

Research Article

Synthesis of Montmorillonite-Silica Nanocomposite Using Millet Husk and Montmorillonite Clay and Optimization of Adsorption Parameters for Congo Red Dye Adsorption

Oboyi Matthew Echeofun , Ernest Isaac* , Ishaku Bingong ,
Joseph Faruk Kpesibe , Emmanuel John 

Department of Chemical Sciences, Taraba State University, Jalingo, Nigeria

Abstract

Dyes are substances that, when applied to a substrate provides color by a process that alters, at least temporarily, any crystal structure of the colored substances. The discharge of these effluents into the receiving environments results in hazardous health problems as most of these dyes have carcinogenic effects on the living organisms. Generally, dyes are classified into three categories: a) anionic: direct, acid, and reactive dyes; b) cationic: basic dyes; and c) non-ionic: disperse dyes. The chromophores in anionic and non-ionic dyes mostly consist of azo groups or anthraquinone types. However, Congo red, are difficult to biodegrade due to their complex aromatic structures, which provide them with physico-chemical, thermal, and optical stability. This study is aimed at synthesizing Montmorillonite-silica nanocomposite, a cost effective adsorbent from millet husk and Montmorillonite-clay with the determination of its optimum adsorption parameters for Congo Red Dye adsorption. Here, synthesis of Montmorillonite-silica nanocomposite and optimization parameters were carried out using standard procedures. The unbiased result demonstrated that the percentage yield was found to be 94.51 %. The optimum adsorption parameters studied were adsorbent dose, adsorbate concentration, pH and Kinetics studies. The optimum adsorption parameters were found to be 8.0 g/L, 2.0 mg/L, 8 and 30 minutes, respectively. Hence, the synthesized Montmorillonite-silica nanocomposite obtained from montmorillonite clay and millet husk ash can serve as a cost-effective adsorbent for the removal of Congo Red Dye from waste waters.

Keywords

CRD, MH, MHA

1. Introduction

Dyes are substances that impart color to a substrate by altering, at least temporarily, the crystal structure of the colored material [8, 9]. Dyes are classified according to their application and chemical structure, and are composed of a group of atoms known as chromophores, responsible for the dye color. These chromophore-containing centers are based on diverse

functional groups, such as azo, anthraquinone, methine, nitro, aril methane, carbonyl and others [12]. In addition, electrons withdrawing or donating substituents so as to generate or intensify the color of the chromophores are denominated as auxo chromes. The most common auxo chromes are amine, carboxyl, sulfonate and hydroxyl.

*Corresponding author: eneszik@gmail.com (Ernest Isaac)

Received: 9 August 2024; **Accepted:** 3 September 2024; **Published:** 10 October 2024



Copyright: © The Author(s), 2024. Published by Science Publishing Group. This is an **Open Access** article, distributed under the terms of the Creative Commons Attribution 4.0 License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.

Generally, dyes are classified into three categories: a) anionic: direct, acid, and reactive dyes; b) cationic: basic dyes; and c) non-ionic: disperse dyes. The chromophores in anionic and non-ionic dyes mostly consist of azo groups or anthraquinone types [5, 6].

Congo red dye is a benzidine-based anionic diazo dye, known to cause allergic reactions and to be metabolized to benzidine, a known human carcinogen, which has caused Congo red to be banned in many countries. Congo red can reduce serum protein concentration and cause platelet aggregation, thrombocytopenia, and disseminated micro embolism [3]. Synthetic dyes, such as Congo red, are difficult to biodegradability due to their complex aromatic structures, which provide them with physico-chemical, thermal, and optical stability [3].

Water contamination resulting from dyeing and finishing in textile industry is a major concern. Discharging large amount of dyes in water resources accompanied with organics, bleaches, and salts can affect the physico-chemical properties of freshwater. In addition to their unwanted colors, some of these dyes may degrade to produce carcinogens and toxic products. The wastewater disposal exacerbates major pollution issues by some factories under unregulated and unsuitable circumstances. Undoubtedly, the urgency of prevention and treatment of pollution is crucial for human life. If a textile mill expels wastewater into the surrounding area without any treatment, it would significantly affect existing water bodies and the adjacent area's soil [10].

Globally, environmental problems associated with the textile industry are those associated with water pollution caused by the direct discharge of untreated effluent and release of toxic chemicals into the aquatic environment. It drastically decreases oxygen concentration in water body due to the presence of hydrosulfides [4].

($\text{FeS} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2\text{S}$) and blocks the passage of light through water body which is detrimental to the water ecosystem.

Current research investigations include the use of millet husk ash (MHA) in silica gels, silicon chip, synthesis of activated carbon and silica, catalysts, zeolites, ingredients for lithium ion batteries, graphene, energy storage/capacitor, carbon capture, and in drug delivery vehicles [1].

Adsorption is a consequence of surface energy which results to the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent [11]. This process differs from absorption, in which a fluid (the adsorbate) is dissolved by or permeates a liquid or solid (the adsorbent), respectively.

In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled by other atoms in the material [6]. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates [7]. The exact nature of the bonding depends on the details of the species involved. But the adsorption process is

generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may occur due to electrostatic attraction [2].

2. Materials and Method

2.1. Sample Collection

Millet husk was collected at Ardo-Kola Local Government Area, Taraba State and sample of Montmorillonite clay was collected from Gombe State, Nigeria.

2.2. Preparation of Millet Husk Ash

500 g of millet husk was washed thoroughly with distilled water. It was dried and subsequently, oven dried at 105 °C and kept for further analysis.

2.3. Preparation of Montmorillonite Clay

The collected clay sample (500g) was washed with distilled; the washed sample was air dried and oven dried at 110 °C. The clay was ground and sieved using a sieve. A weighed of 125 g of the clay-powder was refluxed with 250 mL of 0.5 M H_2SO_4 for 30 minutes. It was then washed with distilled water to expunge its acidity. The clay was then dried in an oven at 105 °C.

2.4. Preparation of Millet Husk Ash

500 g portion of dried millet husk was refluxed with 500 mL sulfuric acid for 30 minutes at 95 °C to remove any metallic impurities. After completion, it was washed thoroughly with distilled water and dried in an oven for 3 hours at 110 °C. The treated millet husk was calcined in a muffle furnace for 5 hours at 600 °C. The obtained white millet husk ash was kept for further preparations.

2.5. Synthesis of Montmorillonite-Silica Nanocomposite

15 g of millet husk ash (MHA) was refluxed with 2 M KOH solution for 30 minutes while stirring. After which the solution was then filtered, where sodium silicate solution was observed and obtained. 60 g of the acidified montmorillonite clay was added into 100 mL solution of the sodium silicate obtained. It was then precipitated with 0.5 M HCl drop-wise and measuring the pH until it was equal to 8.9, it was then kept for 24-hour and then washed with distilled water until the pH was equal to 7. It was then oven dried for 3 hours, ground and sieved.

2.6. Procedures for Optimization of Adsorption Parameters

Adsorbent Dose

Prepare a 2 mg/L solution of Congo red by dilution to mark a known volume of the stock solution in the appropriate volumetric flask.

Measure out 50 mL of 2 mg/L solution of Congo red into a 100 mL conical flask.

Disperse 0.1 g of the montmorillonite-silica nanocomposite into the 50 mL Congo red solution, stopper and shake thoroughly for 60 min.

Filter the content of the flask using a filter paper and store the filtrate in a sample bottle (clearly marked "0.1 g") for spectrophotometric analysis.

Repeat same procedure using 0.2, 0.3, 0.4, 0.5 and 0.6 g of the nanocomposite.

Adsorbate concentration

Weigh out 0.1 g montmorillonite-silica nanocomposite into a 100 mL conical flask and add 50 mL of a 1 mg/L solution of Congo red prepared from the stock solution.

Allow the mixture to stand 60 min with intermittent shaking every 10 min.

Filter the content of the flask using a filter paper and store the filtrate in a sample bottle (clearly marked "1 mg/L") for spectrophotometric analysis.

Repeat same procedure using 2, 3, 4 and 5 mg/L solution of Congo red prepared from the stock solution.

pH

Measure out 50 mL of 2 mg/L Solution of Congo red into a 100 mL conical flask and adjust its pH to the desired value using 1 M HCl solution.

Dispersed 0.1 mg/L of the montmorillonite silica nanocomposite into the 50 mL Congo red solution, stopper and shake thoroughly for 60 min.

Filter the content of the flask using a filter paper and store the filtrate in a sample bottle (clearly marked with the pH value) for spectrophotometric analysis.

Carry out this procedure at pH value of 5, 6, 7 and 8.

Kinetics Studies

Weigh out the equivalent of optimum adsorbent dose (0.4 g) into a 100 mL conical flask and add 50 mL of the Congo red dye solution equivalent to the optimum adsorbate concentration (2 mg/L solution).

Stopper, shake thoroughly and allow to stand for 10 min.

Filter the content of the flask using a filter paper and store the filtrate in a sample bottle (clearly marked "10 min") for spectrophotometric analysis.

Repeat same procedure for varying contact time of 20, 30, 40, 50 and 60 min.

3. Results and Discussion

3.1. Percentage Yield

The percentage yield for the montmorillonite silica-nanocomposite was found to be 94.51% which indicates that a good quantity of the sample was recovered.

3.2. Effect of Adsorbent Dose

The effect of adsorbent dose for Congo red dye was observed that, there was an increase in the amount of Congo Red removed from the aqueous phase as the adsorbent dose increased from 1 g to 8 g. Beyond this concentration, the amount of Congo Red decreased [Figure 2]. A similar observation has been reported [9]. This report according to the authors may be due to aggregation of adsorption sites resulting in a decrease in the total adsorbent surface area of particles available to adsorbate and an increase in diffusion path length. Thus, the optimum adsorbent dose was found to be 8 g.

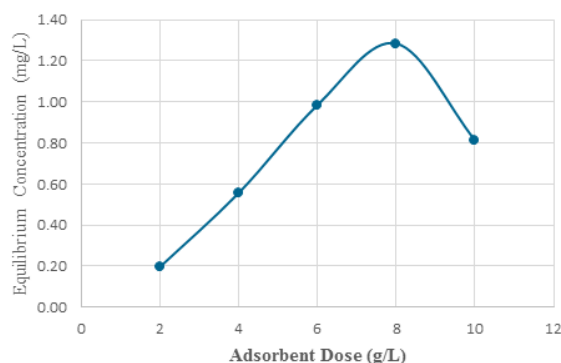


Figure 1. Graph of effect of Adsorbent Dose for the removal of Congo Red Dye at adsorbate concentration of 2 mg/l, contact time of 60 (min), and varied Dosage of 0.1, 0.2, 0.3, 0.4 and 0.5 g.

3.3. Effect of Adsorbate Concentration

The adsorption of Congo red dye on montmorillonite-silica nanocomposite was studied at different initial concentration from 1 mg/L to 5 mg/L. This result was represented in Figure 2., it was observed that there was a high removal of Congo red dye from 1 mg/L to 2 mg/L. Beyond this concentration, the removal of Congo red dye decreases sharply. A similar observation has been reported by (28) where the removal of Congo Red increases with initial concentration and beyond this concentration the amount of Congo Red removed decreased [Figure 2]. The optimum initial concentration was found to be 2 mg/L.

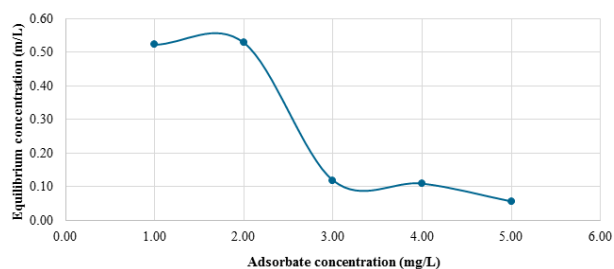


Figure 2. Graph of effect of Adsorbate concentration for the removal of Congo Red Dye at adsorbent dose of 0.1 g, contact time of 60 (min), and varied adsorbate concentration of 1, 2, 3, 4 and 5 mg/L.

3.4. Effect of pH

The adsorption of Congo Red on montmorillonite-silica nanocomposite was carried out at varied pH of 5, 6, 7, 8, and 9. The adsorption of the Congo Red increased from 5 to 8. Beyond this pH it decreased. The optimum pH for Congo Red removal on montmorillonite-silica nanocomposite at adsorbate concentration of 2 mg/L, contact time of 60 (min) and adsorbent dose of 0.1 g/50 mL was found to be 8.

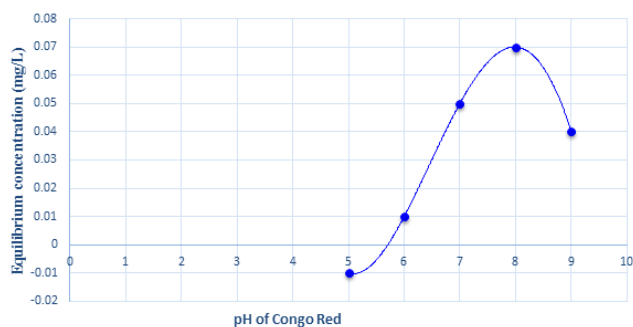


Figure 3. Graph of effect of pH for Congo Red Dye removal at adsorbate concentration of 2 mg/L, adsorbent dose of 0.1 g, contact time of 60 (min) and varied pH of 5, 6, 7, 8 and 9.

3.5. Kinetic Studies

As seen from the experimental results obtained from the adsorption process of Congo red dye on montmorillonite-silica nanocomposite, the percentage removal of the dye increases speedily with the increase of the contact from 10 minutes to 20 minutes. And then decreases at a significant narrow range from 30 minutes to 40 minutes from which it increases rapidly at 50 minutes. Then at 60 minutes, it decreases to the lowest percentage removal and this look so abnormal to account for. Thus, the optimum kinetic studies was found to be 30 minutes.

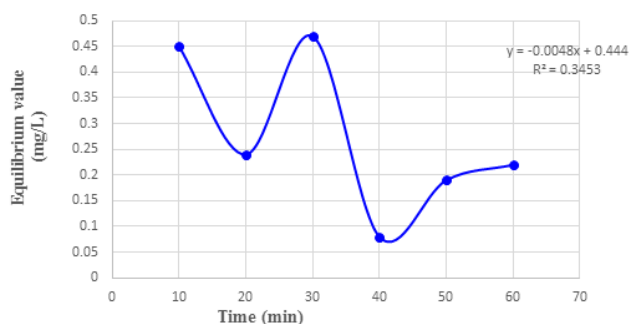


Figure 4. Graph of kinetic studies for the removal of Congo Red Dye at adsorbate concentration of 2 mg/mL and adsorbent dose of 0.4 g/L and varied time of 10 to 60 min.

4. Conclusion

The adsorption process of Congo red was carried out using Montmorillonite silica nanocomposite. From the result, the percentage yield was 94.51%. Optimum adsorbent dose, adsorbate concentration, pH, and kinetic studies were 8 g/L, 2 mg/L, 8 and at 30 minutes, respectively. Hence, Montmorillonite-silica nanocomposite obtained from montmorillonite clay and millet husk ash can serve as an effective adsorbent in the removal of Congo red dye.

Abbreviations

MH	Millet Husk
MHA	Millet Husk Ash
CRD	Congo Red Dye

Author Contributions

Oboyi Matthew Echeofun: Funding acquisition, Investigation, Methodology, Writing – original draft

Ernest Isaac: Funding acquisition, Investigation, Supervision, Writing – review & editing

Ishaku Bingong: Investigation, Writing – original draft, Writing – review & editing

Joseph Faruk Kpesibe: Formal Analysis, Funding acquisition, Resources, Validation, Writing – review & editing

Emmanuel John: Funding acquisition, Methodology, Resources Software

Conflicts of Interest

The authors declare no conflicts of interest.

References

- [1] Adebayo (2009). Preparation of porous silica from chlorite by selective acid leaching. *Applied clay science*, 32, 261-270.
- [2] Basiri H., Yusef O. K., Mohammad JM, Mojtaba S, Shahram S and Sedigheh S. Removal of Congo red dye from aqueous solutions by a low-cost adsorbent: Activated carbon prepared from Aloe vera leaves shell. *Environmental Health Engineering and Management Journal* (1): 29–35.
- [3] Madrakian, T.; Afkhami, A. and Ahmadi, M. (2012) Adsorption and kinetic studies of seven different organic dyes onto magnetite nanoparticles loaded tea waste and removal of them from wastewater samples. *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 99, 102–109.
- [4] Mansoori T, Rohani B, Ahmad PA and Eshaghi Z. (2008). Environmental application of nanotechnology. *Annual Review of Nano Research.*; 2(2): 1-73.

- [5] Moosa A. A., Ali M. R. and Noor A. H. (2016). Adsorptive removal of lead ions from aqueous solution using biosorbent and carbon nanotubes. *American Journal of Materials Science.*; 6(5): 115-124.
- [6] Olayinka O. K., Oyediji O. A. and Oyeyiola O. A. (2009). Removal of chromium and nickel ions from aqueous solution by adsorption on modified coconut husk. *African Journal of Environmental Science and Technology*; 3(10): 286-293.
- [7] Sharma, N.; Tiwari, D. P. and Singh, S. K. (2012). Decolourisation of synthetic dyes by agricultural waste—A review. *Int. J. Sci. Eng. Res*, 3, 1–10.
- [8] Shehu Z. and Danbature W. L. (2018). Montmorillonite-silica nanocomposite for dye removal from solution in *Advances in applied science and technology*, 3: 1-12.
- [9] Shehu Z.; Danbature, W. L.; Ayuba, L. and Balama, B. M, (2018). Adsorption and optimization studies of congo red from solution using montmorillonite-silica nanocomposite. *Current Journal of applied science and technology*, 4: 1-10.
- [10] Zhu, X., Li, S., Zhang, Y., & Wang, H. (2022). Textile wastewater treatment using a novel membrane bioreactor with integrated biochar filtration system. *Water Research*, 221, 118796.
- [11] Jain, P., Gaur, V. K., Luhach, S., & Sharma, P. (2022). A comprehensive review on the treatment of textile wastewater using natural adsorbents. *Environmental Technology & Innovation*, 28, 102854.
- [12] Gökkuş, Ö., & Koseoglu-Imer, D. Y. (2023). Application of membrane processes in textile industry wastewater treatment: A review of recent developments and future perspectives. *Journal of Environmental Management*, 326, 116769.