



Synthesis and Kinetic Investigation of Fe-Mn Binary Metal Oxide for Adsorption of Black Reactive 5 Dye

Hesam Malekzadeh
Department of Chemical Engineering
Sahand University of Technology
Sahand New Town, Tabriz, Iran.
H_Malekzadeh99@sut.ac.ir

Mohammad Zabihi
Department of Chemical Engineering
Sahand University of Technology
Sahand New Town, Tabriz, Iran.
Zabihi@sut.ac.ir

Morteza Faghihi
Chemical and Process Research Group
Niroo Research Institute
Tehran, Iran.

Abstract— In the present study, a bimetallic nanocomposite of Fe-Mn was synthesized using a facile co-precipitation method. The prepared sample was characterized using XRD analysis to determine the important formed phases. The removal efficiency of Reactive Black 5 (RB5) dye using the fabricated Fe-Mn binary metal oxide was measured to be about 84.8% under the normal condition. The achievements indicated that the bimetallic adsorbent Fe-Mn can be effectively utilized for removal of the anionic ions from aqueous solutions. Furthermore, the adsorption kinetic was also investigated which showed that the second order kinetic equation had the good conformity with the experimental data. Therefore the electrostatic adsorption was carried out for uptake of dye.

Keywords; Nanostructure; Bimetal Oxide; Adsorbent; Reactive Black 5; Kinetics



1. introduction

In various industries, including textiles, paper, leather, food, and cosmetics, a wide range of dyes, exceeding 10,000 in number, are utilized[1]. The presence of reactive dye in wastewater can be visually detected by humans at levels as low as approximately 0.005 mg/l[2, 3]. Therefore, wastewater that surpasses these limits cannot be tolerated due to aesthetic reasons. Reactive Black 5 (RB5) dye belongs to the category of azo acidic reactive dyes and finds extensive use in the dyeing industry[4]. This particular dye class possesses high solubility in water and carries a negative charge when introduced into aquatic environments. It is worth noting that many azo dyes are nonbiodegradable, leading to the inhibition of photosynthesis in plants and posing potential toxicity and carcinogenic risks to humans[5]. Among various methods for removing dyes from wastewater, the adsorption process stands out as highly effective. This method offers advantages such as cost-effectiveness and sludge-free clean operation compared to alternative approaches[6].

The Fe-Mn binary oxide was synthesized by one-step co-precipitation method for the adsorption of anionic aqueous solution[7]. the adsorbent (Fe-Mn binary oxide) exhibited an 84.8% efficiency in removing of RB5 dye, we also calculated maximum adsorption capacity of the Fe-Mn binary oxide for RB5 dye which was approximately 56.49 mg/g. The primary objective of this study was to synthesize Fe-Mn binary oxide using a simple co-precipitation method and cost-effective materials. The synthesized bimetal oxide was then employed for the removal of RB5 dye from aqueous solutions, while also examining the kinetics of the process. Additionally, the prepared sample underwent characterization using XRD analysis.

2. Experimental

2.1. Materials

Reactive Black 5 (C₃₄H₂₅N₉Na₂O₇S₂, abbreviated as RB5), potassium permanganate (KMnO₄), iron (II) sulfate heptahydrate ((FeSO₄·7H₂O), sodium hydroxide (NaOH)

2.2. Synthesis of Fe-Mn binary oxide

Fe-Mn binary oxide was synthesized using a straightforward co-precipitation method. Initially, a solution was prepared by dissolving 0.015 mol of potassium permanganate (KMnO₄) and 0.045 mol of iron (II) sulfate heptahydrate (FeSO₄·7H₂O) individually in 200 mL of deionized water. Throughout the process, a vigorous magnetic stirring was applied. The FeSO₄ solution was gradually added to the KMnO₄ solution while simultaneously introducing a 5 M NaOH solution. This addition of NaOH was essential to maintain the pH of the solution in the desired range of 7 to 8. Following the addition, the resulting suspension underwent continuous stirring for a duration of 1 hour. Subsequently, the suspension was left to age at room temperature for 12 hours. To ensure the purity of the product, the suspension was subjected to multiple washes with deionized water until no SO₄²⁻ ions were detected. Once the washing process was complete, the suspension was filtered and then dried at 105 °C for 4 hours. The final dry material was crushed into a suitable form and then stored in a desiccator for future use. This synthesized Fe-Mn binary oxide is now ready for further applications and experimentation.

2.3. Dye adsorption experiment

We conducted an experiment to remove RB5 (a dye) from water using 0.05g of Fe-Mn binary oxide. The experiment's conditions were kept constant, including the initial concentration of RB5 (50 mg/l), the volume of the polluted water (50 mL), the temperature (25°C), and a pH of 7. To measure the concentration of RB5, we used UV-vis spectroscopy, and we also calculated the removal efficiency of RB5 using a specific equation (eq. 1).

$$Re\% = \frac{C_0 - C_e}{C_0} * 100 \quad (1)$$

Where C₀ and C_e are the initial and the equilibrium concentration of RB5, respectively.

3. Result and discussion

3.1. XRD Analysis

The XRD pattern of the Fe-Mn binary adsorbent (Fig.1) revealed the absence of distinct crystalline peaks, indicating that the Fe and Mn oxides within the Fe-Mn binary composite primarily exist in an amorphous form. This suggests that the coexistence of these elements during the synthesis process hindered the formation of crystalline manganese oxide and iron (III) oxide[8, 9].

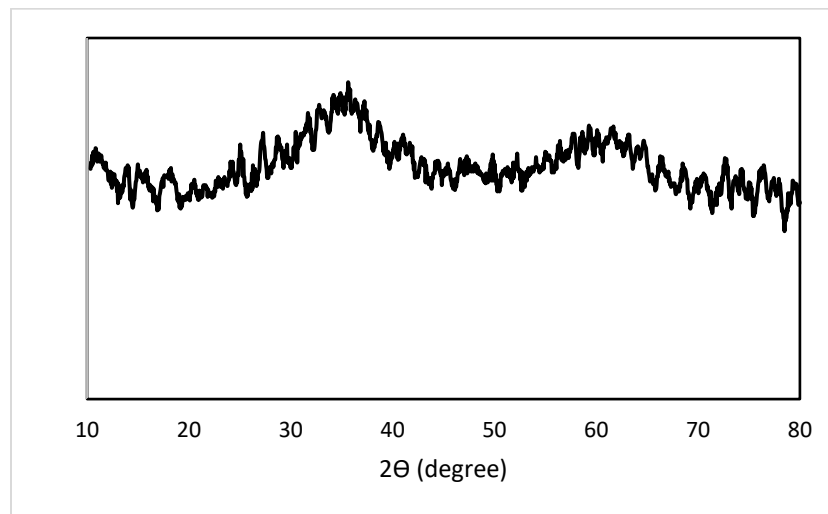


Figure 1. XRD analysis of Fe-Mn binary oxide

3.2 Kinetics

Figure 1 depicts the adsorption kinetics of RB5 on the Fe-Mn binary oxide. The adsorption process can be divided into two distinct steps: an initial rapid step followed by a slower one. Within the first 20 minutes, the adsorption rate was observed to be fast, whereas after this period, the adsorption rate significantly decreased.

Upon examining Figure 2, it is evident that the pseudo-second-order model aligns well with the experimental data. The pseudo-second-order kinetics model (equation 2) exhibited a strong fit with a high correlation coefficient (R² = 0.9983), as summarized in Table 1.

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

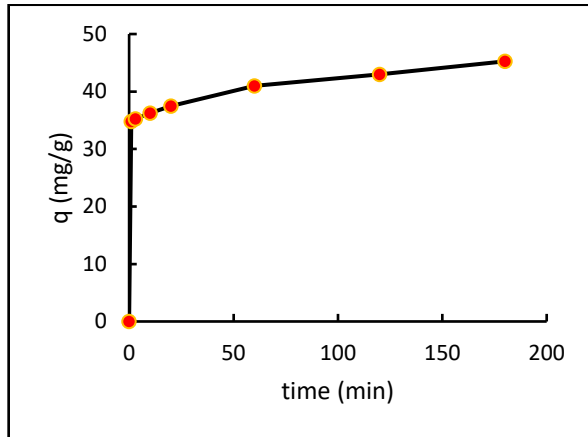


Figure 2. Adsorption kinetic of RB5 on Fe-Mn binary oxide

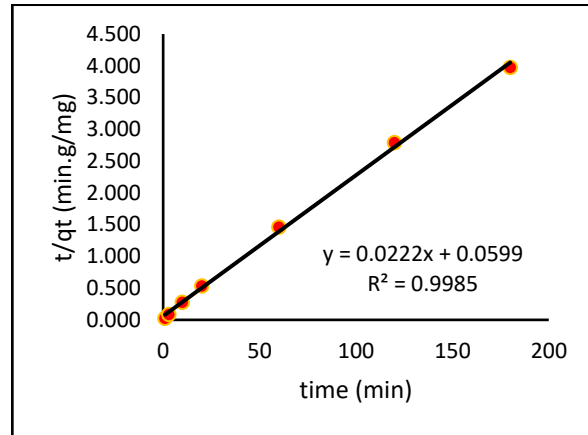


Figure 3. Pseudo-second-order kinetic model

Table 1. Kinetic parameters for Adsorption of RB5

Kinetic model	Parameters	Fe-Mn binary oxide
Pseudo-first-order	K1	0.030
	q _e	10.336
	R ²	98.78
Pseudo-second-order	K2	0.0083
	q _e	45.04
	R ²	99.85

4. Conclusion

In this research, the Fe-Mn binary oxide was synthesized using the cost-effective co-precipitation method, which utilizes abundant and readily available materials. Our study demonstrates that the Fe-Mn binary oxide adsorbent is highly effective in treating anionic aqueous solutions like RB5. The XRD analysis revealed the absence of distinct crystalline peaks, indicating that our Fe-Mn binary oxide exists in an amorphous form.

To evaluate the kinetics of the adsorption process, we compared the experimental data with pseudo-first-order and pseudo-second-order equations. The comparison of the correlation coefficients derived from these kinetics models indicated that the pseudo-second-order equation provides a more accurate representation of the RB5 adsorption process.



5. References

- [1] Pormazar, S.M. and A. Dalvand, 2022 *Adsorption of Reactive Black 5 azo dye from aqueous solution by using amine-functionalized Fe₃O₄ nanoparticles with L-arginine: Process optimisation using RSM*. International Journal of Environmental Analytical Chemistry, **102**(8): p. 1764-1783.
- [2] Amin, M., A. Alazba, and M. Shafiq, 2015 *Adsorptive Removal of Reactive Black 5 from Wastewater Using Bentonite Clay: Isotherms, Kinetics and Thermodynamics, Sustainability*. 7 15302-15318. DOI.
- [3] Almeida, C., et al., 2009 *Removal of methylene blue from colored effluents by adsorption on montmorillonite clay*. Journal of colloid and interface science, **332**(1): p. 46-53.
- [4] Jović-Jovičić, N., et al., 2013 *Synergic adsorption of Pb²⁺ and reactive dye—RB5 on two series of organomodified bentonites*. Journal of contaminant hydrology, **150**: p. 1-11.
- [5] Erdem, B., M. Erdem, and A.S. Özcan, 2016 *Adsorption of Reactive Black 5 onto quaternized 2-dimethylaminoethyl methacrylate based polymer/clay nanocomposites*. Adsorption, **22**: p. 767-776.
- [6] Gupta, V., 2009 *Application of low-cost adsorbents for dye removal—a review*. Journal of environmental management, **90**(8): p. 2313-2342.
- [7] Zhang, G., et al., 2009 *Adsorption behavior and mechanism of arsenate at Fe–Mn binary oxide/water interface*. Journal of Hazardous Materials, **168**(2-3): p. 820-825.
- [8] Zhang, G., et al., 2007, *Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal*. Water research, **41**(9): p. 1921-1928.
- [9] Song, Y.-f., et al., 2017 *Removal of tungsten from molybdate solution by Fe–Mn binary oxide adsorbent*. Transactions of Nonferrous Metals Society of China, **27**(11): p. 2492-2502.