Kinetics and Equilibrium Studies of Electro Adsorption of Remazol Red on Modified Stainless Steel Electrode

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Abstract. Remazol Red B compounds are dyes including azo groups. These compounds are reactive and often used in the textile industry. About 70% of dyes are synthetic azo dyes, representing a highly diverse group of dyes characterized by nitrogen to nitrogen double bonds (so called azo bonds, -N=N-). Many azo dyes and their metabolites are recalcitrant in nature and can be highly toxic to both terrestrial and aquatic life. The electroadsorption of remazol red from aqueous solution has been investigated. Batch electroadsorption experiments were performed and kinetic and equilibrium was tested. The result shows that Stainless steel electrode can remove remazol red from aqueous solution. To predict the adsorption phenomena and to determine the characteristic parameters for process design, three kinetic models: Pseudo first order, pseudo second order and Elovich, and three equilibrium of adsorption model: Langmuir, Freundlich and Jovanovic were applied to experimental data. The Kinetic and Equilibrium of the adsorption were found to fit the Elovich and Freundlich model.

Keywords: remazol red, electroadsorption, Kinetics model, Equilibrium model.

1. Introduction
Currently, there are more than 100,000 synthetic dye structures and more than 0.7 million tons of dyes are used in textile, paper, food, pharmaceuticals, cosmetics every year [1], [2] [3] [4]. Textile industry's liquid waste can be easily observed, because its liquid waste has a dense color. Chemical substances that are often used in textile industry are reactive dyes, their used around 45% [5]. Approximately 10-15% of dye materials used will be left and wasted into the environment. Disposal of wastewater into rivers or oceans can cause damage to water ecosystems as well as human life [6]. The release of dyes into the environment may constitute a small proportion of water pollution, but dyes in effluent are highly visible and undesirable [7]. Therefore, the color removal of the textile wastewater of the textile industry becomes a very important aspect of waste treatment.

Remazol Red B compounds are dyes including azo groups. These compounds are reactive and often used in the textile industry. About 70% of dyes are synthetic azo dyes, representing a highly diverse group of dyes characterized by nitrogen to nitrogen double bonds (so called azo bonds, -N=N-) [8]. Many azo dyes and their metabolites are recalcitrant in nature and can be highly toxic to both terrestrial and aquatic life [9].

Various experiments have been conducted to remove dyes from textile waste either biologically, physically or chemically. Physical methods are carried out by coagulation, flocculation, filtration, and
adsorption, but these methods still have deficiencies such as the formation of sludge in large quantities, low efficiency and high operating costs. While chemicals for color removing typically use strong oxidizing agents such as H$_2$O$_2$, O$_3$ and Fenton reagent or Advanced Oxidation Process (AOP) [10] [11] [12] [13]. The electro-adsorption consists of the metal parts of the anode and cathode pairs using electrochemical principles. The research of electro-adsorption method is used for the desalination process [14], treatment of liquefied water in iron and steel industry [15] and tetracycline adsorption process using synthetic carbon electrode and aniline composite and obtaining adsorption efficiency of 95.11% [16]. Pirkarami et al [17] has also conducted photo-electro adsorption studies on azo dye compounds (Acid Red 98, Acid Orange 2 and Acid Blue 92) and as much as 96% of the dyestuff in the waste can be absorbed on the electrode surface. Based on the research of Pirkarami et al [17], modified anodes with polyaniline coating were used for this study. The porous solid of a given adsorption process is a critical success or failure of the process depends on how the solid performs in both equilibria and kinetics. This research investigated an electro-adsorption process using types of dyes commonly used in textile industry such as Remazol Red (Azo type).

2. Experimental Details

For polyaniline film coating, a stainless steel sheet was polished with sandpaper. Subsequently, hydrochloric acid (1 M HCl) and 0.4 M aniline were poured in a beaker glass. The solution was stirred for 5 min before the sheet was dipped in it. The solution was then subjected to a bias potential of 2 V for 1 hour at room temperature. After electropolymerization, the color of electrode changed from bright white to dark gray, indicating the formation of polyaniline film. Then, the electrode was cleaned using distilled water.

Synthetic waste made by dye powder (Remazol Red) is dissolved into aquaest according to predetermined concentration variations of 450; 600; 750 mg / L. To determine the efficiency of electro adsorption process 5 mL of samples were taken out from the solution every 20 minutes for spectrophotometric measurement. The linear relationship between dye concentration and dye removal efficiency was determined through Eq (1):

\[
\text{Efficiency (\%) } = \frac{A_0 - A}{A} \times 100
\]

where $A_0$ and $A$ are the absorbance of the waste before and after electroadsorption process.

The amount of remazol red adsorbed at equilibrium, $q_e$ (mg/g), was calculated by the following mass balance relationship:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

3. Results and Discussion

Remazol Red (C$_{27}$H$_{18}$O$_{16}$N$_7$S$_5$Na$_4$Cl) having molecular weight of 984.2 g/mol, was used as adsorbate in this study. Remazol red was chosen as a model of dyes largely used in the industry. Its structure, reported in Figure 1, is responsible for the high solubility in water (70 g/L).
3.1. Adsorption Kinetic

Different kinetic models including pseudo first order, pseudo second order and Elovich model were tested.

3.1.1. Pseudo First Order. Lagergen (1898) presented a first-order rate equation to describe the kinetic process of an adsorbate from the liquid phase. It is believed to be the earliest model to the adsorption rate based on the adsorption capacity. In recent years, it has been widely used to describe the adsorption of pollutant from wastewater [18], [19]. The linear form of pseudo-first order equation is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_{p1}}{2.303}t$$  \hspace{1cm} \text{(3)}

Where $q_e$ and $q_t$ (mg/g) are adsorption capacities at equilibrium and time t (minutes), respectively $K_{p1}$ (min$^{-1}$) is the pseudo first order rate constant for the kinetic model.

![Figure 2. Pseudo First Order Kinetic Rate Model](image)

3.1.2. Pseudo Second Order. Ho’s second order rate equation has been called pseudo second order rate equation to distinguish kinetic equations based on adsorption capacity from concentration of solution [20].

The linear equation of pseudo second order kinetic model is:

$$\frac{t}{q_t} = \frac{1}{k_{p2}q_e^2} + \frac{1}{q_e}t$$  \hspace{1cm} \text{(4)}

![Figure 3. Pseudo Second Order Model](image)
3.1.3. Elovich. A kinetic equation of chemisorption was established by [21] and it has been widely used to describe the adsorption of gas onto solid systems [22], [23]. Recently it has also been applied to describe the adsorption process of pollutants from aqueous solution [24]. The linear equation of Elovich kinetic model is:

\[ q_t = \alpha \ln(a\alpha) + \alpha \ln t \]  

(5)

![Figure 4. Elovich Model](image)

Kinetic parameter of that model is shown at Table 1. From Table 1, the correlative coefficient of remazol red was 0.9988 which is better than that of both the pseudo-first order and pseudo second order models.

| Kinetic Model        | Parameter | Value  | R²   |
|----------------------|-----------|--------|------|
|                 |           |        |      |
| Pseudo First Order  | \( k_p1 \) | 0.021879 | 0.9896 |
| Pseudo First Order  | \( q_{cal} \) | 6.443176 |      |
|                     | \( k_p2 \) | 0.089017 | 0.9934 |
| Elovich             | A         | 0.785848 | 0.9988 |
|                     | A         | 1.2674   |      |

3.2. Adsorption Equilibrium

Adsorption equilibrium is the most important piece of information in understanding an adsorption process. No matter how many components are present in the system, the adsorption equilibria show how much those components can be accommodated by a solid adsorbent.

3.2.1. Langmuir Isotherm. The Langmuir adsorption equilibrium [25] has been used to predict the performance of different adsorbent and is based on the assumption that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules. The linear form of the Langmuir equilibrium equation can be expressed as follows:

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \]  

(6)

From Figure 5. The correlation coefficient (R²) equals to 0.9896 indicating an adsorption of remazol red is monolayer adsorption.
3.2.2. **Freundlich.** The Freundlich sorption [25], gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies, and is expressed by the following equation:

\[
\log q_e = \log K_f + \frac{1}{n_f} \log C_e
\]  

(7)

Freundlich equation is obtained by assuming that the surface topography is patchwise, that is sites having the same adsorption energy are grouped together into one patch. Each patch is independent from each other that are there is no interaction between patch. Other assumption is that on each patch adsorbate molecule only adsorbs onto one and only one adsorption site, hence the Langmuir equation is applicable for the description of equilibria of each patch.
3.2.3. Jovanovic. An adsorption surface assumption, considered in Jovanovic isotherm model [26] corresponds to another approximation for monolayer localized adsorption without lateral interactions. The nonlinear relationship of Jovanovic model is:

\[ q_e = q_m \left(1 - e^{-k_j C_e}\right) \]  

(8)

![Figure 7. Jovanovic Adsorption Model](image)

The correlation parameter coefficient of adsorption equilibrium model was expressed in Table 2. From Table 2, Freundlich model has better correlative parameter value (0.9997) than Langmuir and Jovanovic models. The parameter of each models were calculated from the slope and intercept of the linear plot as shown in Figure 5, 6 and 7.

| Isotherm Model | Parameter | Value   | R²     |
|---------------|-----------|---------|--------|
| Langmuir      | K_L       | -0.0069 | 0.9919 |
|               | q_m       | 1.2195  |        |
| Freundlich    | K_f       | 26.3633 | 0.9997 |
|               | n_f       | 7.0422  |        |
| Jovanovic     | k_j       | -0.249  | 0.9974 |
|               | q_m       | 17.1843 |        |

4. Conclusion
Stainless steel electrode was successfully utilized for the removal of Remazol Red from solution by electroadsoption. The kinetics data were tested using pseudo first order, pseudo second order, and Elovich model. The equilibrium data were also analyzed using the Langmuir, Freundlich and Jovanovic model. Kinetic and equilibrium studies showed that the adsorption of Remazol Red onto stainless steel electrode followed Elovich and Freundlich model.

Notation
- A: Absorbance of remazol red solution
- A₀: Initial absorbance of remazol red solution
- C₀: Initial Remazol Red Concentration (mg/L)
- C_e: Equilibrium Remazol Red Concentration (mg/L)
- C_t: Remazol Red Concentration at (t) time (mg/L)
- k_p1: Rate constant of the pseudo first order (min⁻¹)
- k_p2: Rate constant of the pseudo first order (g/mg.min)
- K_F: Freundlich adsorption capacity constant (L/mg)
Kj : Jovanovic adsorption capacity constant (L/mg)
K_L : Langmuir adsorption capacity constant (L/mg)
m : Mass of adsorbent (g)

n_F : Freundlich adsorption intensity constant
q_e : Amount of Remazol Red adsorbed at equilibrium (mg/g)

q_t : Amount of Remazol Red adsorbed at (t) time (mg/g)
V : Volume of Solution (L)

Greek :
α : Initial sorption rate constant (mg/g min)
β : Extent of surface coverage and activation energy for chemisorptions (g/mg)

5. References

[1] M. Shahid M, Shahid-Ul-Islam and F. Mohammad, "Recent Advancements in natural dye applications: a review," Journal of Clean. Prod., pp. 310-331, 2013.

[2] K. Yamajala, M. Nair and N. Ramisetty, "Methods for the analysis of azo dyes employed in food industry - a review," Food Chem, pp. 813-824, 2016.

[3] N. Z. Sekuljica, N. Z. Prlainovic, A. B. Stefanovic, M. G. Zaza, D. Z. Cickaric, D. Z. Mijin and D. Knezevic-Jugovic, "Decolorization of anthraquinonic dyes from textile effluent using horseradish peroxidase: Optimization and Kinetic Study," Journal of Sci. World, 2015.

[4] A. R. Tehrani-Bagha and K. Holmberg, "Solubilization of Hydrophobic dyes in surfactant solutions," Mater (Basel), pp. 580-608, 2013.

[5] O. Tunch, H. Tanaci and Z. Aksu, "Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye," Journal of Hazardous Materials, pp. 187 - 198, 2009.

[6] P. Baskaralingam, M. Pulikesi, V. Ramamurthi and S. Sivanesan, "Modified hectorites and adsorption studies of a reactive dye," Applied Clay Science, pp. 207-214, 2007.

[7] P. Nigam, G. Armour, I. M. Banat, D. Singh and R. Merchant, "Physical Removal of Textile Dyes and solid state fermentation of dye-absorbed agricultural residues," Bioresour. Technol, vol. 72, pp. 219-226, 2000.

[8] H. Zollinger, Colour Chemistry: Synthesis, properties and applications of organic dyes and pigments, Weinheim: VCH Publishers, 1991.

[9] R. G. Saratate, G. Saratate, J. Chang and S. Govindwar, "Bacterial decolorization and degradation of azo dyes: a review," Journal of Taiwan Ins. Chem. Eng., pp. 138-331, 2011.

[10] C. R. Holkar, A. B. Pandit and D. V. Pinjari, "Kinetics of biological decolorization of anthraquinone based Reactive Blue 19 using an isolated strain of Enterobacter sp.F NCIM 5545," Bioresource Technology, pp. 342-351, 2014.

[11] T. Robinson, G. McMullan, R. Merchant and P. Nigam, "Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative.," Bioresour Technol, pp. 247 - 255, 2001.

[12] P. C. Vandevivere, R. Bianchi and W. Verstraete, "Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies," J. Chem. Tech. Biotechnol, pp. 289-302, 1980.

[13] Y. Anjaneyulu, N. S. Chary and D. Raj, "Decolorization of Industrial effluents available methods and emerging technologies-a review," Rev. Environ. Sci Biotechnol, pp. 245-273, 2005.

[14] Y. Liu and J. Zhou, "The Study of Modified PAN-based Carbon Fiber Felt as Electrode in the Electro-adsorption Desalination," International Journal of Electrochemical Science, vol. 8, pp. 4864-4872, 2013.

[15] Z. Yun-Hua, G. Fu-Xing, L. Meng, W. Di-Hua, H. Zhong-Mai and G. Yun-Peng, "Treatment of Reused Comprehensive Wastewater in Iron and Steel Industry With Electrosorption Technology," Journal of Iron and Steel Research, vol. 18, pp. 37-42, 2011.
[16] N. Li, S. Yang, J. Chen, J. Gao, H. He and C. Sun, "Electro-adsorption of tetracycline from aqueous solution by carbonized pomelo peel and composite with aniline," Applied Surface Science, vol. 386, pp. 460-466, 2016.

[17] A. Pirkarami, M. E. Olya and N. Y. Lemaee, "Decolorization Of Azo Dyes By Photo Electro Adsorption Process Using Polyaniline Coated Electrode," Progress in Organic Coatings 76, pp. 682-688, 2013.

[18] B. Hamed and M. El-Khaiary, "Batch removal of malachite green from aqueous solutions by adsorption on oil plm trunk fibre: Equilibrium isotherms and kinetic studies," Journal of Hazardous Materials, pp. 237-244, 2008.

[19] I. Tan, A. Ahmad and B. Hameed, "Adsorption of basic dye on high-surface area activated carbon prepared from coconut husk: Equilibrium, Kinetic and thermodynamic studies," Journal of Hazardous Materials, pp. 337-346, 2008.

[20] Y. Ho, "Review of Second-Order models for adsorption systems," Journal of Hazardous Materials, pp. 103-111, 2006.

[21] J. Zeldowitsch, "Uber den mechanismus derkatalytischen oxydationvon CO an MnO2," Acta Physicochemical URSS, pp. 364-449, 1934.

[22] W. Rudzinski and T. Panczyk, "Kinetics of isothermal adsorption on energetically heterogenous solid surfaces: a new theoretical description based on the statistical rate theory of interfacial transport," Journal of Physical Chemistry, pp. 9149-9162, 2000.

[23] J. Heimberg, K. Wahl, I. Singer and A. Erdemir, "Superlow friction behavior of diamond-like carbon coatings: time and speed effects," Applied Physics Letters, pp. 2449-2451, 2001.

[24] C. Cheung, J. F. Porter and G. McKay, "Sorption Kinetic analysis for the removal of cadmium ions from effluents using bone char," Water Research, pp. 605-612, 2001.

[25] O. Hamdaouia and E. Naffrechoux, "Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters," Journal of Hazardous Material, pp. 381-394, 2007.

[26] S. Rangabhashiyam, N. Anu, M. N. Giri and N. Selvaraju, "Relevance of isotherm modeles biosorption of pollutants by agricultural by products," Journal of environmental Chemical Engineering, pp. 2398-2414, 2014.

[27] C. Hessel, C. Allegre, M. Maisseu and F. Charbit, "Guidelines and legislation for dye house effluents," J. Environ, pp. 171-180, 2017.

[28] A. Paz, J. Carballo, M. J. Perez and J. M. Dominguez, "Biological treatment of Model dyes and Textile Wastewaters," Chemosphere, pp. 168-177, 2017.

[29] P. Nigam, G. Armour, I. M. Banat, D. Singh and R. Marchant, "Physical removal of textile dyes and solid state fermentation of dye adsorbed agricultural residues," Journal of Biorase Technology, pp. 219-226, 2000.