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Copolymer Clay Nanocomposite: Synthesis, Characterization and Removal of Congo red dye

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Abstract - *Oxidative polymerization technique was used to synthesize a novel polymeric nanocomposite GTF for the removal of congo red dye from an aqueous medium. The nanocomposite GTF was prepared by precipitation technique in various compositions. The oxidative polymerization technique offers effortless incorporation of clay into the copolymer GTF. The morphological characteristic features, functional groups were studied using FT-IR, SEM, UV-spectroscopic methods. Further studies have been carried out to analyze the efficiency of the synthesized nanocomposite for the removal of dye under visible light irradiation in different parameters viz dose, concentration, time, pH. This study has been repeated for the unmodified copolymer GTF. The results revealed that, GTF with clay exhibited a greater dye removal rate than the unmodified GTF due to the presence of clay which enhances the porosity the polymeric nanocomposite. Studies have been done to determine the optimum time and optimum concentration for the removal of dye.*

Key Words: **GTF, Congo red, Clay, Nanocomposite, Porosity etc**

1. INTRODUCTION

Polymer molecules are also named as monomers, and combine reaction are termed polymerizations. There may be hundreds, thousands, tens of thousands, or more monomer molecules linked together in a polymer molecule. Polymers, sometimes called macromolecules. For example, plastics are synthetic polymers, and they are all around you. Industry makes plastics into such things as fibers, structural materials, and protective films. Except for fuels, more plastics are manufactured in the world than any other organic material. One-third of all industrial chemists work in the polymer industry. Another way that polymers affect your life is in the natural chemistry of the life processes. Proteins and enzymes are polyamide polymers. Proteins are an important part of the structure of all animals, and enzymes catalyze the chemical processes that make those bodies function. For plants the structural material is cellulose and the storage energy medium is starches. Both RNA and DNA are polymers of individual nucleic acids. These two classes of molecules control the genetic make-up of our body. Generally, the size and stereochemistry of the polymer molecule determine the properties of that molecule. The main part of an adsorption method is to control the water pollution in less investment cost. This technique is based on the removal of Congo red dye from wastewater. Congo red one of the toxic chemicals and it is soluble in water. So it's our prime duty for our researchers to remove the toxic substances by adsorption method.

2. MATERIALS AND METHODOLOGY

The chapter discusses a detailed account on the experimental procedure adopted for the synthesis of a Polymeric Nanocomposite (PNC) involving Gallic acid /Thiosemicarbazide/formaldehyde (GTF) doped with clay. All of the strains used for the test of anti-microbial were stored in 80°C in a freezer. The synthesized PNC were characterized by physico-chemical analysis, FTIR, UV-Visible spectroscopic analysis and scanning electron microscopy in order to confirm the structure of the PNC and morphology of the developed nanocomposite. The polymeric nanocomposites were further studied for the Congo red dye removal in various conditions like change in concentrations of the dye, adsorbent dosage, and pH as a function of time. Congo red is dissolved in distilled water to form different concentration. Solvents (acetone, methanol, ethanol) were purified by standard procedure before use.

2.1 Materials

Double distilled water and Acetone were used throughout the experiments. The monomers and chemicals used for the synthesis are listed in below table.

Table -1: Monomers and chemicals used for synthesis

Chemicals	Molecular weight (g/mol)	Manufacture source	Chemical formula	Purity
Gallic acid	170.12	MERCK	$C_7H_6O_5$	99.0
Thio-semicarbazide	91.132	MERCK	CH_5N_3S	99.0
Hydrochloric acid	36.46	MERCK	Hcl	37
Formaldehyde	30.026	MERCK	CH_2O	37
Sodium hydroxide	39.997	MERCK	NaOH	99

2.2 Synthesis of polymeric nanocomposite

Polymeric Nanocomposite was synthesized by oxidative polymerization involving monomer (2g) of Gallic acid was dissolved in (20ml) Dimethyl formamide, (2g) of Thiosemicarbazide was dissolved in (20ml) Dimethyl formamide and (8ml) of Formaldehyde (37%) were mixed together in a round bottom flask. The reaction was conducted at 80°C for about 4 hours maintained by an water bath where polycondensation takes place. A condenser was fixed over the round bottom flask. The reaction was stopped when a suspension of the polymer was formed. Clay is added to increase the size of the pores. The polymer was beaten in crushed ice cubes and allowed to settle for 24 hours. Finally, the precipitate was filtered off and washed with water several times and acetone followed by filtration to remove unreacted monomers and impurities. The polymer obtained was filtered in a Buchner funnel and dried in hot air oven at 50°C. The dried polymer was crushed in a mortar to obtain powder form.

2.3 Adsorption studies

The adsorption of Congo red onto GTF was carried out by batch method. The adsorption experiments were carried out in 250 ml conical flasks. 0.1 g of GTF was added to 50 ml of congo red solution of known concentration. At constant temperature the solution was stirred continuously for a certain time to achieve equilibration time. The value should be taken for 2 hours with 10 minutes time Interval. The adsorption was determined using UV-visible spectrophotometer at 497nm. Various parameters such as Ph, initial concentration and adsorbent dosage were change in order to optimize the adsorption process. The percent adsorption is

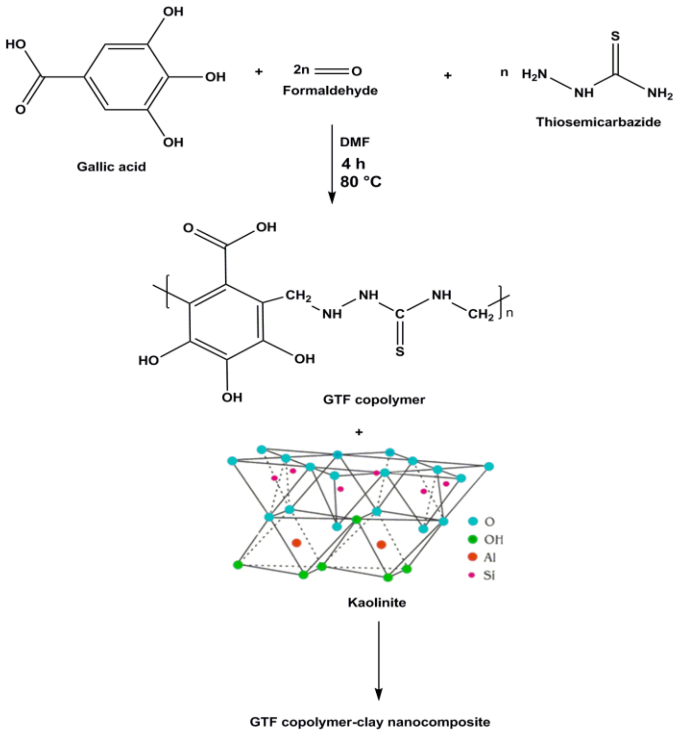
$$Percentage\ adsorption = \frac{(C_O - C)}{C_O} \times 100$$

Where C_0 are the initial concentration of Congo red in solution respectively. C is Congo red concentration at the end of adsorption. Concentration of Congo red solution (50, 60, 70, 80 ppm).

3. RESULTS AND DISCUSSION

3.1 characterization of GTF

A novel bio-based polymeric resin (GTF) was synthesized by Gallic acid and thiosemicarbazide and formaldehyde doping with clay as shown in scheme 1.



SCHEME -1: Synthesis of GTF copolymer – clay nanocomposite.

The synthesized polymeric resin was insoluble in water. The elemental analysis results for the synthesized resin indicated that the molar ratio of Gallic acid to formaldehyde was 1:2. The FTIR spectrum of the synthesized GTF copolymer is depicted in the Figure and the spectral data are presented in Table.

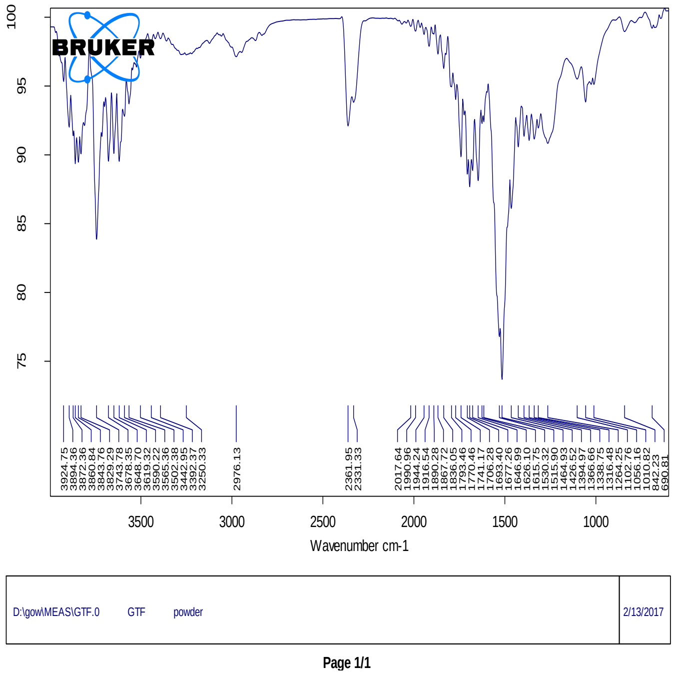


Fig -1. FTIR spectrum of GTF Copolymer

The basic characteristic peaks of GTF were appeared at 3843.76 cm^{-1} is assigned to -NH stretching vibrations for (Azarudeen, et al., 2011). The band appeared at 2976.13 cm^{-1} are assigned to $-CH_2$ stretching vibration for the above mentioned GTF copolymer (Azarudeen, et al., 2012 and Ahamed, et al., 2013) respectively. A characteristic band at 1102.76 cm^{-1} is assigned to C-N stretching vibrations (Mukhopadhyay, et al., 2013). The band appeared at 1530.32 cm^{-1} are assigned to >C-C (aromatic) vibrations. The characteristic peaks appeared at 1693.4 and 1741.17 cm^{-1} are assigned to >C=O & >C=S vibrations respectively. The FTIR spectra of the synthesized polymeric nanocomposites are depicted in the Figure and the spectral data are presented in Table. The basic characteristic peaks of polymeric nanocomposites were appeared at 3829.33 cm^{-1} is assigned to -NH stretching vibrations for (Azarudeen, et al., 2011). The band appeared at 2975.55 cm^{-1} are assigned to $-CH_2$ stretching vibration for the above mentioned PNCs (Azarudeen, et al., 2012 and Ahamed, et al., 2013) respectively. A characteristic band at 1033.01 cm^{-1} is assigned to C-N stretching vibrations (Mukhopadhyay, et al., 2013). The band appeared at 1530.32 cm^{-1} are assigned to >C-C (aromatic) vibrations. The characteristic peaks appeared at 1677.5 and 1741.9 cm^{-1} are assigned to >C=O & >C=S vibrations respectively.

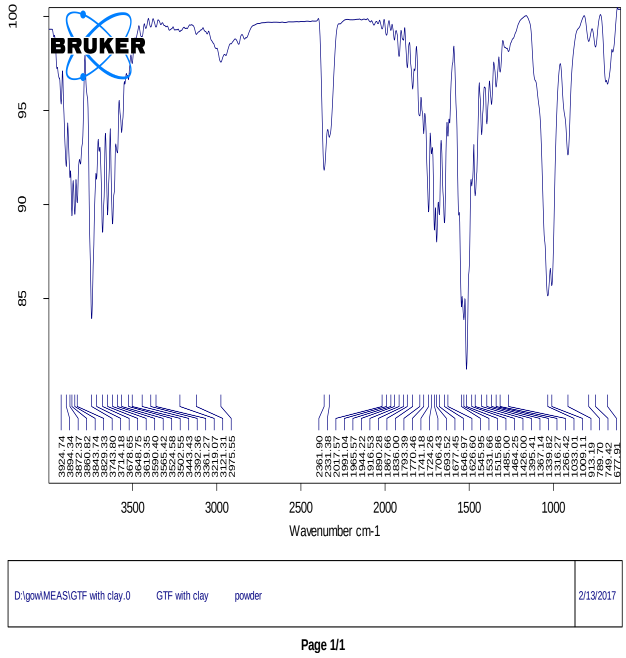


Fig -2. FTIR spectrum of GTF Copolymer – Clay Nanocomposite

On comparison between the data obtained between the GTF copolymer and GTF-clay, the observations clearly evidences the copolymer has interacted well with the clay to form polymeric nanocomposites. It is observed due to the changes in the IR frequencies.

3.2 Removal study of Congo red from aqueous medium by batch method

3.2.1 Effect of Concentration of dye

The effect of dye concentration was evaluated by varying the concentration of the dye solution from 50-80 ppm. Various adsorbent dosages were taken to check the dye removal rate for an estimated time of 2 h. The results obtained for 0.1g of adsorbent dosage are shown in FIGURE. On increasing the concentration of the dye solution, the rate of removal of dye decreases for a particular adsorbent dosage because as the concentration increases, the number of dye molecules increases stating that the surface of the polymeric nanocomposites can accommodate only for a particular amount of dye molecules (M. Sangareswari, M. Meenakshi Sundaram, 2015).

Table -2: Dye removal data for (0.1g) concentration

S.No.	TIME (Min)	REMOVAL OF DYE (%)			
		50 ppm	60 ppm	70 ppm	80 ppm
1	10	4.60	4.69	0.13	9.5
2	20	12.85	6.39	1.95	14.08
3	30	17.49	11.0	1.98	23.78
4	60	21.04	16.35	5.91	-
5	90	22.35	17.7	9.52	-

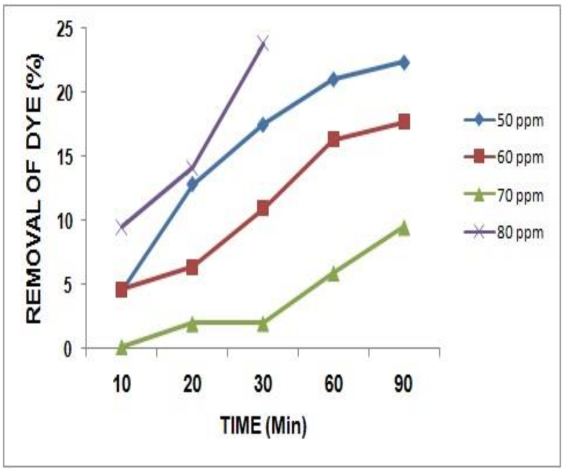


Chart -1: Dye removal data for (0.1g) concentration

3.2.2 Effect of pH of dye

The above studies were done to determine the optimum concentration and adsorbent dosage. From the above studies, the optimum conditions were taken as 50 ppm dye solution and 0.1 g of adsorbent dosage. The effect of pH on the removal of dye for the optimum conditions is evaluated by varying the pH value (2, 4, 6 and 8) of the dye solution. The obtained results are shown in Figure. From the results, it is clear that the removal rate of the dye is very high for the pH values 2, 4, 6 and 8 because, at the acidic nature of the dye solution, the number of H^+ ions present is high. Thus under acidic conditions, the surface of the PNC is highly protonated that takes up the anionic dye molecules at a faster rate which decolorizes the dye solution. But for alkaline conditions at the pH value of 8, the surface of the PNC is highly deprotonated because of the presence of OH- ions. The dye solution being anionic in nature, the molecules of the dye and the surface of the PNC gets repelled. This resulted in very low removal rate (Umar Ibrahim Gayaa Abdul Halim Abdullaha, 2007).

Table -3: Dye removal data for pH

S.No.	TIME (Min)	REMOVAL OF DYE (%)			
		pH 2	pH 4	pH 6	pH 8
1	10	2.1	3.4	5.78	2.8
2	20	4.1	19.4	10.34	5.46
3	30	7.3	20.8	11.20	7.01
4	60	27.7	24.4	13.03	-
5	90	44.6	35.52	15.54	-
6	120	61.9	45.49	23.87	-

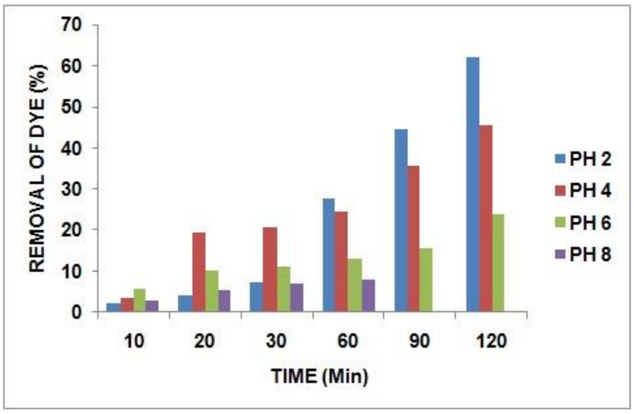


Chart -2: Dye removal data for pH

3.2.3 Effect of adsorbent dosage of dye

The effect of adsorbent dosage on the removal of dye is evaluated by conducting studies like variation of the dosage from 0.1 to 0.75g of PNC. This variation was done for all the concentrations of the dye (50-80 ppm). The obtained results for adsorbent dosage of 0.1, 0.5 and 0.75 g for all the concentrations of dye solution are shown in Figure. On increasing the dosage from 0.1 to 0.5 and 0.75 g, the dye removal rate increases. This is because the surface area increases due to increase in PNC particles. This provides more pores which take up the dye molecules thus decolorizing the dye solution (T. Robinson, B. Chandran, P. Nigam, 2001).

Table -4: Dye removal data for (0.5g) adsorbent dosage

S.No.	TIME (Min)	REMOVAL OF DYE (%)			
		50 ppm	60 ppm	70 ppm	80 ppm
1	10	44.3	43.55	26.77	26.77
2	20	45.7	42.38	29.77	27.45
3	30	48.61	43.29	33.81	28.60
4	60	51.01	49.21	34.59	29.40
5	90	53.14	50.52	40.41	34.08

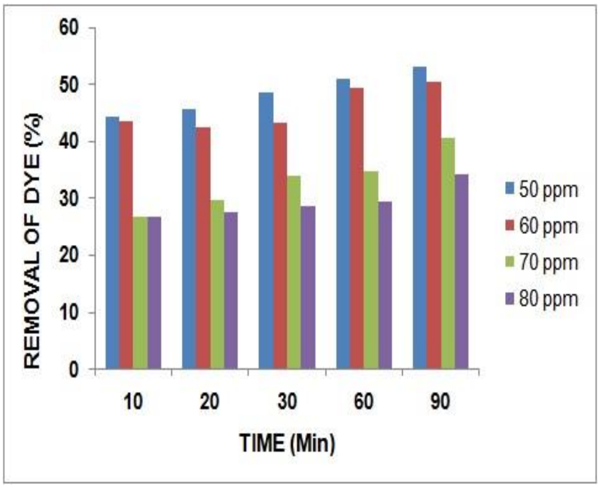


Chart -3: Dye removal data for (0.5g) adsorbent dosage

Table -5: Dye removal data for (0.75g) adsorbent dosage

S.No.	TIME (Min)	REMOVAL OF DYE (%)			
		50 ppm	60 ppm	70 ppm	80 ppm
1	10	51.37	45.49	37.94	28.12
2	20	52.71	50.94	40.10	32.43
3	30	59.24	52.03	46.93	36.18
4	60	62.93	59.95	50.22	40.56
5	90	72.30	60.64	52.73	43.85

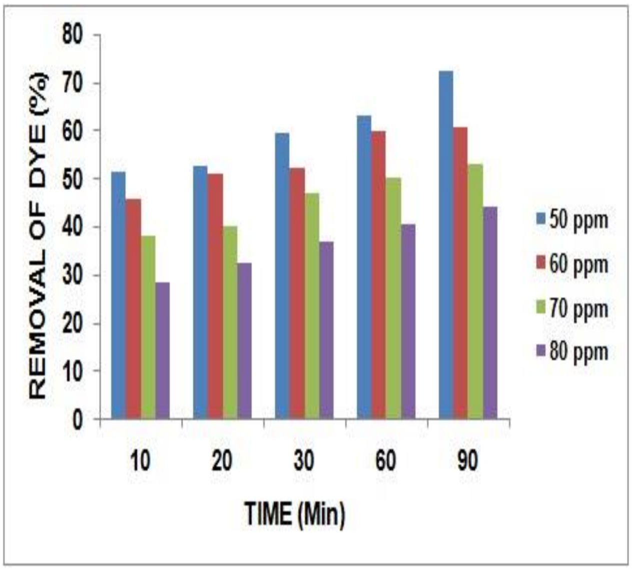
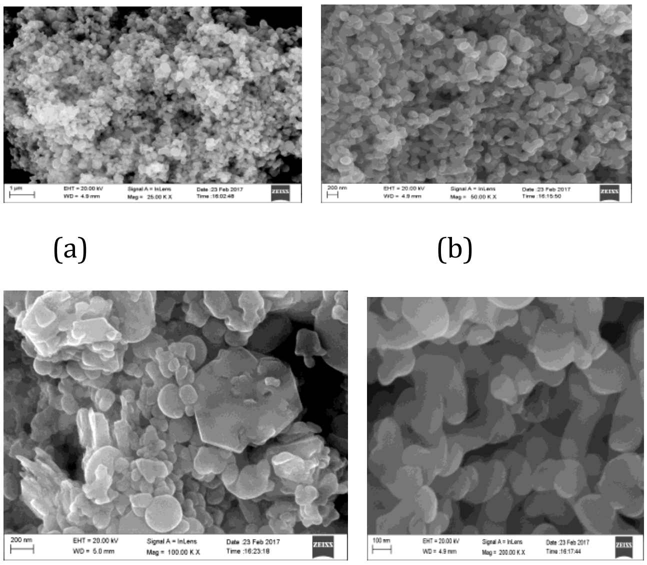


Chart -4: Dye removal data for (0.75g) adsorbent dosage

3.3 MORPHOLOGICAL STUDIES

The structural morphology of the PNC was examined from SEM micrographs by taking images at various magnifications. The structure of the PNC is tubular and has a non-uniform surface. The SEM micrographs confirm the prepared PNC are nano in size.



(a) (b) (c) (d)

Fig -3: SEM images of (a and b) is GTF and (c and d) is GTF-Clay

The structure of the PNC is tubular and has a non-uniform surface. The SEM micrographs confirm the prepared PNC are nano in size. On x50 K magnification, images (A) and (B) reveal that average size of the particles is 200 nm, which comes in the nano range. On magnifications from x100 K images (C) reveal that size of the particles is 100 nm. At x200 K magnification, image (D) shows that pores are present even at the interior surface of the PNC which increases the adsorption capacity and hence increasing the removal rate of the dye. Thus the results from SEM micrographs, confirms that adsorption capacity of the PNC is very high due to high porosity and reveals that it is nano in size proving that the surface area of the PNC is very large that enhances the dye removal rate even at room temperatures.

4. CONCLUSION

A new bio based polymeric resin GTF was synthesized and used for the removal of congo red dye. Polymer composite has been successfully synthesized via condensation polymerization technique with the GTF copolymer and Kaolin clay. The synthesized polymeric composite has been confirmed through FTIR and SEM analyses. The observed frequencies in FTIR clearly illustrate the polymer formation. From the SEM images, it could be confirmed that the high porous nature of clay composite is responsible for better removal of Congo red than the polymeric sample. On increasing the concentration of the Congo red dye, decreases the removal of dye by the adsorbent. On decreasing the pH (to the acidic level), increases the removal of dye. This is because the Congo red dye is also acidic in nature. On increasing the adsorbent dosage, increases of the removal of dye is observed. In view of all outcomes, it may be concluded that GTF could be a potential candidate for the removal of Congo red dye.

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