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Adsorption of Methylene Blue and Tetracycline from Municipal Water and Surface Water Samples Using Zno-Curcumin-GO Composite

Nabanita Chakraborty[12], Swati Ghosh Acharyya[2], Roy Anindya[1]
[1] Department of Biotechnology, Indian Institute of Technology Hyderabad,
Hyderabad, Telangana, India, 502284
bo21resch11005@iith.ac.in; sgase@uohyd.ac.in
[2] School of Engineering Sciences and Technology, University of Hyderabad,
Gachibowli, Hyderabad, India, 500046
anindya@bt.iith.ac.in

Abstract – A graphene oxide, ZnO, and curcumin composite, (ZnO-cur)-GO, was synthesized by the chemical precipitation method for methylene blue (MB) and tetracycline (TC) adsorption. The morphological and chemical characterization was established by FESEM, TEM, XRD, FTIR, and Raman spectroscopy. TEM confirmed the formation of ZnO nanorods. The composite was rich in oxygen functional groups and had a mesoporous structure. The removal of organic pollutants followed the Langmuir and the Freundlich isotherms for TC and MB, respectively. The maximum removal efficiency was 98.5% and 99% in 10 min. From the supplied municipal and surface water samples, (ZnO-cur)-GO adsorbed 97% and 96 % of MB and TC. The maximum adsorption isotherms are 2000 mg/g and 1200 mg/g, respectively, which is much higher than the reported literature. Nitrate, phosphate, and cationic surfactant adsorption were also studied for the composite in 10 min, where 50%, 80%, and 99.5% removal was noted, respectively. The adsorption mechanism employed H-bonding, electrostatic attraction, and π-π bonding, accompanied by the adsorption into the pores of the mesoporous material.

***Keywords*: Tetracycline, methylene blue, curcumin, ZnO, graphene oxide, adsorption**

1. Introduction

Chemical waste, including dyes, heavy metals, and antibiotics, damages the ecosystem by invading our rivers due to untreated industrial discharge effluent [1, 2]. To protect the environment, it is now essential to eliminate the pollutants and prevent their release at the site of origin. Tetracyclines (TCs) are reportedly the most widely used broad-spectrum antibiotics in numerous nations [2]. Methylene blue is toxic because of its chemical stability and physiological toxicity[3]. Adsorption appears to be one of the technologies most commonly utilized in wastewater treatment facilities because of its easy, efficient, and cost-effective operation [4]. The literature indicated advancement in nano-adsorbents by functionalization to make them more effective towards selective adsorption capabilities by modifying the large surface areas that offer more adsorption sites [3]. GO has an enormous specific surface area and an abundance of oxygen-containing groups, such as epoxy, hydroxyl, and carboxyl groups, which give it exceptional adsorption properties [3, 5].

A graphene oxide-ZnO-curcumin nanocomposite was synthesized using the chemical precipitation method to perform tetracycline (TC) and methylene blue (MB) adsorption from water, with high adsorption and good material reusability. The ability of the composite to remove MB and TC from supplied municipal water and treated drinking water, which are commonly found in wastewater containing dyes and antibiotics, respectively, was evaluated. The π-π interaction, H-bonding between the ring structures, and the electrostatic attraction between oxygenated functional groups governed the adsorption mechanisms. The optimum pH for adsorption, adsorbent dosage, and life cycle of the composite was optimized by minimizing the contact time. Removal of pollutants in a binary system was also established.

2. Materials and Methods

Tetracycline (T3258-25G) 98-102% HPLC grade from Sigma Aldrich and 1000 ± 4 mg/L of Methylene Blue (aqueous) from Qualigens, together with 99.5% pure graphite powder and curcumin (Curcuma longa). Alfa Aesar provided us with potassium hydroxide flakes, zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$, and further pure (KOH) salts. Membrane filters with 0.22 μm pore diameters were the source of Minimac Systems Pvt. Ltd. The successful synthesis of the composite was verified by characterization of the contact angle (ADCAM-02 of Apex Instruments), FTIR (Frontier Perkin Elmer), RAMAN (Model Alpha 300 of WITEC), FESEM (FEI manufactured Nova Nano SEM-450), and XRD (Bruker made D8 Advance). UV-Vis spectrometry for pollutant analysis was done using UV-1780, Shimadzu.

2.1. Material synthesis and characterizations

2 mg of curcumin was stirred at 80˚C until the curcumin dissolved. Next, 0.1 M zinc nitrate salt [$Zn(NO_3)_2$] was added, followed by 0.2 g of graphene oxide. ZnO growth was ensured by the chemical precipitation method using KOH, and the solution was allowed to rest for 12 hours. The composite was centrifuged and vacuum-dried. The morphological and chemical characterizations were reported in previous literature [6].

2.2. Adsorption studies

Batch adsorption experiments were carried out to remove pollutants. Stock solutions of various concentrations were prepared after optimizing the parameters such as pH, contact time, and the adsorbent concentration. The removal efficiency of the adsorbent was determined using equation (1) [7]:

$$\eta\left(\%\right) = \frac{Co - Ce}{Co} X100 \quad (1)$$

where η (%) = metal ion removal efficiency, C_o = initial metal ion concentration (mg/L) and C_e = equilibrium metal ion concentration after reaction (mg/L). The adsorption isotherm for the composites was determined using the Langmuir (eq. 2) or the Freundlich isotherm (eq. 3) models[8].

$$\frac{Ce}{q_e} = \frac{C_e}{q_m} + 1\ /\ (K_L q_m) \quad (2)$$

$$\ln q_e = \ \ln K_F + \left(\frac{1}{n}\right) lnC_e \quad (3)$$

where the maximum adsorption capacity is denoted by q_m (mg/g), the amount of pollutant adsorbed per gram of adsorbent is represented by C_e (mg/L), the equilibrium concentration of pollutant is indicated by C_e (mg/L), the Langmuir constant, K_L (mg/L), is the affinity between the solute and the adsorbent, and the Freundlich constants, n, and K_F, indicates sorption intensity and adsorption capacity, respectively [5]. UV-Vis spectroscopy was employed to analyse the filtrate pre- and post-adsorption. MB and TC peaks were noted at 665 nm and 357 nm, respectively.

3. Results and Discussion

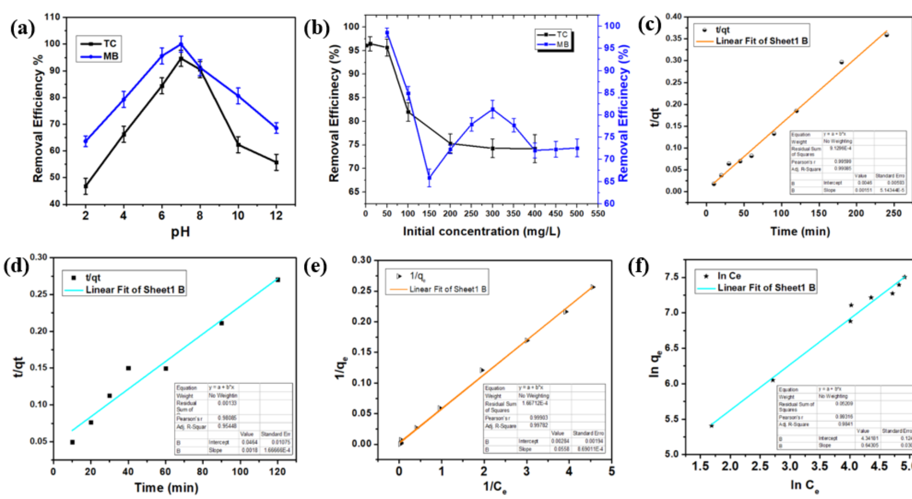

Fig. 1: (a) pH for adsorption of MB and TC; (b) Removal efficiency of MB and TC; pseudo-second-order kinetics is followed by (c) TC and (d) MB; e) TC follows the Langmuir isotherm, f) MB follows the Freundlich isotherm

3.1. Adsorption studies

The optimum pH for pollutant removal was optimized, and it was seen that adsorption efficiency was > 90% for both pollutants in the pH range of 6-8 (Fig. 1a), with the highest removal at neutral pH. By varying the initial concentration, the removal efficiency was seen as 99.9% and 98.5% for 50 mg/L MB and 10 mg/L TC (Fig. 1 b), respectively, in 10 min. TC and MB followed second-order kinetics (Fig. 1c and 1d) and Langmuir (R^2= 0.99) and Freundlich isotherms (R^2=0.98), respectively (Fig. 1e and 1f). For MB adsorption, the mesoporous structure of the material was responsible, in addition to the H-bonding between the ring structures, electrostatic attraction, and π-π bonding, governing adsorption of both pollutants. Similar mechanisms were reported before [4, 8, 9]. The maximum adsorption isotherm established is 2000 mg/g and 1200 mg/g, for MB and TC, respectively.

3.2. Real-time studies

To establish the efficiency of the (ZnO-cur)-GO in real-time systems, MB and TC removal experiments were carried out for municipal water and real-time samples by artificial addition of pollutants in the lab. The removal efficiency of the composite for all samples is represented in Table 1. The adsorption efficiency dropped only by 1-2 % for the real-time water samples despite the ionic interference due to the difference in adsorption isotherms, along with the metal chelating capacity of TC [8]. FTIR analysis was conducted for the composite pre- and post-adsorption (Fig. 2) to understand the functional groups involved in the adsorption process. It was observed that the -OH groups at 3394 cm^{-1}, the carboxylic group at 1576 cm^{-1}, and zinc at 543 cm^{-1} completely disappeared after organic pollutant adsorption on the composite. These groups controlled the adsorption mechanism by electrostatic attraction, H-bonding, and ionic interaction. The C-N groups appeared post-adsorption, which was attributed to the methyl-NH_3^{2+} in the molecular structure [8].

Table 1: Removal Efficiency (%) of MB and TC from different water samples in 10 min.

Sample Location	MB removal percentage (%)	TC removal percentage (%)
DI (control)	99.9	99
Supplied Municipal Water	99	97.4
Ganga River	98.26	97.2
Bompally Industrial Area Stream	97.62	95.6
Rudhraram Industrial Area	97.47	96

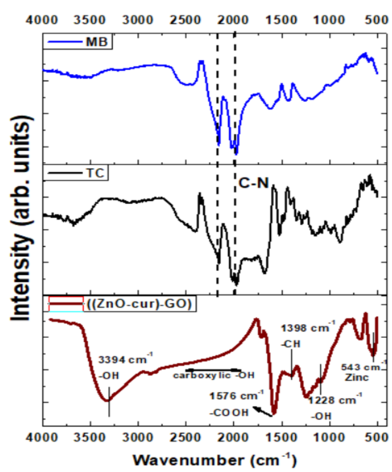

Fig. 2: FTIR spectra of composite pre- and post-adsorption of MB and TC

Nitrate, phosphate, and cationic surfactant removal experiments were also carried out for the particular composite to analyse the basic grey water contaminant removal efficiency. In 10 minutes, 50%, 80%, and 99.5% removal was observed for nitrate, phosphate, and cationic surfactant, respectively. The composite was effective in removing cationic pollutants.

4. Conclusion

The chemically synthesized graphene oxide-ZnO-curcumin composite, (ZnO-cur)-GO, efficiently removed methylene blue and tetracycline. ~ 99 ± 1 % of the pollutants were removed for lab-scale experiments. 97-99 % of MB and > 96% of TC were removed from supplied municipal and surface water in 10 minutes. Thus, this composite was efficient for real-time MB and TC removal at higher dosages. Also, nitrate, phosphate, and cationic surfactant adsorption tests were conducted at lab-scale, where 50%, 80%, and 99.5% removal was observed. The mesoporous structure, enriched oxygen-functional groups, and π-π bonding contributed to the adsorption process.

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