endothermic and chemically in nature. The possible explanation of this increase in percentage removal of dyes onto ZnO $_{NPs}$ could be due to the availability of more active sites and activation of the adsorbent surface at higher temperatures.

3.6. Effect of Doped (Ag) ZnO $_{NPs}$ Dose

The capacity of the ZnO $_{NPs}$ to degrade dye was examined after they were doped with various concentrations of Ag. Figure 7 depicts the effect of Ag dosage doped on ZnO $_{NPs}$ on the removal of azo dyes from aqueous solutions. From the plot it can be seen that the percent removal of the E124, E122, E110 and E102 dyes is enhanced with increasing the doping dose of Ag onto ZnO $_{NPs}$. The increased removal of E124, E122, E110 and E102 dyes were found to be poor after a dose of 1 % Ag for all azo dyes. The optimum dose of Ag doped on ZnO $_{NPs}$ was at 1% Ag which achieved a removal percent of 93, 84.7, 98.4 and 91.5 for E124, E122, E110 and E102 respectively. This complies with literature studies [26], which found that the addition of Ag $_{NPs}$ decreases the Energy band gaps of ZnO, i.e. the presence of Ag $_{NPs}$ downshifts the Fermi level of ZnO toward the valence band. As a result, the driving force for electron injection from dye-excited state to ZnO conduction band is increased.

4. Conclusions

ZnO $_{NPs}$ proved to be very suitable and effective adsorbent for removing azo dyes from aqueous solutions. The optimal treatment conditions for the removal of azo-dyes were: 5ppm initial concentration of dye solution, treatment time of 80 min, 0.08g of ZnO $_{NPs}$, pH 7 and temperature of 40^0C. A removal percent between 85 and 98.5 was achieved when applied ZnO $_{NPs}$ was doped with 1% (Ag) dose. This method is of great advantage since it is harmful and inexpensive when compared with photcatalyst radiation procedure.

References

[1] B. Okutucu. (2020). Wastewater Treatment Using Imprinted Polymeric Adsorbents Waste in Textile and Leather Sectors.

[2] Q. Jia, S-M. Wong, and K-B, Chua. (2019). In vitro and in vivo inhibition of infectivity of human enterovirus 71 by a sulfonated food azo dye, brilliant black BN. Journal of Virology. 93(17): e00061–e00019

[3] D. Shao, W. Zhou, T.J. Bouma, T. Asaeda, Z.B. Wang, X. Liu, T. Sun and B. Cui. (2019). Physiological and biochemical responses of the salt-marsh plant *Spartina alterniflora* to long-term wave exposure. Ann Bot 125:291–300

[4] D. Georgiou, C. Metallinou, A. Aivasidis, E. Voudrias, and E. Gimouhopoulos. (2004). Decolorization of azo-reactive dyes and cotton-textile wastewater using anaerobic digestion and acetate-consuming bacteria. Biochemical Engineering Journal. 19: 75-79.

[5] C. Maximo, M.T.P. Amorim, M. Costa-Ferreira. (2003). Biotransformation of industrial reactive azo dyes by Geotricum sp. CCMI 1019. Enzyme and Microbial Technology. 32: 145-151.

[6] E.V. Veliev, T. Ozturk, S. Veli, and A.G. Fatullayev. (2006). Application of diffusion model for adsorption of azo reactive dye on pumice. Polish Journal of Environmental Studies. 15: 347-353.

[7] C.L. Yang and J. McGarrahan. (2005). Electrochemical coagulation for textile effluent decolorization. Journal of Hazardous Materials. 127: 40-47.

[8] C. O'Neill, A. Lopez, S. Esteves, F.R. Hawkes, D.L. Hawkes, et al. (2000) Azo-dye degradation in an anaerobic-aerobic treatment system operating on simulated textile effluent. Applied Microbiology and Biotechnology.53: 249-254.

[9] P. Rajaguru, K. Kalaiselvi, M. Palanivel, and V. Subburam. (2000). Biodegradation of azo dyes in a sequential anaerobic-aerobic system. Applied Microbiology and Biotechnology. 54: 268-273

[10] P.L. Gilkey, D.T. Bolshakov, J.G. Kowala, L.A. Taylor, S. O'Donnell, D.R. Marenda, and L.K. Sirot. (2018). Lethal effects of erythritol on the mosquito Aedesaegypti Linnaeus (Diptera: Culicidae). Journal of Applied Entomology. 142:873–881.

[11] M. Rafatullah, S. Ismail, and A. Ahmad. (2019). Optimization study for the desorption of methylene blue dye from clay based adsorbent coating. Water. 11:1304

[12] J. Racyie, M. Rimeika, and H. Bruning. (2009). pH effect on decolorization of raw textile wastewater polluted with reactive dyes by advanced oxidation with UV/H_2O_2. Environmental Protection Engineering. 35: 167-177.

[13] E. Zablocka-Godlewska, W. Przystas, E. Grabinska-Sota. (2009). Decolorization of triphenylmethane dyes and ecotoxicity of their end products. Environmental Protection Engineering. 35: 161-169.

[14] L. Dabek, E. Ozimina, and A. Picheta-Oles. (2012). Dye removal efficiency of virgin activated carbon and activated carbon regenerated with fenton's reagent. Environmental Protection Engineering. 38: 5-13.

[15] J. Kawiecka-Skowron, and K. Majewska-Nowak. (2011). Effect of dye content in a treated solution on performance of the UF ceramic membrane. Environment Protection Engineering, 37(2), pp.5-12.

[16] N.M.A. Ghalwa, A.M. Saqer and N.B. Farhat. (2016). Removal of Reactive Red 24 Dye by Clean Electrocoagulation Process Using Iron and Aluminum Electrodes. Journal of Chemical Engineering and Process Technology. 7:1

[17] S. Baruah, and J. Dutta. (2009). Nanotechnology applications in pollution sensing and degradation in

agriculture: a review. Environmental Chemistry Letters. 7(3), 1-14.

[18] G.L. Hornyak, J. Dutta, H.F. Tibbals, and A.K. Rao. (2008). Introduction to nanoscience. CRC Press.

[19] J. Kim, and K. Yong. (2012). A facile, coverage controlled deposition of Au nanoparticles on ZnO nanorods by sonochemical reaction for enhancement of photocatalytic activity. J. Nanopart. Res. 2012, 14, 1-10.

[20] S.K.K. Shaat, H. Musleh, J. Asad, N. Shurrab, A. Issa, A. Al-Kahlout and Naji Al Dahoudi. (2019). IntechOpen 1-26.

[21] N. Mohan, N. Balasubramanian, and C.A. Basha. (2007). Electrochemical oxidation of textile wastewater and its reuse. Journal Hazardous Materials. 147: 644-651.

[22] M. S. Hamada. (2021). Zinc oxide nanoparticles for the decolourization of e124 dye from aqueous solution. International Journal of Advanced Research in Engineering and Technology (IJARET). 12, 40-47,

[23] O. Moradi, K. Zare. 2011. Fullerenes, Nanotubes and Carbon Nanostructures, 19, 628.

[24] F. Ishtiaq, H.N. Bhatti, A. Khan, M. Iqbal, and A. Kausar. (2020). Polypyrole, polyaniline and sodium alginate biocomposites and adsorption-desorption efficiency for imidacloprid insecticide. International Journal of Biological Macromolecules. j.ijbiomac.2020.01.022.

[25] H.A. Kiwaan, T.M. Atwee, E.A. Azab, and A.A. El-Bindary. (2019). Journal of the Chinese Chemical Society 66(1), 89–98.

[26] M.N. Zafar, Q. Dar, F. Nawaz, M.N. Zafar, M. Iqbal, M.F. Nazar. (2018). Effective adsorptive removal of azo dyes over spherical ZnO nanoparticles. Journal of Materials Research and Technology. 8(1), 713-725.