Parameters Affecting Dye Adsorption - Using Graphene Coated Sand (GSC)

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ABSTRACT

Adsorption is most commonly applied process for the removal of pollutants such as dyes and heavy metals ions from wastewater. The present work talks about preparing graphenic material attached sand grains called graphene sand composite (GSC) by using ordinary sugar as a carbon source. Physical morphology and chemical composition of GSC was examined by using (FTIR, SEM, EDAX and XRD). Efficiency of GSC in the adsorption of organic dyes from water was investigated using reactive green dye with different parameters such as (ph, temperature, contact time and dose). Adsorption isotherm was also studied and the results showed that the maximum adsorption capacity of dye is 28.98 mg/g. This fast, low-cost process can be used to manufacture commercial filters to treat contaminated water using appropriate engineering designs.

Keywords: ***GCS, CNTs, wastewater, Reactive green dye.***

1. INTRODUCTION

Deficiency of fresh water is one of the most severe worldwide issues.[1] Moreover, this issue was further complicated by varied waterborne contaminants, such as heavy metals, microorganism's and natural organic matters.[2,3] Over years, efforts have been devoted in water treatment researches to lessen the deterioration of water body qualities around the world.[4] There are several methods used to remove contaminants such as, coagulation,[5] chemical precipitation,[6] chemical reduction,[7] ion exchange,[8] membrane separation,[9] biological treatment,[10] and adsorption.[11-14]

Among all these methods, adsorption is commonly the most adaptable and feasible process because of its low preliminary cost, simple design, easy to operate and insensitivity to toxic material.[15] In specific, potential of various nanomaterials as adsorbents are extensively studied on laboratory scale. The distinctive physical and chemical properties of those materials attributable to the presence of physical and chemicals active groups on their surfaces favouradsorption for many pollutants.[16] Carbon compounds are the most absorbent used to remove dye and heavy metals pollutants.[17] Following the detections of carbon nanotubes (CNTs) in the previous years.[18] There are several practical application of graphene, such as electronic properties, high electrical, thermal conductivity, quantum hall effect, and application in drug delivery and DNA sensing, have been studied in the early few years ago.[19-20] Numerous studies have been conducted on chemically produced graphene, as well as graphene oxide that can be attached onto the surfaces of river sand to create effective adsorbents that can remove natural dyes,[21] pesticides,[22] and heavy metal ions.[23]

This study involves the producing of graphene coated sand using cane sugar and ordinary river sand. The final product was named graphene sand composite (GSC). To investigate the composition and morphology of the prepared GSC different analytical techniques were carried out on GSC such as X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscopes (SEM), and The Element Energy Disappeared Spectroscopy (EDAX)

2. MATERIAL AND METHODS

2.1 Preparing of graphene coated sand composite (GSC)

GSC was prepared through three stages using sugar as a source of carbon.[24] The first stage was preparing concentration of water - sugar solution and mixing it with river sand, the combination then stirred and heated for 90^{o}C by hot air oven till the sugar hardens on sand grains.The second stage the sample was burned in furnace with N_2 gas atmosphere (to prevent oxidation) at 750^{o}C for three hours. When the temperature reached (186 ^{0}C) which is the melting point of sugar, the sugar was converted to dark brown color and then transformed to carbon. The last stage was activation using a strong acid (H_2SO_4) to get rid of ashes that covered the surface. Then, the composite was filtered, washed with distilled water and dried in oven at 120^{0}C for 2 hours.

Fig. 1 Scheme represents river sand and GSC prepared.

2.2 Fourier Transformation Infrared Spectroscopy (FTIR) of GSC

The FTIR analysis was conducted to determine the functional groups on the surface of GSC. The instrument used to record the FTIR spectra by FTIR instrument with kBr as reference. The spectrum was recorded by using FTIR (WQF-510A FTIR) spectrophotometric in a range of 400-4000cm^{-1}.**Fig. 2** represent the FT-IR of GSC. The spectrum of GSC shows an absorption band at 1620 cm^{-1} corresponding to the C=C stretching illustrating the structure of grapheme.[25] The results of FTIR confirms the formation of the graphinic material from common sugar. The peaks at 1093 cm^{-1}, 3593 cm^{-1} and 795 cm^{-1} were corresponded to the C-O ,O-H and C-O-C stretching that are representing the oxygen functionality present .the peak 777 cm^{-1} was due to C-H stretching.

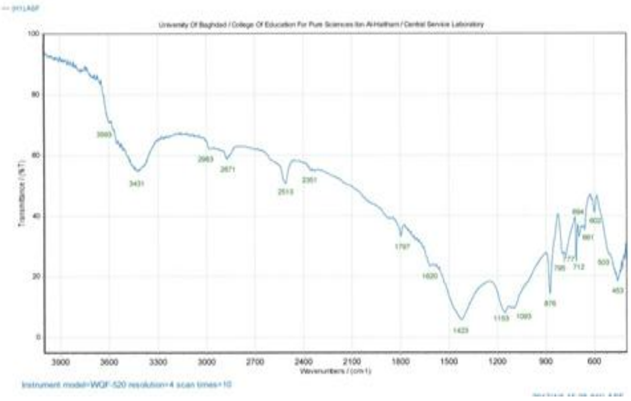

Fig 2: FT-IR analysis of GSC

2.3 SEM and EDAX analysis for GSC

The morphology of GSC was carried out through SEM image. **Fig 3** represents SEM images of sand and GSC, the formation of carbon around the sand can be clearly noticed. Elementary mapping using EDAX analyzer were also carried out and it shows that the surface consists mainly of elements C and O of (73.15%) and (22.98%) percentage respectively, the traces of other elements like aluminum, silicon and calcium shown in **table 1**

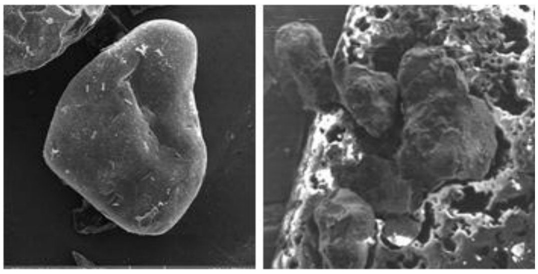

Fig 3 SEM images of sand and GSC

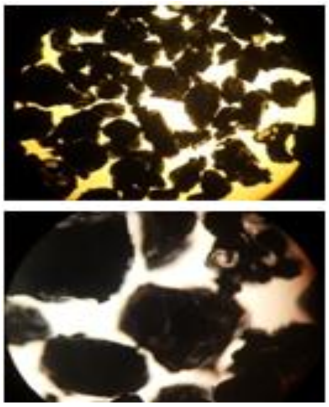

Fig 4 Images of GSC by normal microscope

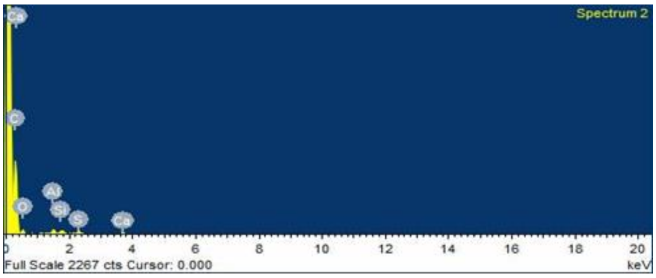

Fig 5: EDAX analysis of GSC

Table 1: percent weight of element on the surface of sand and GSC.

	Sand	GSC
Element	Weight%	Weight%
C	-	73.15
O	47.3	22.98
Al	1.2	1.16
Si	50.2	1.07
S	0.9	0.71
Ca	0.5	0.94
Totals	100.00	100.00

2.4 XRD analysis of GSC

Fig 6 shows the XRD pattern of the powdered GSC sample. The peak at 2Ө =26.61 (002) is observed which represent the existence of graphite layer with d spacing of 0.334 nm.[26] The peaks at 29.38 refer to the existence of SI and other peaks at 45.8, 50.01, 54.84, and 59.88 are characteristic of graphite.[27]

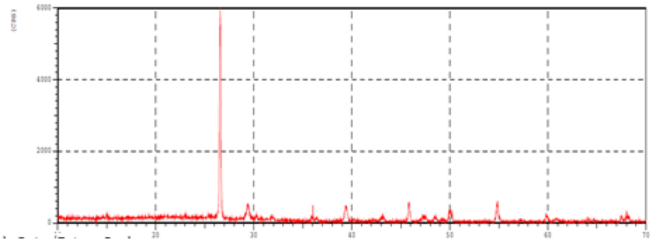

Fig 6: Xrd of GSC sample

3. ADSORPTION EXPERIMENTS

Adsorption of color on GSC was studied using different affecting parameters: pH, Temperature, Contact time and dose to specify the best operation conditions. A certain amount of GSC was added to 50 ml working volume with a constant concentration (50 mg/L). The mixtures were shacked by a shaker (model: VRN-480), then the samples were put in Centrifuge (80-1 table top low, china) at 4000 rpm for 10 min to separate adsorbent elements.

Removal efficiency of dye was calculated using the following equation:

$$\%\text{Removal efficiency} = \frac{C_0 - C_e}{C_0} * 100 \qquad (1)$$

Where C_0 and C_e is the primary and final pollutant concentration (mg/L), respectively.

An adsorption isotherm shows the relation between the amount (by a unit weight) of GSC (adsorbent) and the amount of adsorbate (dye) residue in the solution at equilibrium. Adsorption isotherms are useful in describing the interaction of adsorbate particles with adsorbent surface. In this study, Langmuir and Freundlich models were employed for the treatment of reactive green dye. The adsorption capacity of GSC was examined in a batch reactor. The adsorbent dose and volume of solution were 3g and 0.05L, respectively. The adsorption capacity was calculated using the following equation:

$$\left[q_e = \frac{V_L (C_o - C_e)}{W_o} \right] \qquad (2)$$

Where q_e : Quantity of adsorbate per mass of adsorbent, mg/g

V_L: Working volume of solution, L

W_0: Mass of medium, g

3.1 Effect of pH

Reactive dyes are known to be greatly ionized in aqueous solutions to form colored anions due to the sulfonate groups present in their structure.[28] **Fig 7** shows the removal percentage of reactive green dye with different pH ranging from 2 to 8. As it clear ,the removal percentage increased with the decreased of pH values in dye solution, because At higher pH values, the negative charge ions will increases leading to a competition with the negatively charged anionic active sites where the removal percent decreases. As pH value decreased, the number of positively charged sites on adsorbent were increased such phenomena will increase the interaction with the reactive dye which leads to increasing removal percent.[29] pH value equal to 4 is then used in further experiment.

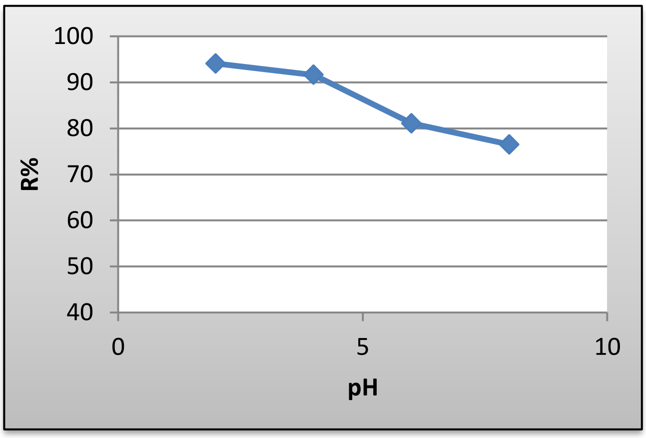

Fig 7 Effect of pH on reactive green removal, C_0=50 mg/L, m=3g.

3.2 Effect of temperature

Fig 8 shows the removal efficiency of dye with temperature reaches highest level (91.64 %) at 25°C and lowest level (62.86 %) at 55°C. The decrease of sorption effectiveness caused by temperature increasing indicated the exothermic nature of the sorption process.[30]

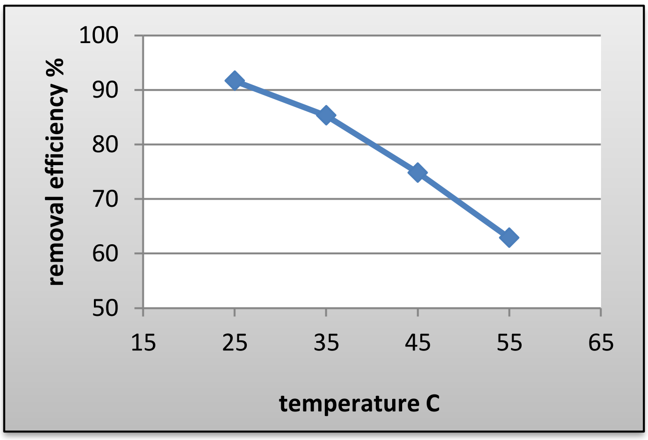

Fig 8 Effect of temperature on reactive green dye, C_0=50 mg/L, m=3g, pH =4.

3.3 Effect of contact time:

Fig 9 illustrates the effect of contact time on the adsorption of reactive green dye by GSC. It shows that the dye was adsorbed rapidly at the beginning (30 and 60 minutes) then the value was constant.[31] The equilibrium time was 120 min and there there was no significant changes in removal after this time because of saturation of absorption sites occured on absorbent.

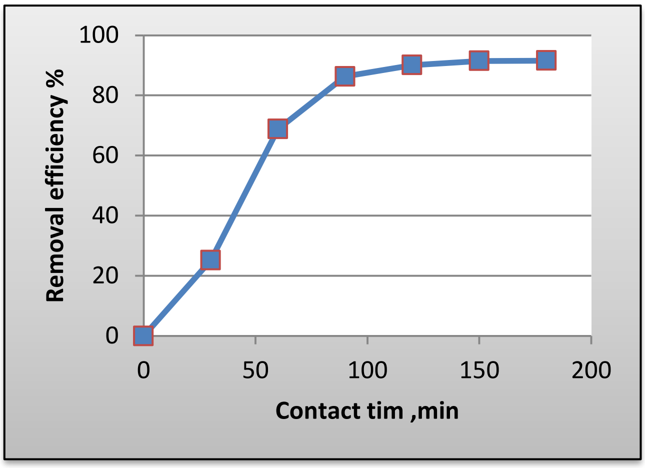

Fig 9 Contact time effect, C_0=50 mg/L , m=3gm, pH =4, T=25^{o}C.

3.4 Effect of dose

Fig 10 shows the removal efficiency increases from 23.8% to 99.44% with an increase of adsorbent dose from 0.5 to 4g, due to increased number of sorption sites available for sorbent solute interaction. Approximately 4 grams of the material removes the dye completely from 50 ml of 50 mg/L dye concentration with 150 min contact time.

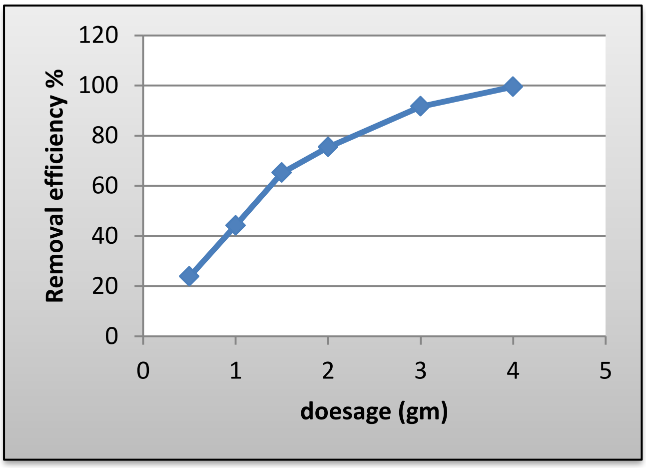

Fig 10 Contact time effect, C_0=50 mg/L , m=3gm, pH =4, T=25^{o}C contact time=150min.

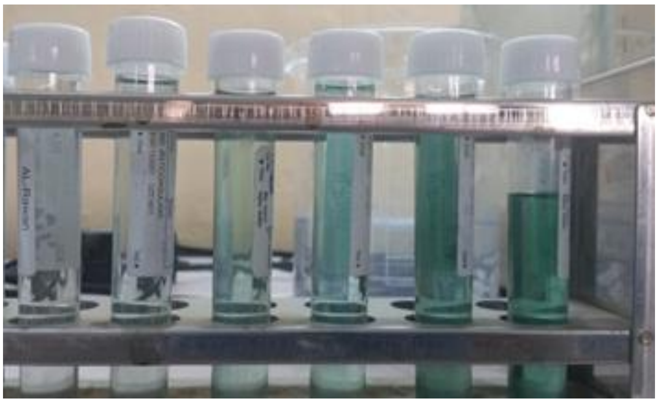

Fig 11 Effect of dose on dye removal

4. ADSORPTION ISOTHEOREAM FOR REACTIVE GREEN DYE

Fig 12 shows relation between effluent concentration (C_e) and the adsorption capacity (q_e). Curve was convex upward which is irreversible and considered favorable. Langmuir and frendlich model was studied for the adsorption of reactive green dye. Langmuir model shown in figure **Fig 13**, (C_e vs C_e/q_e). The maximum adsorption capacity for reactive green dye using GSC was 28.98 mg/g of carbon content. **Fig 14** shows relation between log C_e and log q_e for frendlich model. The measured adsorption capacity (K_F) and adsorption intensity (1/n) for reactive dye was 16.7 mg/g and 0.1338, respectively.

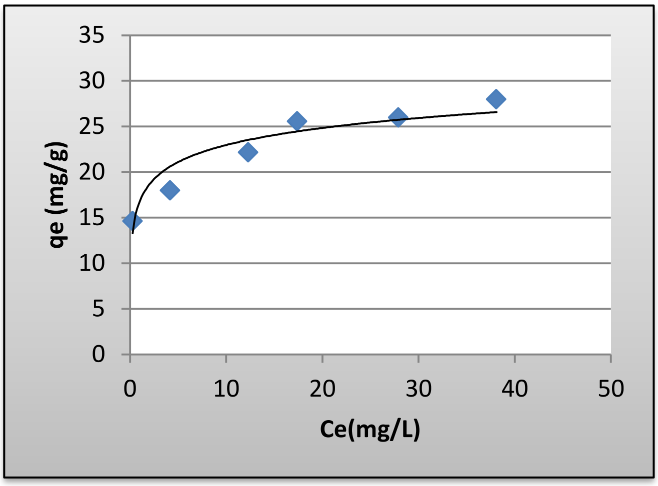

Fig 12 Relation between C_e and q_e curve for the adsorption of reactive dye

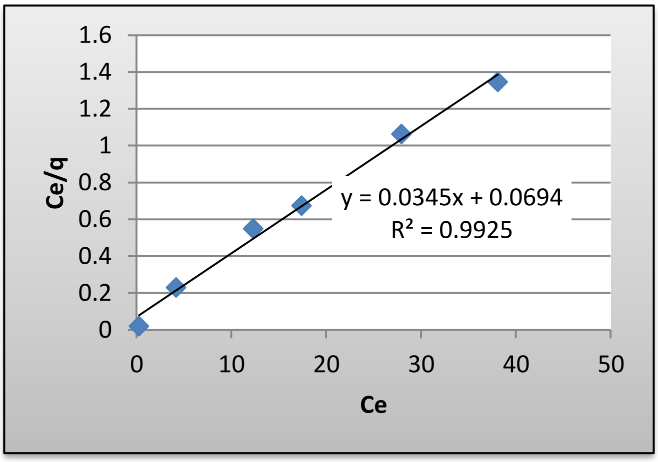

Fig 13 Langmuir model for reactive green adsorption

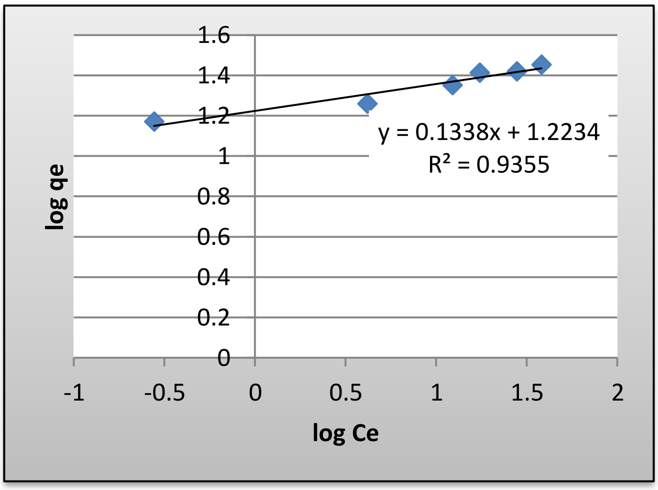

Fig 14 Freundlich plot for reactive green adsorption

5. DISCUSSION & CONCLUSION

Using common sugar, graphenic material has been bio synthesized and attached successfully on sand particles. This study explained low cost filter that was an effective adsorbent for the removal of reactive green dye in batch experiments. Parameters were discussed in details including variation of Ph, Temperature, Contact time and dose. GSC shows the higher removal percent at low pH values and temperature. Langmuir and freundlich models were studied on the removal of dye by GSC. The results showed that the maximum adsorption capacity of reactive green dye was 28.98 mg/g. Materials like GSC are expected to contribute in developing affordable solutions in removal of different pollutants from water.

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