

# Adsorption of Eriochrome Black T on MnO<sub>2</sub>-Coated Zeolite

Dios Marie M. Aguila and Mayzonee V. Ligaray

**Abstract**—The removal of Eriochrome Black T from wastewater model by manganese oxide-coated zeolite was studied. Batch experiments were performed at different contact time. Experimental data were analysed using pseudo-first order, pseudo-second order and intra-particle diffusion models, and it was found out that the rate of adsorption follows the pseudo-first order model. Equilibrium was attained at 12h at 79.2428% removal, and data generated from this were used to analyse the system's isotherms. Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were used. The Freundlich model gave the best fit for the EBT adsorption.

**Index Terms**—Adsorption, zeolite modification, color removal, azo dyes.

## I. INTRODUCTION

Organic colorants are used in industries like textile, cosmetics, and paper production. Comprising 60-80% of the organic dyes used in manufacturing, azo dyes are the most widely used organic colorants [1]. The release of these colorants to other bodies of water has negative effects in the environment due to their toxicity and turbidity levels [1].

Color is considered as pollutant in effluent standards in the Philippines [2] that is why color removal is one of the most important processes in treating wastewater. There have been many processes used in color removal like ion exchange, adsorption and oxidation. However, adsorption has advantages over other methods due to its lower land area requirement, constancy and easy implementation [3], [4]. Commonly used adsorbents are activated carbon, chitin, sand and zeolites [5]-[8].

Due to its relatively low cost, zeolite has been used as adsorbent in many adsorption studies. Moreover, its surface can be modified to adapt to select different adsorbates and to have higher selectivity. Based from studies, adsorbent coated with Mn has larger surface area and is more efficient than uncoated adsorbent [9], [10].

The objective of this study is to determine the effectivity of manganese oxide-coated zeolite (MnZ) in removing an azo dye Eriochrome Black T (EBT) in a wastewater model at its natural pH. Kinetic and isotherm studies have been

performed using batch process.

## II. MATERIALS AND METHODS

### A. Adsorbent Preparation

Powdered zeolite sample mainly composed of mordenite was received from Saile Industries, Philippines. To prepare the sample for modification, it was soaked in tap water for 24 h. Afterwards, it was rinsed with distilled water and oven dried at 373 K. Manganese coated zeolite (MnZ) was prepared using potassium permanganate solution. Placed in a beaker, the zeolite was contacted with boiling KMnO<sub>4</sub>. Then, HCl (37.5% WHCl/WH<sub>2</sub>O) was added dropwise to form MnO<sub>2</sub>. After stirring for 1h, it was then filtered and washed with distilled water until pH 7.0 was reached. It was left to dry at room temperature and stored in a polypropylene bottle until further use.

### B. Adsorbate

Preparation of 1000 ppm stock solution was done using commercial powdered dye Eriochrome Black T, dissolving 1g of the dye to 1L distilled water in a volumetric flask. From the stock solution, 20, 40, 60, 80 and 100 ppm solutions were made. They were stored in glass containers until further use. Table I shows the general characteristics of EBT.

TABLE I: GENERAL CHARACTERISTICS OF EBT [11]

Molecular formula	C <sub>20</sub> H <sub>12</sub> N <sub>3</sub> O <sub>7</sub> SNa
Molecular weight	461.38
Wavelength	530 nm

### C. Batch Adsorption

Batch adsorption experiments were performed in agitated vials in shaking water bath at constant temperature (30 °C) and at 150 rpm. 25 ml of the model wastewater with 20 ppm EBT and 0.1 g of the adsorbent was put in the vials with varying time (10, 20, 30, 40, 50, 60, 120, 240 660, 1080 and 1440 minutes). Subsequently, the suspensions were centrifuged for zeolite separation, and the liquid samples were transferred to clean vials.

The isotherm experiment was evaluated by contacting 0.1 g MnZ and 25 ml of the pollutant at different concentrations (40, 60, 80 and 100 ppm) for 12 hours.

### D. Analytical Methods

EBT concentrations of adsorbed samples were determined using UV-Vis spectrophotometer (Shimadzu UV-Vis Mini 1240) set at 530 nm wavelength. A calibration curve was made from the spectra of EBT samples with known concentrations (5-100 ppm) before the samples' concentrations were determined.

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### III. RESULTS AND DISCUSSION

#### A. Effect of Contact Time

The model wastewater with 20 ppm Eriochrome Black T (EBT) was removed through batch adsorption process with 0.1 g MnO<sub>2</sub> coated zeolite (MOZ) as adsorbent for 24 hours. Fig. 1 shows the %EBT removal of MOZ at a given contact time. Each sample was collected after the following contact times: 10, 20, 30, 40, 50, 60, 120, 180, 240, 660, and 1440 min. After 11 hours the % EBT removal reached 79%. It can be observed in the Figure that during the first few hours of the adsorption process, the %removal of EBT rapidly increases to 70%. This can be attributed to the presence of readily available functional groups of the adsorbent at the start of the experiment. The adsorbate attaches itself to the binding sites on the surface of MOZ until it became saturated. This slowed down the EBT uptake until the system reached equilibrium after 11 hours [12].

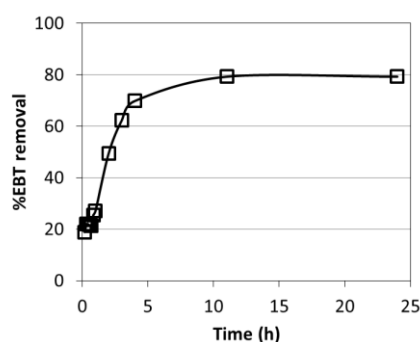


Fig. 1. Removal percentage of Eriochrome black T at a given time by MnO<sub>2</sub>-coated zeolite (MOZ).

#### B. Kinetic Studies

Adsorption kinetics determines the rate-limiting mechanism of the system. The results of the kinetic experiments were fitted using pseudo-first order, pseudo-second order, and intra-particle diffusion models.

Pseudo-first order or the Lagergren model is defined by the following linear equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

where  $q_e$  and  $q_t$  are the adsorption capacities (mg/g) at equilibrium and time  $t$ , respectively and  $k_1$  is the pseudo-first order rate constant (min<sup>-1</sup>) [13]. This model states that the rate-limiting step of the system is physical adsorption. Fig. 2 shows the plot of the results fitted to the pseudo-first order equation.

Chemical adsorption is said to be the slowest mechanism if the results fit the pseudo-second order model. The integrated form of its equation is shown below:

$$t/q_t = 1/(k_2 q_e^2) - (1/q_e)t \quad (2)$$

where  $k_2$  (g/mg min) is the rate constant of the pseudo-second order [14]. Fig. 3 shows the fitted results using this model.

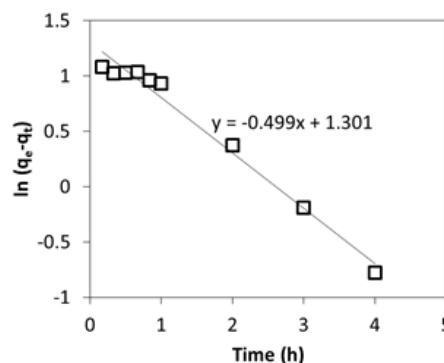


Fig. 2. Pseudo-first order model of the adsorption of EBT on MnO<sub>2</sub>-coated zeolite. Initial concentration of 20ppm; T=30 °C; V=25mL; mass=0.1g.

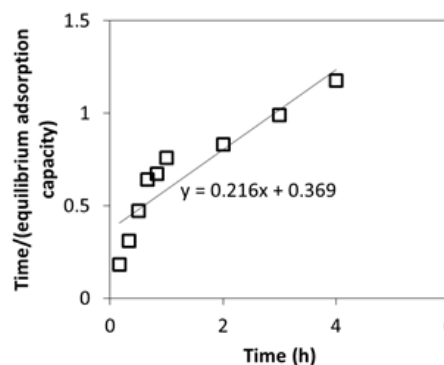


Fig. 3. Pseudo-second order model of MnO<sub>2</sub>-coated zeolite. Initial concentration of 20 ppm; T=30 °C; V=25 mL; mass=0.1g.

Intra-particle diffusion is the third model that was applied as shown in Fig. 4. This model states that mass transfer is the rate-limiting mechanism. Mass transfer is described as the transfer of adsorbate from the aqueous solution into the pores of the adsorbent through its boundary layer. The linear equation of this model is shown below:

$$q_t = k_i t^{0.5} + C_i \quad (3)$$

where  $k_i$  (mg/g min<sup>0.5</sup>) is the intra-particle diffusion rate constant, while  $C_i$  is the thickness of the boundary layer.

TABLE II: RATE OF ADSORPTION, CORRELATION COEFFICIENT, AND THEORETICAL EBT UPTAKE OF PSEUDO-FIRST ORDER, PSEUDO-SECOND ORDER, AND INTRA-PARTICLE DIFFUSION MODELS

Pseudo-first			Pseudo-second			Intra-particle		
$k_1$	$R^2$	$q_{e,theo}$	$k_2$	$R^2$	$q_{e,theo}$	$k_i$	$R^2$	$q_{e,theo}$
0.499	0.980	3.86	0.126	0.833	3.56	3.428	0.948	8.37

Using the equations in the kinetic plots above, the constants and correlation coefficients of the models were computed and are shown in Table II. The pseudo-first order model has the highest correlation coefficient with a value of 0.98, which indicates that physical adsorption is the rate-limiting mechanism of the EBT/MOZ system. The theoretical values of the adsorption capacities of the kinetic

models at a given time were compared to the actual values which were shown in Fig. 5. Adsorption capacity is defined as the EBT uptake of MOZ.

It can be observed in Fig. 5 that the actual values follow the trend of the pseudo-first order model. The experiment yielded a capacity of 3.86 mg/g at equilibrium which is the same with the theoretical  $q_e$  of pseudo-first order. Pseudo-

second order and intra-particle diffusion models yielded  $q_e$  values of 3.56 mg/g and 8.37 mg/g respectively. Both values have significant differences from the actual.

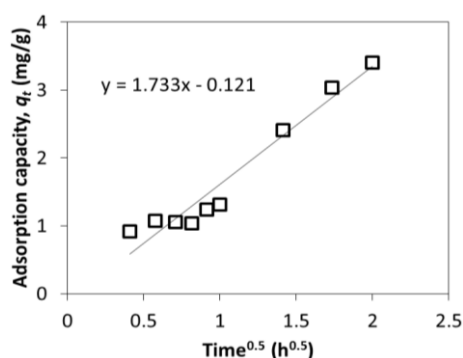


Fig. 4. Intra-particle diffusion model of MnO<sub>2</sub>-coated zeolite Initial concentration of 20 ppm; T=30 °C; V=25mL; mass=0.1g.

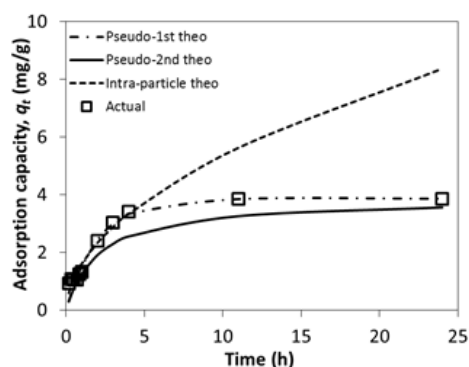


Fig. 5. Adsorption capacity of MnO<sub>2</sub>-coated zeolite.

### C. Isotherm Studies

Isotherm studies were conducted by varying the concentration of EBT, from 40 ppm to 100 ppm. The vials containing 25 ml of EBT solution and 0.1 g of MOZ were agitated at a speed of 150 rpm and a temperature of 30 °C for 12 hours, which allows the EBT/MOZ system to reach equilibrium. This experiment furthers the understanding of the mechanism of how an EBT molecule attaches itself to the surface of MOZ at a constant temperature. Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models were used to fit the results.

The Langmuir model was first introduced by its namesake

in 1918. This model assumes that localised monolayer adsorption occurs during the process. This basically states that the surface of the adsorbent is homogenous with constant adsorption energy throughout the binding sites. Each of these sites can only hold one adsorbate molecule [15]. This model is described in the linear equation below:

$$C_e/q_e = C_e/q_{max} + 1/(K_L q_{max}) \quad (4)$$

where  $C_e$  is concentration of the EBT solution at equilibrium,  $q_e$  and  $q_{max}$  are the equilibrium and maximum adsorption capacities of MOZ respectively, and  $k_L$  is the Langmuir constant. Fig. 6 shows the fitted adsorption equilibria of EBT/MOZ.

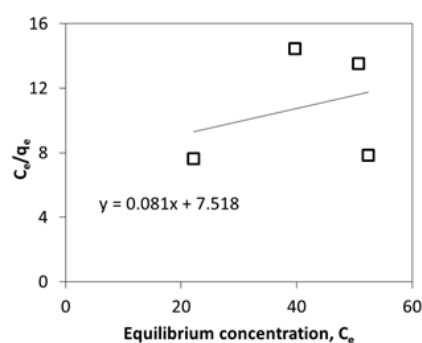


Fig. 6. Langmuir model of the adsorption of Eriochrome black T on MnO<sub>2</sub>-coated zeolite. Contact time=12 hours; T=30 °C; V=25mL; mass=0.1g.

Fig. 7 shows the results fitted using the Freundlich model. This model was the earliest known isotherm equation, published in 1906 [16], and was frequently used in illustrating adsorption of organics from aqueous solutions onto activated carbon. Freundlich assumes that the surface of the adsorbent is heterogeneous [14] which means that the adsorption energy is distributed and that binding sites with the same energy are grouped together in one area, thus; forming patches of sites which are independent of each other [15]. Equation (5) describes this model,

$$\log q_e = \log K_F + (1/n) (\log C_e) \quad (5)$$

where  $K_F$  is the Freundlich constant while  $1/n$  represents the intensity of the adsorbate molecules on the adsorbent.

TABLE III: ADSORPTION PARAMETERS AND CORRELATION COEFFICIENTS OF LANGMUIR, FREUNDLICH, AND DUBININ-RADUSHKEVICH ISOTHERM MODELS

Langmuir			Freundlich			Dubinin-Radushkevich			
$K_L$	$q_{max}$	$R^2$	$K_F$	$1/n$	$R^2$	$\beta$	$Q_m$	$R^2$	$E$
0.011	12.35	0.096	0.342	0.654	0.408	5E-5	4.768	0.287	0.01

The third isotherm model applied was the Dubinin-Radushkevich (D-R) model. It is used to determine the dominant adsorption mechanism that occurred during the experimentation, whether it was physical or chemical adsorption. This can be confirmed by calculating the energy of adsorption which can be derived from the following equations.

$$\ln q_e = -\beta \varepsilon^2 + \ln q_{max} \quad (6)$$

where  $\beta$  is the D-R constant and  $\varepsilon$  is the Polanyi potential which is given by the equation:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (7)$$

where  $R$  is the gas constant (J/K mol) and  $T$  is the temperature in Kelvin. The energy of adsorption can be computed using the equation:

$$E = 1/\sqrt{2\beta} \quad (8)$$

From the equation of the line in Fig. 8, the energy of adsorption was calculated which resulted to 0.01 J/mol. This value falls within the range of physical adsorption (less than 8kJ/mol). Since the kinetic studies determined that physical adsorption was the rate-limiting mechanism, this confirms that only physical adsorption occurred during the process.

Table III shows the parameters and correlation coefficient of the three previously introduced models. Freundlich showed the highest  $R^2$  which states that more than 2 functional groups are present on the surface of the adsorbent and attract the EBT molecules. FTIR results from another literature found that hydroxyl groups,  $\text{NO}_2$  groups,  $\text{C}=\text{C}$ -aromatic, and  $\text{SO}_3^-$  groups from the adsorbent that they used exhibited band changes portraying possible occurrence of adsorption of EBT. This means that it is possible for EBT to attach itself to more than 2 functional groups.

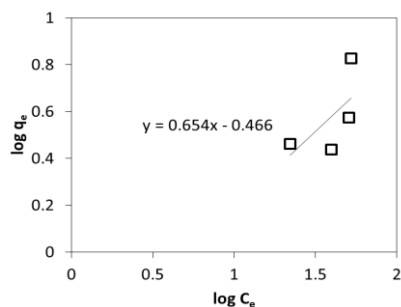


Fig. 7. Freundlich model of the adsorption of Eriochrome black T on  $\text{MnO}_2$ -coated zeolite. Contact time=12 hours;  $T=30^\circ\text{C}$ ;  $V=25\text{ mL}$ ; mass=0.1 g.

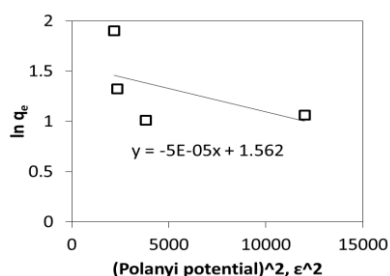


Fig. 8. Dubinin-Radushkevich model of the adsorption of Eriochrome black T on  $\text{MnO}_2$ -coated zeolite. Contact time=12 hours;  $T=30^\circ\text{C}$ ;  $V=25\text{ mL}$ ; mass=0.1 g.

#### IV. CONCLUSION

This study investigated the removal of EBT dye from MOZ, a zeolite composite, and also proved that it is effective in removing the dye which reached up to 79% removal. Batch adsorption studies showed that the maximum removal of EBT took place within 12 hours contact time and remained constant until 24 hours. It indicates that the equilibrium time for EBT/MOZ is around 12 hours.

Kinetic studies show that the results fit the pseudo-first order model with an  $R^2$  of 0.98, which indicates that physical adsorption is the rate-limiting mechanism of EBT/MOZ system. Isotherm studies, on the other hand, showed that Freundlich has the best fit with an  $R^2$  of 0.408. This indicates that EBT was adsorbed by 2 or more functional groups present in MOZ.

#### V. RECOMMENDATIONS

It is recommended to further investigate about the possible occurrence of oxidation of EBT dye by  $\text{MnO}_2$  during the adsorption process. This is a relevant factor in the disappearance of color in the solution. FTIR analysis of MOZ is also recommended to determine the functional

groups that attract EBT molecules.

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