

# Adsorptive Removal of Eosin Y Dye by using PVA/Gelatin/CuO Polymer Nanocomposite Film

M. S. El-Hassan<sup>1</sup>, M.A. ABBO<sup>2</sup>, E.A. HASSN<sup>3</sup>, Ahmed M. Ismaiel<sup>4</sup>

<sup>1,4</sup>Department of Chemistry, Faculty of Science, Jazan University, Jazan, Saudi Arabia

<sup>2</sup>Department of Chemistry, College of Education and science Taif University, Saudi Arabia

<sup>3</sup>Department of Chemistry, College of Science, Sudan University of Science and Technology, Sudan

**Abstract:** The adsorption behavior of eosin yellow (EY) from aqueous solution onto various ratios of PVA/Gelatin/CuO film in batch technique was studied. PVA/Gelatin/CuO film was prepared and characterized by SEM, TEM and FTIR analysis. The effect of pH, dosage of adsorbent, contact time, temperature, and the initial concentration of dye was investigated. The maximum amount of dye removal found about 90% at pH 4, the adsorption dose 0.2mg/L, with the initial dye concentration of 5 mg/L, and the temperature of 25°C, with contact time 60 min.

**Keywords:** Eosin Y, Adsorptive, PVA/Gelatin/CuO, polymer nanocomposite, Film, ratio

## 1. Introduction

Nanotechnology is fundamentally about preparation of nanoscale materials [1]. NPs are subjected in an increased interest, because they combine the features of polymers with a small quantity of nanoparticles (less than 5% by weight) [2]. In the last years significant interest has been devoted to the study of nanocomposite materials obtained through the addition of inorganic fillers with at least one dimension in the scale of nanometer to a polymeric matrix. Indeed, such materials showed important improvements in their properties with just few percent of loading, to be compared with classic composites, where filler content well above 30% are needed to obtain interesting results in properties enhancement [3,4]. Eosin Y, a dye widely used as a biological stain, Eosin B is widely used in the estimation of wide range of proteins in life tissue because in acidic solution Eosin Y make a complex with the proteins and the absorption of the complex formed is proportional to the concentration of the proteins. The stain is harmful if swallowed, inhaled, drunk, or absorbed through skin. Some researchers have tried to remove it by adsorption, but no one has attempted for complete degradation [5].

## 2. Experimental

### 2.1. Materials and Methods

Poly (vinyl alcohol), (molecular weight = 350,600g.mol<sup>-1</sup>). With an average degree of polymerization of 1750±50. Gelatin type (B) derived from bovine skin, with Bloom number 50-300(from the supplier). Copper (II)Oxide (CuO) is black powder, Nanoparticles size is 50nm, with molecular weight of 79.546 g/mol, assay > 99%, melting point 1326°C and density 6.3-6.49g/ml at 20°C obtained from Scientific Fischer chemicals, Germany. Citric acid used in this work, is white powder (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>.H<sub>2</sub>O), with molecular weight of 210.14 g/mol, assay 99.5-100.5%. Eosin yellow, also known as Acid red 87, C.I. 45,380, Bromo fluorescein; Sodium eosin, with Molecular Formula C<sub>2</sub>OH6Br4Na<sub>2</sub>O<sub>5</sub>, and

molecular weight equal 691.58 g/mol Figure 1. All chemicals were obtained from Scientific Fischer chemicals Company.

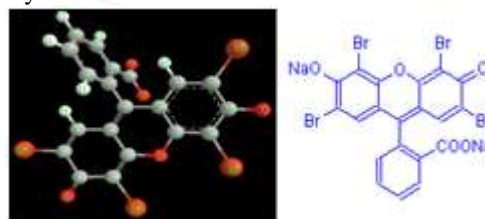


Figure 1: Ball and stick structure of EY.

### 2.2. Preparation of poly (vinyl alcohol)/ Gelatin/Copper Oxide (PVA/Gelatin/CuO) films

Different weights of Copper Oxide (0.01 and 0.1gm) were dissolved in (0.1N) Hydrochloric acid first. These weights were loaded after preparation of PVA/Gelatin powder with different ratios from the two polymers (25/75), (50/50) and (75/25) by weight in 20ml of distilled water with spontaneous stirring. The solution of PVA/Gelatin should be cooled during adding citric acid (0.1M) and Copper Oxide. The solution was then subsequently casted onto plastic dishes to form films. The casted films were dried under ambient conditions. The (PVA/Gelatin/CuO) films have blue-greenish color.

### 2.3 Characterization

The prepared PVA/Gelatin/CuO nanocomposites ratio were analyzed using a Fourier transform infrared (FT-IR) spectrometer (Bruker Optics Ft Tensor 27, Germany). The concentration of dye in solution was measured by a Shimadzu spectro-photometer(UV-1800, ENG 240 V, soft Japan) at maximum wavelength 516 nm.

### 2.4 Equilibrium Studies

Using the batch process in order to evaluate the effect of parameters effects on the amount of dye adsorbed at

equilibrium, the percentage of adsorption was calculated by the following equation.

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

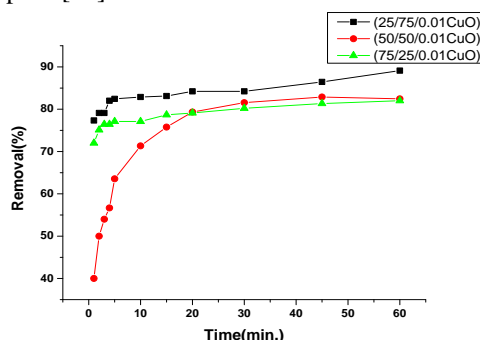
### 3. Result and Discussion

#### 3.1 FT-IR Spectroscopy

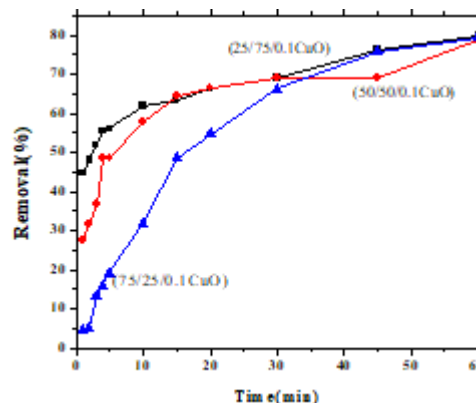
The band at  $3600.26 \text{ cm}^{-1}$  is assigned to O—H stretching vibration of hydroxyl groups observed in a strong broad band. Band at  $2149.16 \text{ cm}^{-1}$  is generally ascribed to the combination frequency of (CH+CC) according to [6]. Carbonyl group C=O was present at  $1745.34 \text{ cm}^{-1}$ . The vibrational absorption peaks of all metal oxides (M—O) bands were observed with low intensity. As well as bands in the low frequency range assigned to the loaded CuO Nanoparticles. The intensity bands at  $868.92\text{-}708.71 \text{ cm}^{-1}$  attributable to Cu—O—Cu in plane vibration according to study [7,8]. The peaks at  $556.55$  and  $434.38 \text{ cm}^{-1}$  are attributed to Cu(II)—O out of plane vibrations[9]

#### 3.2. Effect of time

The investigation of adsorption rate of Eosin Y onto polymer nanocomposite ratios (25/75/0.01 CuO), (50/50/0.01 CuO), (75/25/0.01 CuO) and (25/75/0.1 CuO), (50/50/0.1 CuO), (75/25/0.1 CuO) at constant dose of selected polymer nanocomposite ratios 0.2mg/L. The initial dye concentration was 5 mg/L at a pH of 4.0. Samples were withdrawn at different time intervals at room temperature. From Fig. (2 and 3) It was shown that, the removal percentages (%) of Eosin Y were increases by increasing time. Also, results showed that, the removal percentages (%) of Eosin Y had a sharp increase at the beginning of the reaction for all investigated polymer nanocomposite ratios, followed by a continued slower removal rate and finally reached to the saturation. The removal percentages (%) of Eosin Y onto polymer nanocomposite ratios (25/75/0.01 CuO), (50/50/0.01 CuO), (75/25/0.01 CuO) and (25/75/0.1 CuO), (50/50/0.1 CuO), (75/25/0.1 CuO) were (89%, 82%, 82%) and (80%, 78%, 79%) respectively. This phenomenon can be due to the fact that at the beginning of the dye contact with the sorbent materials, the adsorption of Eosin Y was taken place probably via surface functional groups, there were plenty of binding site available for dye adsorption onto the sorbent surface, so the dye molecules interacted easily in these sites. Until the binding sites were fully occupied, the dye molecules diffused into pores of the adsorbents for further adsorption[10].



**Figure 2:** Effect of contact time for removal of Eosin Y dye by polymer nanocomposite ratios (25/75/0.01 CuO), (50/50/0.01 CuO) and (75/25/0.01 CuO).

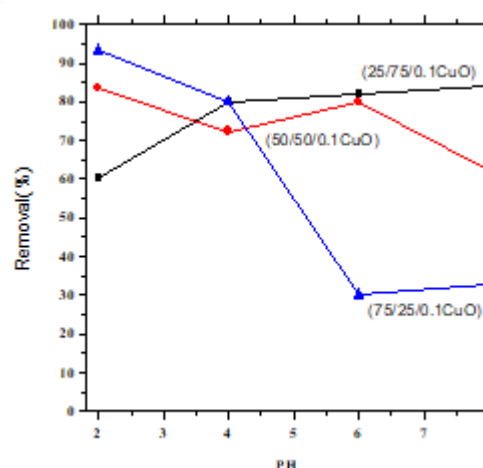


**Figure 3:** Effect of contact time for removal of Eosin Y dye by polymer nanocomposite ratios of (25/75/0.1 CuO), (50/50/0.1 CuO) and (75/25/0.1 CuO).

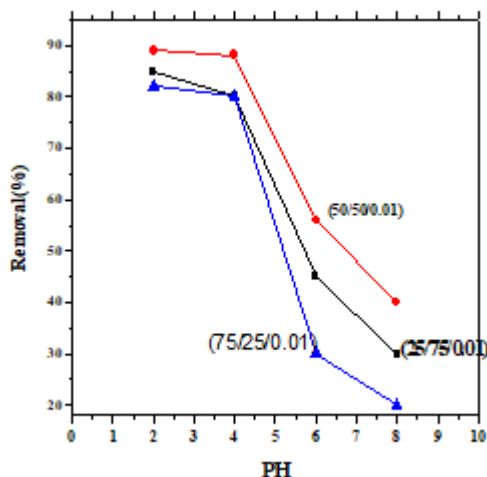
#### 3.3. Effect of PH

The pH is an important parameter affecting the adsorption process. It affects the activities of functional groups on the surface of sorbents and also influences the availability of dye molecules. In order to examine the effect of initial pH value on removal of Eosin Y solution onto polymer nanocomposite ratios (25/75/0.01 CuO), (50/50/0.01 CuO), (75/25/0.01 CuO) and (25/75/0.1 CuO), (50/50/0.1 CuO), (75/25/0.1 CuO), dye adsorption experiments were done at pH range of 2 to 8 using initial dye concentration of 5 mg/L. As it can be observed from (Fig. 4 and 5), the dye removal percentage was decreasing by increasing pH value. It is found that the percentage removal of Eosin Y was higher when the pH is below 5. After pH 5, the adsorption rate decreased.

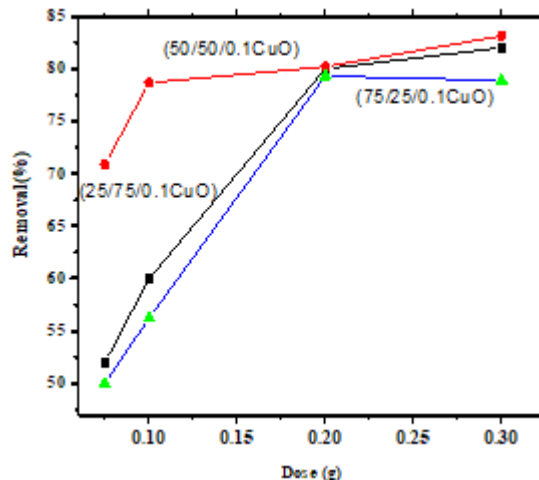
In acidic conditions, the surface of the adsorbent is positively charged due to high concentration of  $\text{H}^+$ , so electrostatic attraction between the adsorbent and the adsorbate (anionic dye) is enhanced. Lower adsorption of Eosin Y under alkaline conditions is due to the presence of hydroxyl ions on the surface of adsorbents competing with the adsorbate for adsorption sites[10].



**Figure 4:** Effect of PH for removal of Eosin Y dye unirradiated polymer blend nanocomposite ratios (25/75/0.01 CuO), (50/50/0.01 CuO) and (75/25/0.01 CuO).



**Figure 5:** Effect of PH for removal of Eosin Y dye on polymer nanocomposite ratios (25/75/0.1 CuO), (50/50/0.1 CuO) and (75/25/0.1 CuO).



**Figure 7:** Effect of polymer nanocomposite dose ratios of (25/75/0.1 CuO), (50/50/0.1 CuO) and (75/25/0.1 CuO) for removal of Eosin Y dye.

### 3.4. Effect of polymer nanocomposite dose

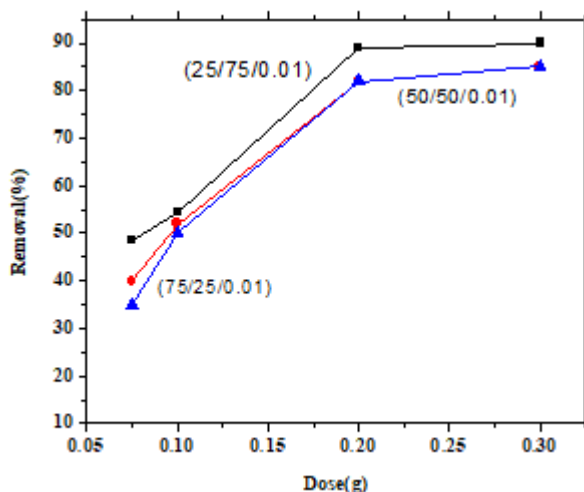
Polymer nanocomposite doses is an important parameter which determines the capacity of polymer nanocomposite for a given initial concentration of dye solution. The effect of polymer nanocomposite doses was investigated by varying of polymer nanocomposite ratios (25/75/0.01 CuO), (50/50/0.01 CuO), (75/25/0.01 CuO) and (25/75/0.1 CuO), (50/50/0.1 CuO), (75/25/0.1 CuO) doses from 0.075 to 0.3 g/L at 5 mg/L dye concentration at PH 4.

Results in Fig. (6 and 7) revealed that by increasing of the polymer nanocomposite ratios (25/75/0.01 CuO), (50/50/0.01 CuO), (75/25/0.01 CuO) and (25/75/0.1 CuO), (50/50/0.1 CuO), (75/25/0.1 CuO) doses, the adsorption capacity (% color removal) increased significantly. With 0.2 g/L of studied polymer nanocomposite ratios, almost all dyes can be removed from the liquid. The increase in the polymer nanocomposite ratios dosage can be attributed to greater surface areas and the availability of more adsorption sites[11].

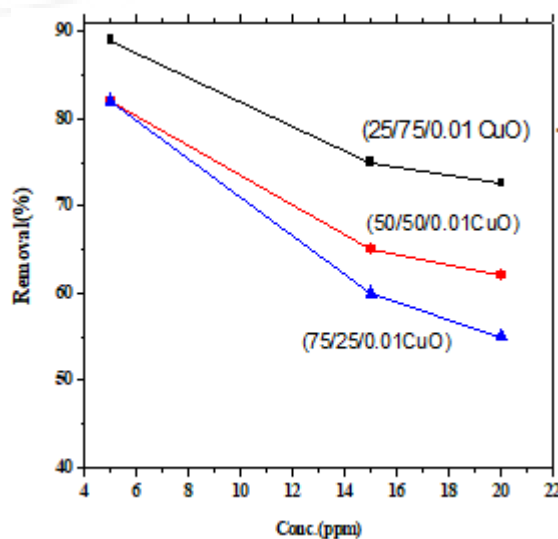
### 3.5. Effect of dye concentration

The effect of concentration on the removal of Eosin Y dye by polymer nanocomposite ratios (25/75/0.01 CuO), (50/50/0.01 CuO), (75/25/0.01 CuO) and (25/75/0.1 CuO), (50/50/0.1 CuO), (75/25/0.1 CuO) is shown in Figure (8 and 9). The applied concentrations were (5 to 20 mg/L).

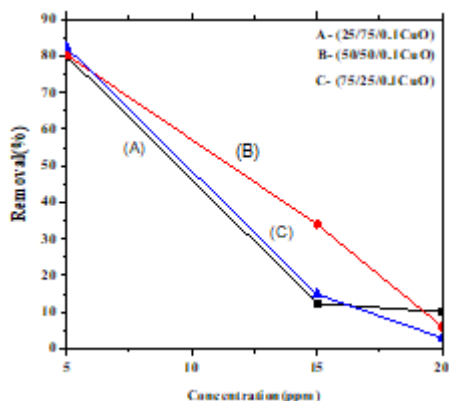
It is observed that, the percentages of removal increase with decreasing the concentration of dye. The amount of dye adsorption decreases from 80% to 10%, while increasing the initial dye concentration from 5 to 20 mg/L. This proved the fact that the concentration gradient is an important driving force to overcome the mass transfer resistances between the liquid and solid phase. This is due to at lower dye concentration, the ratio of solute connecting to the polymer nanocomposite sites is higher, which caused the increase in color removal efficiency, while at higher dye concentration, the lower adsorption percentage was caused by the saturation of adsorption sites[11].



**Figure 6:** Effect of polymer nanocomposite dose ratios of (25/75/0.01 CuO), (50/50/0.01 CuO) and (75/25/0.01 CuO) for removal of Eosin Y dye.



**Figure 8:** Effect of dye concentration for removal of Eosin Y dye on polymer nanocomposite ratios (25/75/0.01 CuO), (50/50/0.01 CuO) and (75/25/0.01 CuO).



**Figure 9:** Effect of dye concentration for removal of Eosin Y dye polymer nanocomposite ratios (25/75/0.1CuO), (50/50/0.1CuO) and (75/25/0.1 CuO).

#### 4. Conclusion

Eosin yellow (EY) is a carcinogenic dye and its exposure may cause adverse effects. Here we prepared polymer nanocomposite ratios (PVA/Gelatin/CuO), for the removal of EY from aqueous solutions. The samples under preparation stage were characterized by FTIR analyses. The systematic adsorption studies were carried out to explore the optimum conditions for the dye removal. Adsorption of dye was highly dependent on pH and 90 % of the dye was adsorbed at pH of 4 within 60min. An adsorbent dose of 0.2 m g/L was needed for the complete adsorption of EY from aqueous solutions.

#### References

- [1] Zhou, B. and Balee, R. Groenendaal, "Nanoparticle and Nanostructure Catalysts": Technologies and Markets, *Nanotech. Law Business*, vol. 2, pp. 222, 2005.
- [2] Peukert, W., Schwarzer, H.C., Gotzinger, M., Gunther, L. and Stenger, F. "Control of Particle Interfaces"—The Critical Issue in Nanoparticle Technology. *Advanced Powder Technology*, vol.14, pp. 411-426, 2003.
- [3] P. B. Messersmith, E.P. Gianannelis " Synthesis and barrier properties of (poly-caprolactone)-layered silicate nanocomposites". *J. Polymer. Sci. A:Polymer. Chem.* Vol. 33, pp. 1047-1055, 1995
- [4] T. J. Pinnavaia, G.W. Beall (Eds.) "Polymer Clay Nanocomposites". John Wiley and sons, New York, 2000.
- [5] H. A. ABD EL-REHIM, EL-SAYED A. HEGAZY, A. M. ALI. "Preparation of Poly (vinyl alcohol) Grafted with Acrylic Acid/Styrene Binary Monomers for Selective Permeation of Heavy Metals". *Journal of applied polymer science*, vol. 74, pp. 807, 1999
- [6] Ali, Z.I.A., F.A. Hosam, A. M. , "Effect of electron beam irradiation on the structural properties of PVA/V<sub>2</sub>O<sub>5</sub> xerogel. *Spectrochimica Acta part A* vol. 72, pp. 868-875, 2009.
- [7] CH LINGA RAJU, J L RAO , B C V REDDY and K VEERA BRAHM AM, " Thermal and IR studies on copper doped polyvinyl alcohol", *Bull. Mater. Sci.*, Vol. 30, No. 3, pp. 215–218, 2007.
- [8] H.P. Oliveira, C.F.O. Graeff, J.M. Rosolen, *Mater. Res. Bull.* 12 and 13, pp. 1891, 1999

- [9] Y.C. Zhang, J.Y. Tang, G.L. Wang, M. Zhang, X.Y. Hu, *J. Cryst. Growth*, 294, 2006.
- [10] J. Huang, K. Huang, S. Liu, A. Wang, C. Yan, "Adsorption of rhodamine B and methyl orange on a hyper-cross-linked polymeric adsorbent in aqueous solution", *Colloids Surf. A*, vol. 330 pp. 55–61, 2008.
- [11] Mahanta, D.; Giridhar Madras, G.; Radhakrishnan, S.; Patil, S. Adsorption of Sulfonated Dyes by Polyaniline Emeraldine Salt and Its Kinetics. *J. Phys. Chem. B*, vol. 112, pp. 10153-10157, 2008.