Adsorptive Elimination of Methylene Blue from Water Using Corncob-Derived Biosorbents

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***Abstract*—The purpose of this work is to investigate the effects of dye removal on the structure and characteristics of graphene oxide. Hummers' approach, which is distinct from the modified Hummers method, was used to extract GO from graphite flakes. Using this technique, an ice bath and sodium nitrate were used to create the experiment. Then, utilizing disodium ethylene diamine tetra acetic acid and the graphene oxide immersion method, EDTA-functionalized corncob (EDTA-corncob) and EDTA/graphene oxide functionalized corncob (EDTA-Graphine Oxide/corncob) were created. SEM and FTIR spectroscopy were used to characterize EDTA-corncob and EDTA-Graphine Oxide /corncob. Based on this, methylene blue was used as the adsorbate while the adsorption characteristics of EDTA-corncob and EDTA-Graphine Oxide/corncob were investigated. The effect of samples on methylene blue's adsorption qualities at various periods, temperatures, and pH levels was used to find the best adsorption settings, and the samples reusability was investigated. The outcomes demonstrated that methylene blue's adsorption ability on EDTA-Graphine Oxide/corncob was greater than that of natural corncob and EDTA corncob. According to this study, EDTA-Graphine Oxide/corncob is a reusable adsorbent that works quickly, cheaply, and effectively to remove dye from waste water.**

***Index Terms*—Dye, Graphene oxide, Hummer's method, EDTA, Corncob**

I. INTRODUCTION

One of today's biggest environmental issues is water contamination. One of the significant and fundamental contaminants in water contamination is dyes. As industrialization progresses more quickly, wastewater containing colors is released from a variety of human activities, posing major environmental risks. The effluent has been disposed of using a variety of physicochemical methods, including electrocoagulation, photocatalysis, flocculation, ozonation, adsorption, and membrane filtering [17]. Liquid-phase adsorption is thought to be the most efficient method of removing organic dyes from wastewater among these many purification processes [20]. Chitosan, leaves, crab shells, waste coal gangue, peach gum polysaccharide, clays, and Cucumis sativus peel are just a few of the materials that have been created for use as adsorbents to remove colours from water [12]. Due to the huge amounts produced, chemical and mechanical stability, high surface area, and structural qualities of biomass waste, such as corncob, there is a great potential for it to build low-cost and environmentally acceptable adsorbents [22, 23]. However, natural corncob's adsorption capability is typically subpar. Hummers' technique, created in 1957 by Hummers and Offeman using a combination of sulfuric acid H2SO4, sodium nitrate NaNO3, and potassium permanganate KMnO4, is still commonly used, frequently with significant changes [7-9]. According to the degree of oxidation and the method of manufacture, graphite oxides show significant changes in their characteristics. As a result, numerous modification techniques have been developed to improve the capacity of adsorbents based on corncob.

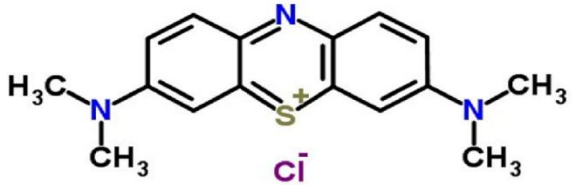


Figure 1 Structure of Methylene Blue

II. MATERIALS AND METHODS

2.1 Preparation of Graphene Oxide

The Hummers method was used to create graphene oxide. Initial mixtures of graphite powder (1g) and

sodium nitrate ($NaNO_3$) (0.5 g) were made in a 100 mL volumetric flask with 25 mL of H_2SO_4 (98%) and were held in an ice bath to maintain a temperature of 0 to 5°C while being constantly stirred. Following three hours of stirring at this temperature, 3 g of potassium permanganate was progressively added to the suspension. To maintain the reaction temperature below 15°C, the rate of addition was carefully managed. At a temperature below 50°C, the mixture is diluted by adding 50 mL of distilled water very slowly in a dropwise method. The mixture is then stirred for two hours with a magnetic stirrer until the solution turns brown. The solution is then given a final treatment with 5 mL of H_2O_2, which causes the color to turn bright yellow. The mixture was ultrasonically processed before being filtered via filter paper. The resultant mixture is centrifuged repeatedly with 10% HCl and then with deionized (DI) water until a gel-like substance appears. Following centrifugation, the gel-like material was dried for 24 hours at 90°C to produce graphene oxide powder.

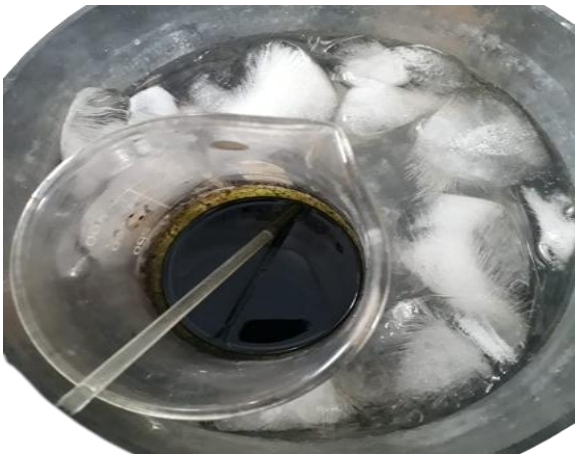


Figure 2 Graphene Mixture kept in Ice Bath

Figure 3 Ultrasonication of Graphite Mixture

2.2 Pre-treatment of corncob

To remove any surface contaminants, the corncobs were carefully cleaned with tap water and distilled water, then dried at 55°C. The dried corncobs were then ground into a powder using a grinder to create corncob powder for storing. 10.0 g of powdered corncob was dissolved in 20% isopropanol, stirred for 24 hours, filtered, colorless washed with 20% isopropanol and distilled water, dried for 24 hours at 55°C, added 0.1 mol/L of sodium hydroxide solution, stirred for 1 hour at room temperature, filtered, added distilled water to stir for 45 minutes, stirred again, washed repeatedly to pH 7.0, and filtered. For storage, the resulting goods were dried at 55°C.

Figure 4 Corncob in Iso-propanol Solution

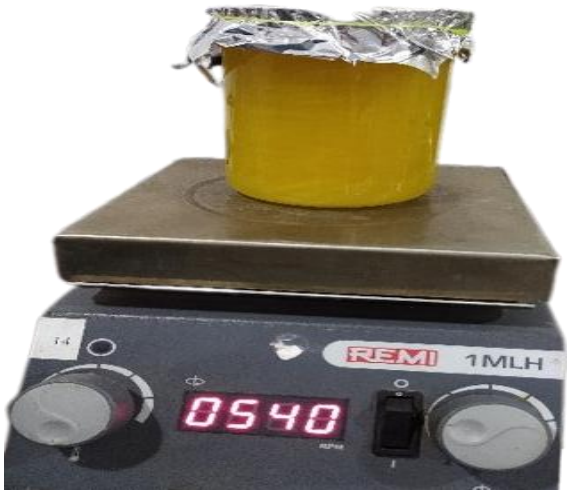


Figure 5 Corncob in NaOH solution

2.3 Preparation of EDTA functionalized corncob/graphene oxide

The prepared corncob powder was filtered, washed, and dried at 55°C after spending 24 hours in a 2.5% EDTA solution. EDTA-corncob was the product that was obtained. Under ultrasound, 0.10 g of GO was

distributed in a 2.5% EDTA solution. After that, a 2.5% EDTA/GO solution was added to the pre-treated corncob powder. It was filtered and cleaned with distilled water after 24 hours. The dried EDTA-GO/corncob sample was kept in reserve after being dried at 55°C.

2.4 Adsorption Studies

A set of 250-mL Iodine flasks were used for the batch tests, each holding a specified amount of adsorbent (0.5g) and 100 ppm of a pH-3 dye solution in 100 ml. The conical flasks were vigorously shaken. A UV-visible spectrometer (systronic) was used to quantify the leftover dye solution's concentration at a wavelength of 700 nm. The following formula was used to determine the percentage of dye removed from the solution:

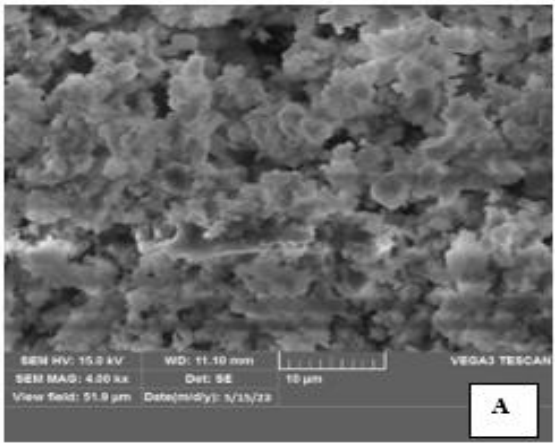
% Removal = C0 - Ct x 100 -------- (1) C0

Where C0 and Ct are the initial and concentration at time‘t’ respectively

III. RESULTS AND DISCUSSION

3.1 SEM Analysis

The prepared EDTA-Graphene Oxide/Corncob composite were analysed by SEM and FTIR. Fig. 6 depicts a scanning electron microscopy (SEM) image of a corncob and a corncob coated with EDTA-graphene oxide. SEM analyses clearly demonstrated the structure of corncob (Fig. 1a and c) and EDTA-Graphene Oxide/corncob (Fig. 1b and d). The porous surface structure of the corncob can be seen in the SEM micrograph (Fig. 1a and c). The structure of the EDTA-Graphene Oxide/corncob is primarily lamellar when compared to the SEM pictures of the corncob.



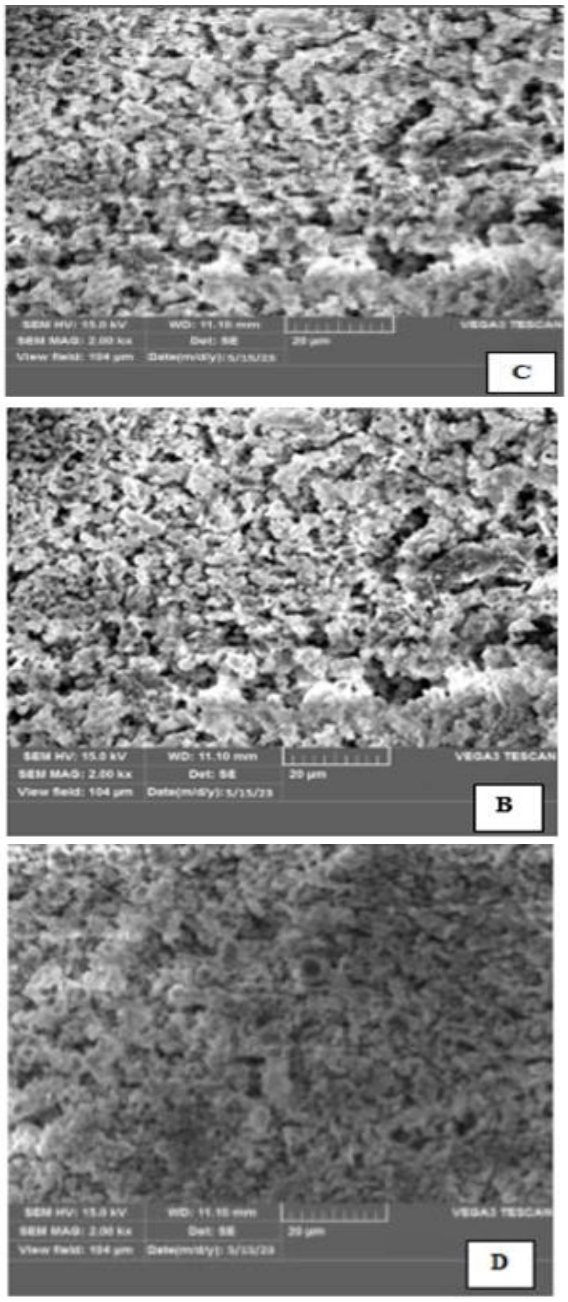


Figure 6 SEM of corncob (a and c) and EDTA-Graphene Oxide/corncob (b and d)

3.2 FTIR Analysis

Figure 7 displays the FTIR spectra of corncob, graphene oxide, EDTA-corncob, and EDTA-graphene oxide/corncob. The distinctive peaks for graphene oxide, which correspond to stretching vibrations of the -OH, C-O-C, C=C, and C=O bonds, are represented by the black color line. All of these functional groups are

anticipated from EDTA and Graphene Oxide (blue and green), and the EDTA-Graphene Oxide/corncob and EDTA-corncob displayed green color peak for N-H (nN-H 26.359cm-1), C=O, N-H (dN-H), and blue color peak for C-O-C (C-O-C, 37.165 cm-1). The presence of these peaks at 26.359 and 42.941 cm-1 in the spectra of corncob that has not been changed (blue line) shows that EDTA and Graphene Oxide have been successfully bonded to the surface of the corncob.

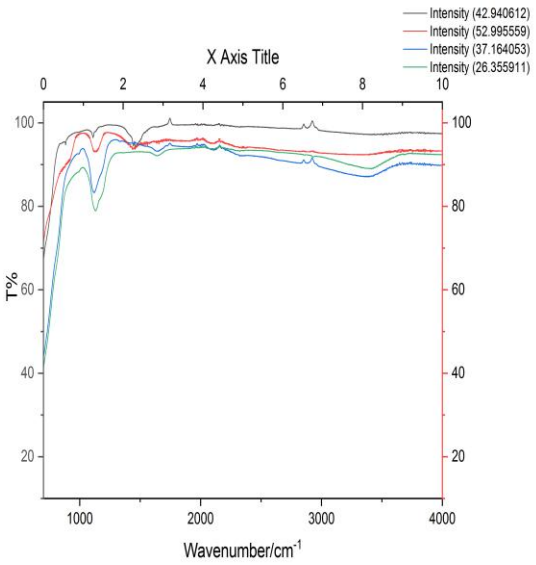


Figure 7 FTIR spectra of adsorbents (black) Graphene Oxide, (red) corncob, (blue) EDTA/corncob, (green) EDTA-Graphene Oxide/corncob

3.3. Adsorption Kinetics

Methylene blue's ability to bind to EDTA corncob and EDTA-Graphene Oxide/corncob over time at 298 K was depicted in Fig. 8. The adsorption capacity of methylene blue on EDTA-corncob and EDTA-Graphene Oxide/corncob grew extremely quickly at 0–100 min and reached equilibrium at 200 min, according to the kinetics data (Fig. 8). The adsorption kinetic data of methylene blue on EDTA-corncob and EDTA Graphene Oxide/corncob were addressed with pseudo-first-order and pseudo-second-order models to describe the adsorption mechanism. The estimated qe was very close to the observed qe, and the adsorption kinetics of EDTA-corncob and EDTA-Graphene Oxide/corncob were nicely represented by pseudo-second order model (R=0.99). This suggested that the adsorption process might be dominated by chemisorption, or chemical bonding, between the active sites of EDTA-corncob and EDTA-Graphene Oxide/corncob and methylene blue.

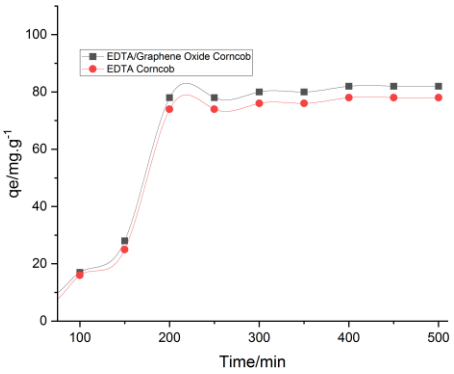


Figure 8 Adsorption Kinetics

3.4 pH Studies

Under the conditions of 100 ppm starting dye solution concentration, 0.5 g 100 ppm of both adsorbent concentration for 200 min, the impact of the initial pH value of the solution on the adsorption process was examined. The pH ranged from 1 to 7. The highest adsorption occurs at acidic pH 3, where MG dye is removed by 86%. This might be because at low pH levels, the surface of the adsorbent is negatively charged, and the electrostatic attraction between the surface and positively charged MB dye molecules causes the adsorption of dye molecules to increase. Adsorption diminishes as pH values rise beyond 3 in the solution. The surface becomes positively charged at higher pH levels. Therefore, there is an electrostatic attraction between the positively charged dye molecules and the positively charged adsorbent surface

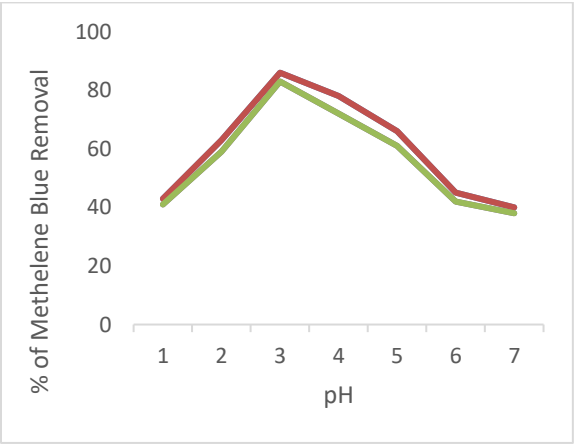


Figure 9 Effect of pH

IV. CONCLUSION

In summary, EDTA/corncob and EDTA-Graphene Oxide/corncob were successfully synthesized and might be employed as effective methylene blue adsorbents. Methylene Blue can adsorb more on EDTA-Graphene Oxide/corncob than it can on EDTA/corncob. The pH at which Methylene blue adhered to EDTA-Graphene Oxide/corncob was around 5.8. It took 200 minutes to reach equilibrium with the adsorption. Adsorption kinetics fits the pseudo-second-order model. Electrostatic attraction was the adsorption mechanism for methylene blue on EDTA/corncob and EDTA-Graphene Oxide/corncob. There was maximum removal of Methylene Blue, 74 % take place, when the concentration of adsorbent is 2 gm. The highest absorption of 80% removal at contact time of 200 min. Maximum dye removal 80 % occurred at 100 ppm concentration of Methylene Blue. So EDTA Graphene Oxide/Corncob can be used for the removal of Methylene Blue from aqueous solution very effectively and economically.

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