Equilibrium studies of the Removal of Trypan blue using modifier Polyurethane Foam

Hala A. Kiwaan, Mervat A. Elsonbati, Shireen K. Elzakzouk, Nasser A. Elghamaz, Elhossein A. Moawed

Abstract—In this work, the efficiency of PUF-COOH@MnO_2 sorbent for the removal of Trypan blue dye (TB) from wastewater was studied through anadsorption process. The effects of various parameters such as solution pH, initial TB concentration and contact time were examined. Adsorption isotherms followed Langmiur.

Index Terms—PUF-COOH@MnO_2, Trypan blue dye, removal, wastewater, isotherm.

1 Introduction

Industrial wastewater containing toxic dye effluents and its byproducts formed through oxidation, hydrolysis or other chemical reactions has raised severe environmental threat [1]. Primarily, there are two methods for removal of toxic dye from wastewater, i.e., adsorption of dye on a suitable substrate and degradation of dye to nontoxic metabolites [2]. Thus, it is significant to treat dye effluent before releasing them into the environment. To date, a variety of chemical, physical and biological approaches have been developed for separation and removal of dyes from wastewater, such as adsorption [3–6], precipitation and coagulation [7–9], photocatalytic degradation [10,11], ion exchange [12], and membrane filtration [13,14]. Among these methods, membrane filtration technology plays a crucial role in meeting the requirements for wastewater treatment due to its relatively simple operation, low cost, and high efficiency [15,16]. Currently, one of the most attractive aspects in the field of membrane filtration is the innovation of membrane materials [17].

Polyurethane foam (PUF) is a three dimensional porous material which is commercially available. The material has been used as the support substrate in various applications due to its highly mechanical durability and excellent elasticity [17].

Adsorption is favored by its efficiency and universally applicable , for the remediation of organic and inorganic compounds, even at low concentration. Adsorption has advantage of its relative ease of operation both in batch and continuous operation, regeneration and reusability of adsorbent [18].

- *Elhossein A. Moawed is professor in the chemistry department, Faculty of Science, Damietta University, Egypt, Corresponding author, Fax: 0020572403868. E-mail: eamoawed@yahoo.com.*
- *Nasser A. Elghamaz is professor in the physics department, Faculty of Science, Damietta University, Egypt, E-mail: elghamaz@yahoo.com*
- *Hala A.Kiwaan is assistant professor in the chemistry department, Faculty of Science, Damietta University, Egypt, E-mail: hkiwaan@gmail.com*
- *Mervat A. Elsonbati is assistant professor in the environmental sciences department, Faculty of Science, Damietta University, Egypt, E-mail: mervat.mossad@yahoo.com*
- *Shireen k. Elzakzouk is currently pursuing a Philosophy Doctor's degree program in analytical chemistry in Damietta University, Egypt, E-mail: aserreda00@gmail.com*

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In the present work, the treatment of Polyurethane foam (PUF) by potassium permanganate in acidic medium is novel stable composite (PUF-COO@MnO_2). The aim of the study was was also deals with removal of trypan blue (TB) dye from the wastewater by using PUF-COO@MnO_2. The effects of contact time, initial dye concentration, temperature, pH on the adsorption of TB onto PUF-COO@MnO_2 was examined. The experimental sorption data were carried out with equilibrium models.

2 Experimental

2.1 Material and methods

2.1.1 Pretreatment of polyurethane foam (PUF)

PUF sheet white density (d=12 Kg/m^3) was cutter to similar small cubes (0.125 cm^3). The cubes were socked 6 h in HCl then NaOH. Squeezing cubes very well was getting rid of remaining HCl or NaOH. Finally, PUF cubs were washed with distilled water then leave cubs to dry in air and ready to use in reactions.

2.1.2 Treatment of Polyurethane foam

The cubes PUF was oxidized by addition 5 g KMnO4 and add to the bottle then 200 ml of distilled water acidified with H2SO4 (0.1 M) and shacked for 3-5 h, the intense purple permanganate ion will gradually disappear as it is reduced from manganese (VII) to manganese (IV) which precipitates as brown manganese dioxide. Then washed with oxalic acid to remove of excess of $KMnO_4$ followed by distilled water and finally air-dried.

2.1.3 Preparation of stock solution

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Stock solution of Trypan blue ($C_{34}H_{24}N_6O_{14}S_4Na_4$, 960.81) dye was prepared by dissolving accurately weighted pure dye in distilled water to the concentration 1g/L. The working solution was obtained by diluting the dye stock to the require concentration.

2.2 Characterization

Morphology of PUF-COO@MnO_2 was investigated using a JEOL (JSM-6510LV, USA) scanning electron microscope.
FT-IR spectra were performed by a JASCO (FTIR-410 spectrometer) in the 4000-400 cm-1 spectral range .
The absorbance measurements were performed using a JASCO (V-630 UV-VIS Spectrophotometer, Japan). UV-Vis absorption spectra of ZnONPs was recorded in the solid state .
The crystallinity was determined using an XRD Brucker D8 diffractometer equipped with aCu Kα radiation (λ=1.5418 Å) with 40 kV voltage and 40 mA current.Surface area and Pore size were determined by BET and BJH techniques using a NOVA 3200 (USA). TGA technique using SDTQ 600, (USA) .

2.3 Recommended procedures

The adsorption of TB onto PUF-COO@MnO_2 was investigated using a batch experiments. 0.1 g of PUF-COO@MnO_2, was added to 25 mL of the TB solution, then the solution was shaken, filtered and the remaining TB concentration in solution was analyzed at λ_{max}= 608 nm. Best condition for removal of TB can be determined by studing effects of pH, contact time and initial TB concentration. Concentration of pollutants is measured before and after time of shacking 0.1 g of adsorbent with TB solutions to give C_o, C_e.

The percentage of dye removal (%E) and adsorption capacity (q_e) were calculated from the following equations:

$$\%E = ((C_0 - C_e)/C_0) \times 100 \quad (1)$$

$$q_e = (C_o - C_e)\ V/m \quad (2)$$

Where, C_o is the initial SA concentration, C_e is the concentration of TB in solution at equilibrium, V is the volume of TB solutions and m is the mass of adsorbent.

3 RESULTS AND DISCUSSION

3.1 Optimum conditions for TB removal using PUF-COO@MnO_2

3.1.1 pH

The effect of the pH on the removal of TB onto PUF-COO@MnO_2 was studied (Fig. 1). The sorption behavior of TB (anionic dye) at different pH values shows that the maximum removal percentage of TB in strong medium pH 3 then decreased at pH 5 followed by at pH 9 followed by decreased at pH 13. Accordingly, the electrostatic attraction between TB and PUF-COO@MnO_2 would happen at pH 3 lead to the TB completely removal from the solution at pH (1-3), increasing negative charges on the PUF-COO@MnO_2 surface the removal of TB was decreased which results in electrostatic repulsion between with PUF-COO@MnO_2. The obtained data showed that the removal process rely on the functional groups of dye [19].

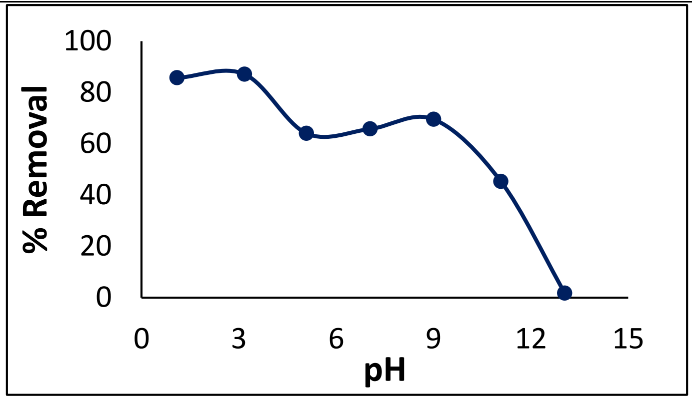

Fig. 1 Effect of pH for removal of TB dye onto PUF-COO@MnO_2

3.1.2 Contact time

The effect of contact time on the removal of TB onto PUF-COO@MnO_2 was investigated at pH=3 (Fig. 2). The maximum removal percentage of T.B dye onto PUF-COO@MnO_2 was found to be 120. It was noticed that the initial removal rate of dye is very rapid, where about 61-89.6% of the total dye concentration was extracted from the solution at the first 5 minutes. Then the rate slowed down progressively with time and the equilibrium extraction is reached within a period of 5 to 30 min then increase little from 82% to 89.6%.

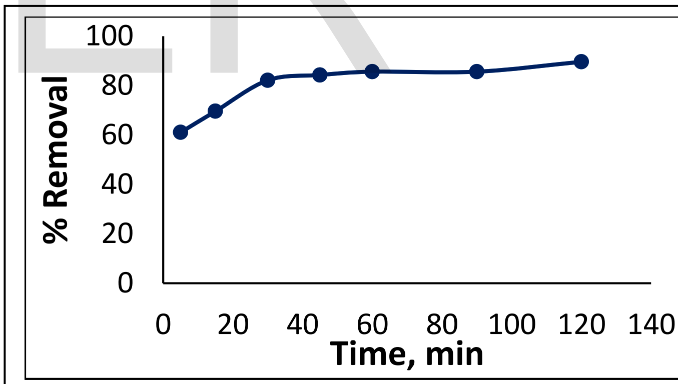

Fig.2 Effect of time on TB removal using PUF-COO@MnO_2 at pH=3

3.1.3 Initial TB concentration

We should study the effect of initial TB dye concentration on the removal process onto PUF-COO@MnO_2 to determine the sorption capacity Q (the amount of dye removed by 0.1g of sorbent) and that by plotting relation between the amount of adsorbed dye per unit mass PUF-COO@MnO_2 (Q) against initial TB dye concentration at pH=3, non-buffer and 9 (Fig. 3). The sorption capacities of PUF-COO@MnO_2 TB dyes were estimated to be (269) mg/g. It is noted that sorption Capacity increased with increasing TB dye concentration.

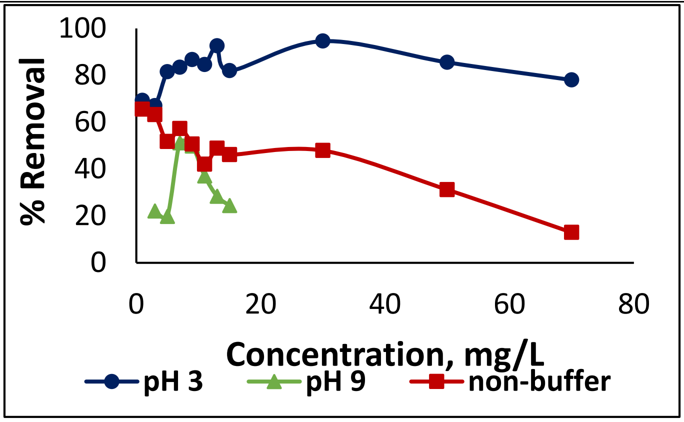

Fig.3 Effect of initial TB concentration on removal using PUF-COOH@MnO_2

3.1.4 Effect of temperature

Fig. 4 shows that the removal percentages were increased with the temperature increase. The explanation is when temperature increase that effect on the bonding between TB and PUF-COO@MnO_2 which makes it to be strong and increase removal process [19].

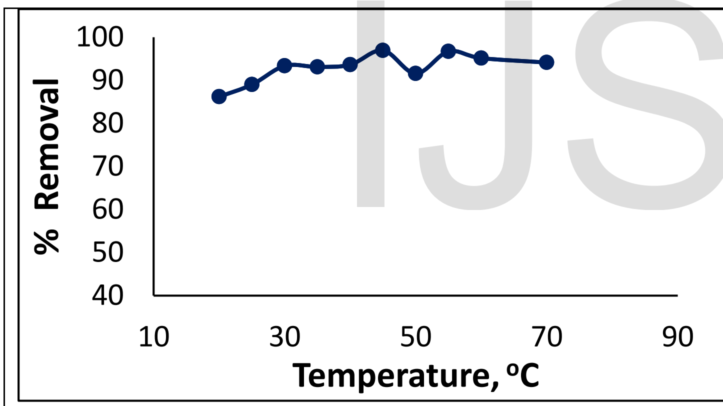

Fig.4 Effect of temperature for removal of TB dye onto PUF-COO@MnO_2

3.2 Equilibrium studies

Langmuir(3) and Freundlich (4) isotherms were applied to study the removal behavior TB using PUF-COO@MnO_2.

$$C_e/q_c = (1/K_L b) + (C_e/K_L) \quad (3)$$

$$Log\, q_c = Log\, K_F + 1/n\, Log\, C_e \quad (4)$$

Where q_c is the amount of dyes adsorbed at equilibrium and C_e is the TB concentration at equilibrium. K_L and b are Langmuir constants [21], while K_F and n are Freundlich constants [22]. Langmuir isotherm is based on an assumption of monolayer sorption, independent energy of sorption and initially free sites. The Freundlich model is an empirical equation assuming heterogeneous surface energy. Additionally, the Dubinin-Radushkevich isotherm ($\ln Q_c = \ln K_{D-R} - \beta\varepsilon^2$) [23] is employed to distinguish physical or chemical sorption at heterogeneous surface. The plot of *Ce/Qc* vs. Ce for the data according to Langmuir model give a bad linear relationship with TB which is confirmed by the low value of the correlation coefficient (R^2 = 0.31) (Fig. 5) (Table 1) and the result demonstrated that the Freundlich equation provides an accurate description of the experimental data for TB onto PUF-COO@MnO_2(Fig. 5). From the obtained data multilayer sorption was observed on the removal of TB onto PUF-COO@MnO_2. Also, the value of 1/n (1.062) is above one, referring to the heterogeneous surface structure with a non-uniform distribution of heat sorption over the surface of PUF-COO@MnO2 [24].

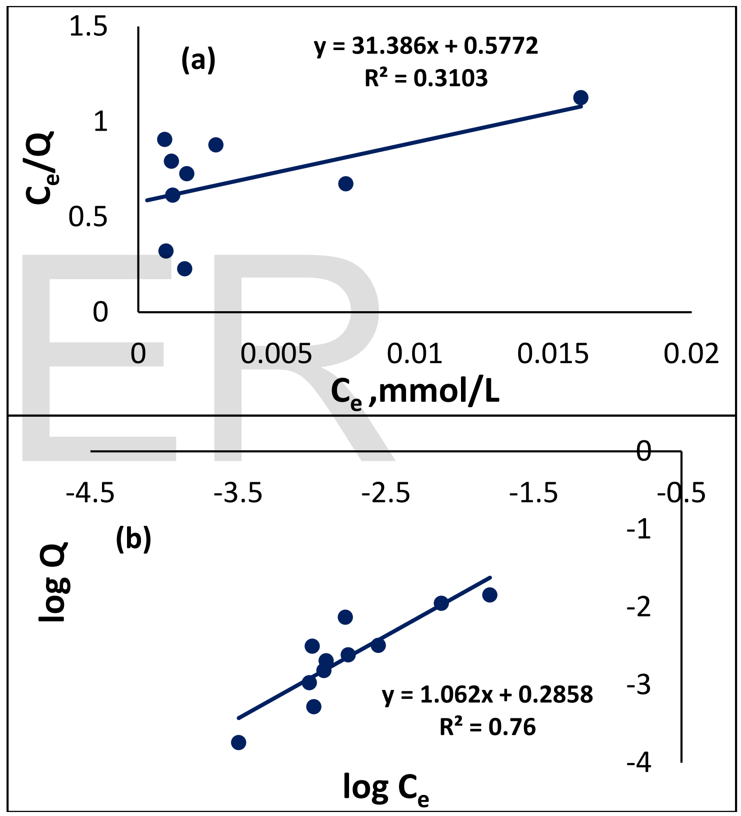

Fig.5 (a) Langmuir and (b) Freundlich isotherm Models for removal of TB dye

The Dubinin-Radushkevich isotherm model is more generalized model as compared to Langmuir isotherm. This model is based on the fact that there is no homogeneous surface or constant adsorption potential. It is used for estimation of the activation energy (ΔE) [19]. The results of the TB concentration onto PUF-COO@MnO_2 were analyzed using Dubinin-Radushkevich equation where K_{DR} is the maximum amount of dye retained onto the solid sorbent (Fig. 6), β is a constant related to the energy of transfer of the solute from the bulk aqueous solution onto the solid sorbent and ε is Polanyi potential. The value of β for sorption TB concentration onto PUF-COO@MnO_2 is (-0.0149) kJ^2mol^{-2} respectively. The value of sorption energy (activation energy, ΔE), were correlated to β (E=1/√-2β). The value of (E) evaluated for PUF-COO@MnO_2 is (5.8) kJ mol^{-1} (Table 1).

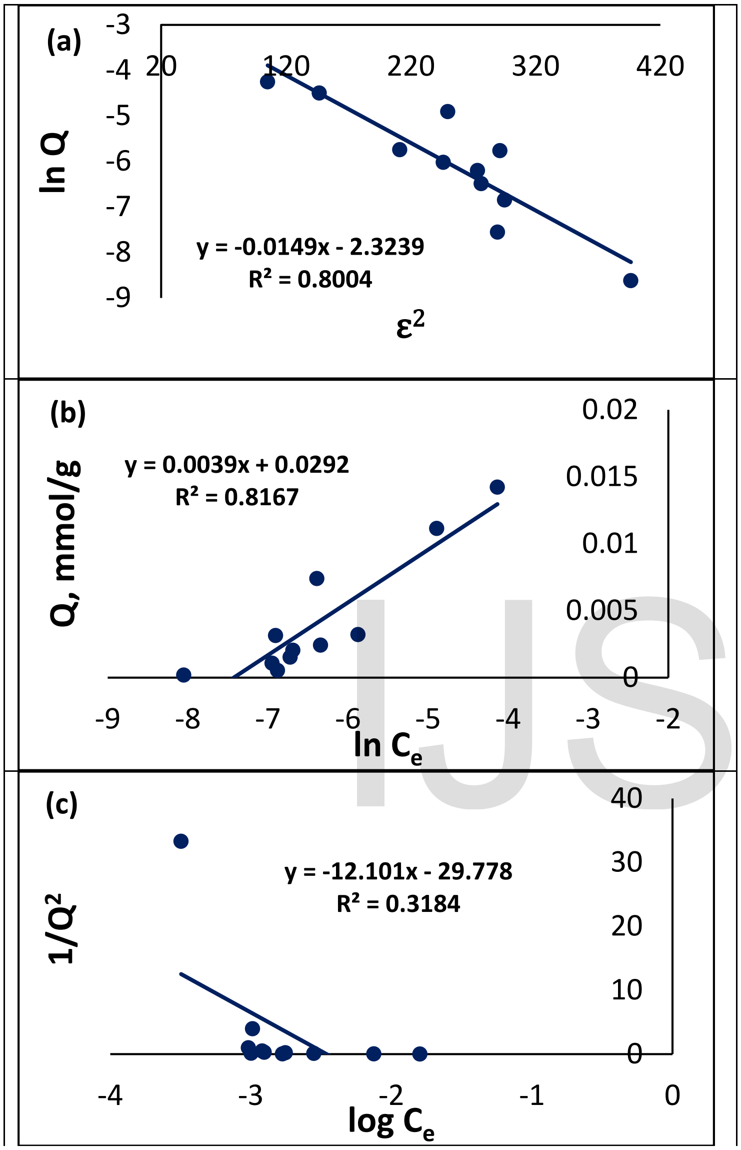

Fig.6 (a) Dubinin-Radushkevich, (b) Temkin and (c) Harkins-Jura isotherm models for removal of TB dye

Table 1. Comparison between correlation coefficient parameters for the sorption isotherms models

Dye	Langmuir	Freundlich	Dubinin-Radushkevich	Temkin	Harkins-Jura
TB	0.31	0.76	0.8	0.817	0.318

Temkin isotherm model suggests an equal distribution of binding energies over the number of the exchanging sites on the surface. Temkin equation is based on the effect of some direct adsorbate–adsorbate interactive relation on sorption isotherm and due to these interactions the decrease in the heat of the adsorbent of all the molecules in the adsorbed surface is linear rather than algorithmic. B value is corresponding to the heat of sorption, and A is the equilibrium binding constant. The values of R^2 for TB suggesting that the experimental data is fitted better to Temkin isotherm model (R^2 = 0.817) onto PUF- COO@MnO_2 (Fig. 6). The values of correlation coefficient of the Harkins-Jura isotherm model are (R^2 =0.318) for TB (Fig. 6).

4 Application

PUF-COO@MnO_2 was applied for the removal of trypan blue dye from waste water samples, collected from Ezbat EL-borg in Damietta Government was examined. A 25 mL aliquot of water sample was spiked with different amounts of tested dye. Then the solutions were shacked for 1h, the remaining concentration of dye in the supernatant solution was determined. The removal percentage of dyes from the water samples was 85-91%. The results show that the PUF-COO@MnO_2 is a suitable sorbent proven to be useful in removing TB dye from environmental samples. The RSD% values found to be 3% (n=6) which is considered relevant (less than10%) for real samples. The obtained data conferred susceptible accuracy of the developed method based on the satisfactory values of RSD.

5 Conclusion

The present work is concerned with the preparation of new composite PUF-COO@MnO_2 from polyurethane foam. This is a new and efficient composite for removing TB dye from aqueous solutions. Adsorption TB was analyzed at different conditions of pH, contact time, temperature and initial dye concentrations. The removal percentages of dye onto PUF-COO@MnO_2 at optimum conditions show that it is highly efficient. The average capacity of PUF-COO@MnO_2 composite is 0.28 mmol g−1 for 85% removal of TB dye. To describe the sorption mechanism isotherm models were applied, namely, Freundlich, Langmuir and Dubinin-Radushkevich sorption. The dye removal isotherm for TB dye was described the Freundlich equation was found to be well suited for the adsorption process of TB on PUF-COO@MnO_2. The PUF-COO@MnO_2 composite was successfully applied for removing TB dye from wastewater samples with relative standard deviation 3 %.

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