Synthesis and Application of Polyacrylamide/Cellulose Gel/Fuller's Earth Composite for Removal of Methylene Blue from Water

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ABSTRACT: *In this study, eco-friendly composite material polyacrylamide/cellulose hydrogel reinforced with fuller's earth (PAAm/CG/FE), has been synthesized and used for the effective adsorption of the Methylene Blue (MB) dye. The synthesis of PAA/CG/FE composite followed the free radical polymerization method. Chemical compositions and morphology of the synthesized composite have been characterized by Fourier Transform InfraRed (FT-IR) Spectroscopy and Scanning Electron Microscope (SEM). Thermal stability has been determined by TGA analysis. Batch adsorption experiments have been carried out by varying different parameters viz. contact time, pH of the solution, and temperature in order to determine the maximum dye adsorption capacity of the composite. Introducing cellulose and fuller's earth into the polyacrylamide eventually enhanced the structural stability, thermal stability, and MB adsorption capacity. Based on the experimental data, adsorption kinetics has been found to be well correlated with the pseudo-second-order kinetic model. It has been found that the equilibrium adsorption isotherm data perfectly followed the Langmuir isotherm model and maximum adsorption capacities were found to be 48.30 and 56.17 mg/g for PAAm and PAAm/CG/FE composite, respectively. Furthermore, the prepared composite exhibits good reusability, and it is an economic, eco-friendly, and nontoxic material.*

KEYWORDS: *Waste cotton fiber; Polyacrylamide; Fuller's earth; Methylene blue; Adsorption; Wastewater treatment; Polymer composite.*

INTRODUCTION

Water pollution is a serious environmental problem existing on the earth for both aquatic and nonaquatic life.

There has been tremendous focus on the development of newer materials to tackle the latest challenges arising

in the field of waste-water treatment. Advancement in technology has confirmed the presence of various organic and inorganic impurities in wastewater, present in trace amounts can affect all living organisms which ultimately leads to the destruction of the ecosystem. Moreover, different types of heavy metals (inorganic), chemicals, and dyes (organic) are continually discharged into water bodies which cause toxicity and adverse effects on living organisms, as these are very harmful because of their non-biodegradability, bio-accumulative behavior, and high toxicity [1, 2]. Synthetic dyes have been widely used in different industries like leather, plastic, dying, cosmetics, textile, petroleum, paper, and foodstuff industry. According to the Food Safety and Standards Act (FSSA) in Indian law, Methylene blue is not a food-safe dye and should not be present in any food items [3]. The presence of Methylene Blue (MB) dye in water also reduces sunlight transmittance and dissolved oxygen content and eventually upsets the biological activity. Therefore, owing to these noxious properties of MB dye, it causes water pollution and could pose a threat to the ecosystem when released in water sources. Methylene Blue (MB) is used in large amounts as a basic dye in various industries. This can cause a number of harmful effects on living beings, such as eye injury, burning sensation, nausea, profuse sweating, vomiting, methemoglobinemia, mental confusion, etc. It is highly toxic and has carcinogenic properties. Due to its complex aromatic structure, it is stable and difficult to biodegrade and photodegrade under natural conditions. Its chemical formula is $C_{16}H_{18}N_3SCl$ and molecular weight is 319.85 [4, 5]. In recent time, apart from using conventional adsorbent materials for MB removal, a number of scientific studies have been carried out towards the development of low-cost composites for MB dye adsorption [6-7]. *M. Saghanejhad et al.* synthesized a metal-organic framework (MOF) MIL-68(Al) for ultrasonic-assisted adsorption of MB and rhodamine B. The MOF are used as porous coordination polymers and are soft analogues of zeolites [8]. *F. Marahel et al.* worked on ultrasonic-assisted MB adsorption and a neural network model for MB dye adsorption by Mn-doped PbS nanoparticles. It is a low-cost and promising adsorbent for proper adsorption of MB dye in a short time [9]. *L. Wang et al.* synthesized chitosan-*g*-poly (acrylic acid)/attapulgite composite for fast removal of MB dye from its aqueous solution [10]. *C. Zhou et al.* worked towards the synthesis of partially hydrolyzed polyacrylamide/cellulose nanocrystal nanocomposite hydrogels for the adsorption of MB dye [11]. *Y. Bulut et al.* synthesized a crosslinked Chitosan/Bentonite composite for fast adsorption of MB dye from wastewater [12]. For the synthesis of all these composite materials, researchers have taken low-cost, biodegradable, and non-toxic materials. All composites effectively removed MB dye from its aqueous solution in a single use. Many low-cost adsorbents have been studied for the effective adsorption of dyes for wastewater treatment.

A number of methods have been used for the removal of MB from water *viz.* electro-coagulation, ozonation or oxidation, biological treatment, coagulation and flocculation, membrane separation, and adsorption. Out of these methods, adsorption is a low-cost, effective, simple, and easy-to-operate method for wastewater treatment [13]. The use of several adsorbents for the removal of MB dye has been reported in the literature, such as activated carbon [14] carbon nanotube [15] nanoparticle and polymer-based adsorbents [16] chitosan composite [17] natural clay[18] mesoporous silica [19] graphene oxide and modified graphene oxide [20] magnetic adsorbents [21], metal-organic framework[22-24], agricultural waste [25], animal waste [26] etc. Clay and cellulose are natural materials that have been used as adsorbents. They can be used in modified or unmodified form.

In the past few years, natural clay composites have drawn significant attention, owing to the biodegradability, nontoxicity, low cost, and reusability of materials [27, 28]. Fuller's Earth (FE) is a sedimentary, stiff clay and has high magnesium oxide content including aluminum, silicon, and a trace amount of other minerals. It consists of different kinds of sepiolite like natural zeolites, dioctahedral smectites, and loughlinite having a fibrous nature with fine channels. It is widely used as an adsorbent in refining oils, bleaching, petroleum cleaning, and decolorization due to having an efficient absorptivity nature. It is found naturally in the Mihaliccik region of Turkey. The minerals present in it have an excellent capacity to adsorb heteroaromatic cationic dyes. FE has a large micro pore volume, and large cages which is helpful in the adsorption-desorption process [29, 30]. Cellulose, a biopolymer containing hydroxy groups is helpful in wastewater treatment. It is an abundant natural material and can be used as an easily available and low-cost material for the water treatment process. It has been used by many

researchers to make different types of composites for water treatment [31]. *Liu et al.* studied cotton cellulose for adsorption of boron from a desalination plant [32]. *B. Wanassi et al.* investigated an eco-friendly composite of phenolic resin and waste cotton fiber as green precursors for the synthesis for removal of the Alizarin Red S dye from textile effluents [33]. A chitosan-cotton composite has been prepared by an easy and economical "Pad-dry process" for the adsorption of acid dyes from an aqueous solution by *M. Jabli et al.* [34]. In comparison with raw cotton, cotton-based materials have shown better results for the removal of adsorbate. It can easily form composite materials. *Niu et al.* studied on the preparation of cotton-based fibrous adsorbents for the adsorption of harmful metal ions. It is a very promising material as it can be easily recycled after completing adsorption from wastewater [35]. A. Yang prepared and studied the low-cost novel MOF@cotton fiber composite for the effective removal of uranium. The recycling experiment on composite showed that it can be used more than five times with less than 10% efficiency loss [36]. It is a biopolymer having a large surface area and its polymerization capacity depends upon materials and synthesis procedures. Cellulose gel has been prepared from waste cotton fiber collected from cotton textile mills. A large amount of waste cotton fiber is generated by the cotton textile industry due to rapid development and high capacity of production. Recycling of waste cotton fiber to prepare composite reduces the problem of textile waste disposal and the economic issue of waste-water treatment [37-39].

Polymer hydrogels can retain various types of dissolved solute molecules and water due to its three-dimensional crosslinked, porous polymeric network of flexible chains. The ionic functional groups are responsible for the adsorption of cationic dyes. Hence, the composite of clay/cellulose gel with PAAm has potential applicability for the effective adsorption of various water pollutants like heavy metal ions, dyes, etc [40, 41].

In the present study, a novel adsorbent material *viz.* PAAm/CG/FE composite has been synthesized from low-cost and eco-friendly materials like polyacrylamide, cellulose gel and Fuller's earth. This composite has been used for the removal of MB dye from water. The experimental findings confirm that the PAAm/CG/FE composite is a biodegradable and recyclable material. The composite has been successfully used for the removal

of MB dye from an aqueous solution. The effect of contact time, pH of MB solution, MB concentration and temperature on the adsorption capacity of composite have been investigated. The controlling mechanism of adsorption has been examined by the kinetic studies and isotherm studies.

EXPERIMENTAL SECTION
Materials

Acrylamide (AAm) (purity 99%), Potassium persulfate (KPS) (98%), Copper acetate (99%), paraformaldehyde, HCl, and Methylene Blue (MB) were purchased from SRL Pt. Ltd. (India) and are used as such. Waste cotton fiber was collected from the local textile factory for the preparation of cellulose gel. Fuller's Earth (FE) was purchased through Amazon.com and milled and passed through a 320 mesh screen, dried at 80 °C for 4 h before use. The molecular structure of MB is shown in Fig. 1. All solutions for the study were prepared in distilled water. The stock solution of MB (500 mg/L) was prepared by dissolving 250 mg of MB in 500 mL deionized (DI) water. The pH of MB solution was adjusted with dil. HCl or NaOH according to the requirement.

Synthesis of cotton cellulose gel

Waste cotton fiber was washed with mild non-ionic surfactant followed by washing with distilled water. Now it was dried in an oven at 70 °C for 8 h. The preparation of Cellulose Gel (CG) was done by alkali oxidation, and mechanical amine gelation by a reported method [42]. Cotton (6 g) was dispersed in a solution of 2.1 M NaOH and 2.5 M urea at -10 °C in a beaker to destroy the polymeric structure of cellulose (Fig. 2). The whole material has been stirred on a magnetic stirrer at 200 rpm. The urea $(CO(NH_2)_2)$ gelled the open-ended chains of cellulose.

Synthesis of N,N'-Methylenebisacrylamide

The crosslinker used for making a hydrogel network is N,N'-Methylenebisacrylamide. It has been synthesized by the general procedure described in the literature. [43] Acrylamide (2 g), paraformaldehyde (0.35 g), and copper acetate (0.01g) were added in a three-neck round bottom flask. Subsequently, conc. HCl (0.4 mL) was added to the mixture and the reaction mixture was refluxed in a water bath at 90 °C for 100 mins. The synthesized N,N'- Methylenebisacrylamide crosslinker was obtained as a yellow solid precipitate followed by crystallization with hexane-methanol solution.
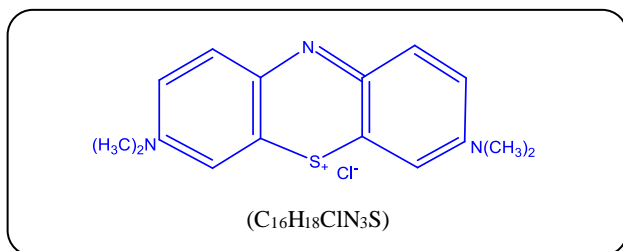
Fig.1: Molecular structure of Methylene Blue.

Fig. 2: Preparation of cellulose gel from cotton fibre.

At last, crosslinker was dried at room temperature of 32 °C for 48 hrs (Yield = 1.24 g, 62%).
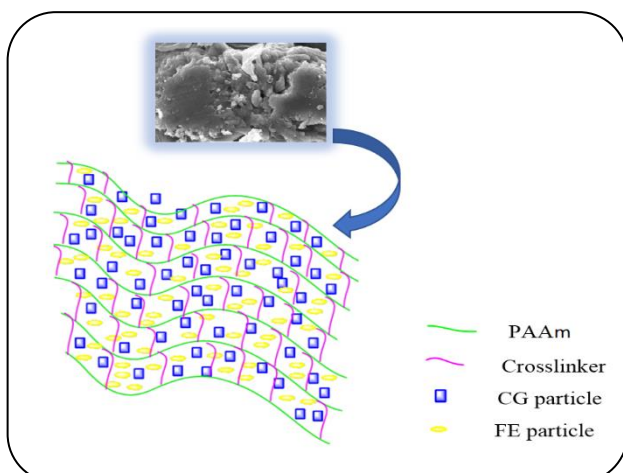

Fig. 3: Schematic representation of the structure of PAAm/CG/FE composite.

Synthesis of PAAm/CG/FE composite

The polyacrylamide/cellulose gel/fuller's earth (PAAm/CG/FE) composite has been synthesized by the free radical polymerization method [45]. Fig. 3 shows the schematic representation of the structure of PAAm/CG/FE matrix. The procedure of synthesis was as

follow, 0.4 g FE and 0.6 g CG was mixed in 40 mL water in a two-neck round bottom flask with stirring for approx. 20 mins. After that acrylamide monomer (2 g) , potassium persulphate (0.042 g), and N,N'- Methylenebisacrylamide crosslinker (0.050 g) were added to the flask with stirring. The reaction was carried out under a nitrogen atmosphere at 80 °C for 140 minutes. The synthesized, gel-like composite material was washed with distilled water and then dried at 70 °C in an oven for 72 h. The yield of the composite was about 99 %. The synthesized composite has been cut into small pieces of 2 mm size.

Characterization of PAAm/CG/FE composite

The FT-IR spectra of the synthesized composite before and after MB adsorption were taken on Spectrum GX (Parkin Elmer, U.S.A.) model FT-IR apparatus in the range 4000-400 cm^{-1}. The samples for testing were prepared by using the KBr pressed pellet method. The surface morphological structure of the composite was obtained by Scanning Electron Microscopy (SEM), (ESEM EDAX XL-30, Philips, Netherlands). Samples for analysis were coated with a thin film of platinum with a sputter coater. The elemental analysis of the composite has been done by EDS. A digital pH meter (Orion 900S2 model) was used to prepare the solutions of different pH values. The surface charge of the prepared composite was studied by Zeta potentials (Malvern Instruments Ltd., Zetasizer ver. 7.11). The thermal stability of the composite was checked by TGA analysis. Table 1. Shows the chemical composition of fuller's earth clay characterized by XRF (AxiosMAX, Panalytical Netherlands).

Adsorption analysis of prepared composite

All batch experiments for adsorption studies were performed on a magnetic stirrer with a constant stirring speed of 50 rpm. The effect of contact time on the removal of MB dye was studied in 50 mL conical flask, 25 mL of MB solutions (100 mg/L, pH 7) with 0.05 g of PAAm/CG/FE composite adsorbent at 30℃ for 10-120 min contact time range. The effect of pH on MB dye adsorption was investigated by adjusting the pH of 100 mg/L of initial concentration MB solution over the different pH values ranges from range 2-12 and 0.05 g of composite at 30 °C for 80 min. The influence of temperature on dye adsorption was carried out for 80 min in the 25 mL of dye solution [46].

Table 1: Chemical composition of the fuller's earth sample (Determined by X-ray fluorescence technique).

Sr. No	Metal	Concentration (%)
1	Na_2O	0.9
2	MgO	3.855
3	Al_2O_3	9.383
4	SiO_2	56.562
6	SO_3	5.055
7	K_2O	0.717
8	CaO	0.247
9	TiO_2	0.974
10	V_2O_5	0.137
12	MnO	0.168
13	Fe_2O_3	19.041
14	Rb_2O	0.184
15	SrO	0.1
17	ZrO_2	0.212

(100 mg/L, pH 7) with temperature range 30-40 °C. The effect of concentration has been studied also with 25 mL MB dye solution (pH 7, 80 min) with concentration range 50-250 mg/L. All experiment were repeated three times to determine and average has been reported to ensure experimental accuracy.

The MB adsorption amount was determined quantitatively with the help of a Lambda 19 (Perkin Elmer, U.S.A.) model UV-Visible spectrophotometer, at 660 nm wavelength. The adsorption capacity (q_e) and percentage removal R (%) of MB by composite was calculated by given equation [45]:

$$q_e = \frac{C_0 - C_e}{w} \times V \tag{1}$$

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

Whre, C_0(mg/L) and l concentration and the equilibrium concentration of MB. V(l) shows the volume of the MB solution, and w(g) is the adsorbent weight.

Kinetic study of PAAM/CG/FE composite

The MB removal kinetics was determined with the help of standard kinetics models such as pseudo-first-order, pseudo-second-order, and intraparticle diffusion models

The pseudo-first-order model in linear form is shown by Eq. (3).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3}$$

Where, q_e and q_t are the amount of MB dye adsorbed mg/g on composite at equilibrium, and t is for instantaneous. time, respectively. The kinetic rate constant (k_1) of pseudo-first order reaction can be obtained from the slope of $\log(q_e-q_t)$ versus t plot. The linear form of the pseudo second order is represented as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

Where, k_2 represents the pseudo second order rate constant, and q_e values are obtained from the slope of the plot between t/q_t versus t. The linear form of intra particle diffusion is shown by given Eq. (5),

$$q_t = k_p t^{1/2} + C \tag{5}$$

Where k_p and C represent the rate constants and determined by the slope and intercept of the plot between q_t versus $t^{1/2}$.

Adsorption isotherm models

To study isothermal adsorption, the adsorption experiments were performed in concentration range 50-300 mg/L at pH 7. Experimental data were fitted with different adsorption isotherm models such as Langmuir and Freundlich isotherm models to obtained equilibrium adsorption values. The Langmuir adsorption model explains about homogeneous adsorption of MB dye by monolayer adsorption on the composite without interacting each other, it is defined by Eq. 6. [47-49].

$$q_e = q_{max} \frac{bC_e}{(1 + bC_e)} \tag{6}$$

Where, q_{max} denotes maximum MB adsorption per unit mass of adsorbent in mg/g. The straight-line curve plotted between Ce/qe versus Ce gives slope and intercept values which determines related constants values of Langmuir equation as shown in Eq. (7).

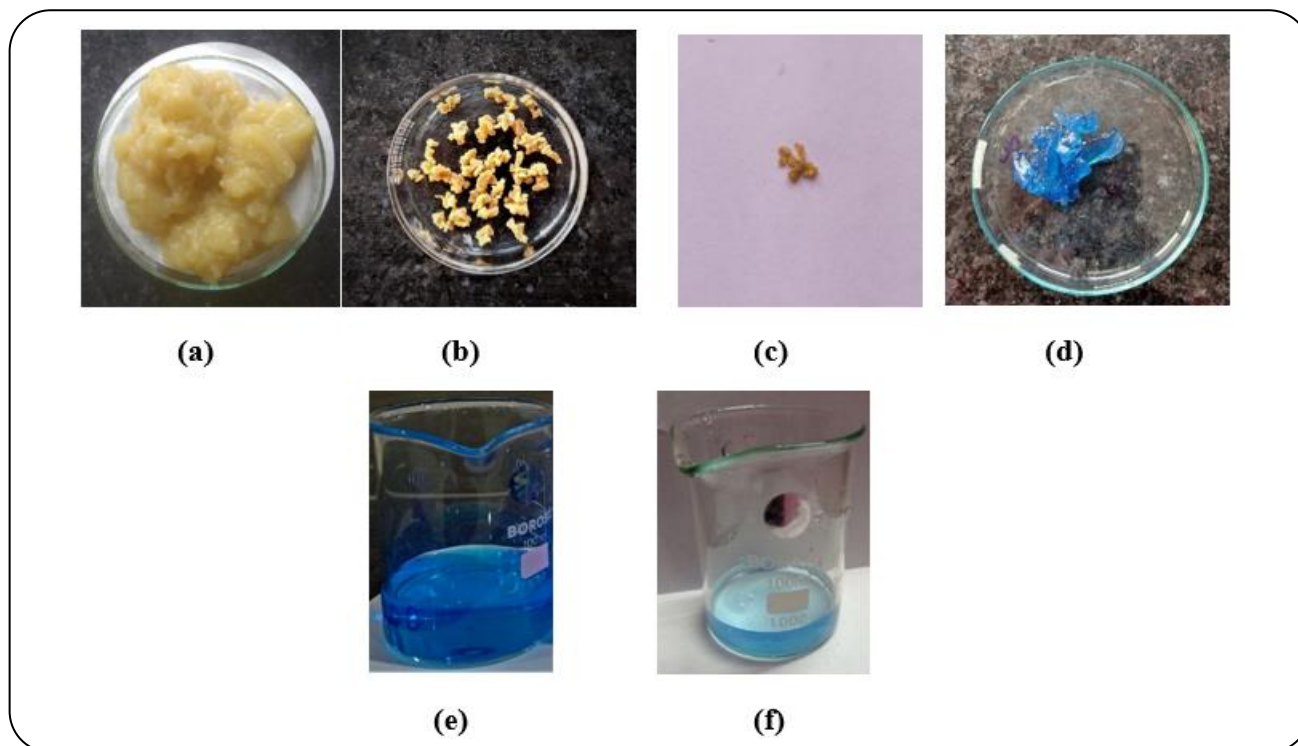$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{Kq_m} \tag{7}$$

Fig. 4: Picture of (a) freshly prepared composite (b) composite after drying (c) composite before adsorption
(d) after adsorption (e) MB solution before adsorption (f) MB solution after adsorption

Where, C_e = equilibrium concentration of adsorbate in the solution (mg/L), q_e = adsorbate amount adsorbed on the adsorbent at equilibrium (mg/g), q_m = monolayer adsorption capacity (mg/g), and K = Langmuir adsorption equilibrium constant (mg/L), which is related to the energy of adsorption.

The Freundlich isotherm model describes the non-ideal, reversible and multi-layered adsorption. This empirical model refers to the heterogeneous surface of the adsorbent. The linear form of Freundlich isotherm is represented by the following equation;

$$\log q_e = \frac{1}{n}\log c_e + \log K_f \tag{8}$$

Where q_e is the quantity of ion adsorbed at equilibrium (mg/g). C_e is the concentration of adsorbate at equilibrium (mg/L). K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent, respectively. The Freundlich isotherm constants are calculated from the plot of log q_e versus log C_e.

The average relative errors (ARE%) are calculated by using equation 9. This equation can determine about relative goodness of fitting of the data obtained from experiment with model equations.

$$ARE = \frac{100}{N}\sum_{1}^{N}\frac{|q_{cal} - q_{exp}|}{q_{exp}} \tag{9}$$

Where, N represents the number of experimental data points. qexp and qcal are experimental equilibrium value and model respectively having unit mg/g.

Reustability study of composite

Regeneration of the used PAAm and PAAm/CG/FE composite was performed by contacting a 0.05 g of MB-adsorbed PAAm and composite samples with 25 mL of 0.05 M of HCl solution separately for 80 min at room temperature. After 80 min desorbed samples were removed from the acid solution and centrifuged. Now samples were washed three times with distilled water and dried in oven at 75 °C for 8 h. This procedure was repeated four times. The adsorption capacity of adsorbant was analyzed at the optimized conditions.

RESULTS AND DISCUSSION
Physical appearance of the prepared adsorbent

Fig. 4 shows the digital images of prepared composites before and after the adsorption process. Prepared

composite exhibits better swelling properties (Fig. 4 d) after adsorption, the high adsorption affinity towards the crosslinked matrix of the composites. Fig. 4 (e) and 4 (f) exhibit the removal of MB from water.

FT-IR of PAAm/CG/FE composite

FTIR spectra of the composite before and after adsorption of MB dye shows different characteristic bands in the range of 4000-400 cm^{-1} before and after adsorption (Fig. 5). The stretching vibrational peak of the carbonyl group has been found at 1667 cm^{-1}. The broad band at 3439 cm^{-1} is due to the N-H vibration of the amide group. The bands at 1416, 1318, 1184 cm^{-1} are due to the presence of cellulose in the composite. The bending mode of Si-O-Si is indicated by 469 cm^{-1} band. All functional groups of materials in composite are involved in MB adsorption and this has been confirmed by broaden the spectrum of composite after MB adsorption [50-52].

SEM analysis of PAAm/CG/FE composite

The surface morphology of the PAAm/CG/FE composite before and after the MB adsorption has been studied by SEM images and indicated in Fig. 6(a). As shown in Fig. 6(a) uniform even surface reveals the successful formation of the composite. The Cellulose Part (CG) and Fuller's Earth (FE) particles in the composite are highlighted by a yellow rectangular box and a green circle, respectively. Fig. 6(b) at a little higher resolution shows the presence of craters in the surface of the composite, which can be useful in the adsorption of MB dye. In Fig. 6 (c) and (d), after adsorption of MB, some rough layered texture is observed, confirming the uniform adsorption of MB dye on the surface of the composite. The smooth surface morphology of the composite before adsorption was changed after adsorption of MB and no other major changes were observed in post-adsorbed samples, reflecting the excellent properties of adsorbent like easy and fast bonding of ions to the functional groups of composites. The elemental distribution in composite has been revealed by EDX analysis and shown in Fig. 6 (e). EDX confirmed the presence of inherent elements like C, O, Na, and Si belonging to fuller's earth, as shown in Table1. No other major impurity was found in the composite. The presence of Pt on the surface of the composite was observed due to the Platinum coating on the sample.
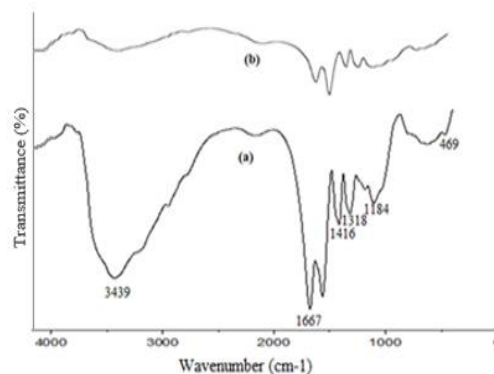

Fig. 5: FTIR spectrum of PAAm/CG/FE composite (a) before and (b) after adsorption.

Thermal analysis

TGA thermogram (Fig. 7) reflects the degradation of composite material over temperature ranges from 25-600 ºC. PAAm/CG/FE thermogram, shows weight loss occurring in three stages. First stage corresponds to the loss of water (20 %) present in the form of hydrogen bonded water with the porous surface of the composite in the temperature range 60-130°C. The second stage from 130 -180 °C shows ~ 12% weight loss in this range. This may be due to decomposition of the amide side groups and the crosslinker.

The third stage ranges between 180-480 °C during which weight loss of 32% occurs due to the complete decomposition of the main backbone of poly acrylamide [53]. Similar trends was observed for the pure polyacrylamide (PAAm), but the relative thermal stability shown by final composite materials is ~ 10 % higher than that of polyacrylamide, which may be due to the addition of FE as filler exhibiting high thermal stability due to the presence of inorganic metal-oxides in FE. After the third stage no further weight loss occurs during TGA analysis upto 600 °C.

Zeta potential analysis

The adsorption mechanism of MB dye is better understood by the determination of surface charge of the adsorbent which is determined from zeta potential study. The zeta potential variation is shown in Fig. 8, which depicts the surface of the adsorbent is negatively charge which increased up to pH 10 and then almost becomes alter. The maximum Zeta potential value recorded for
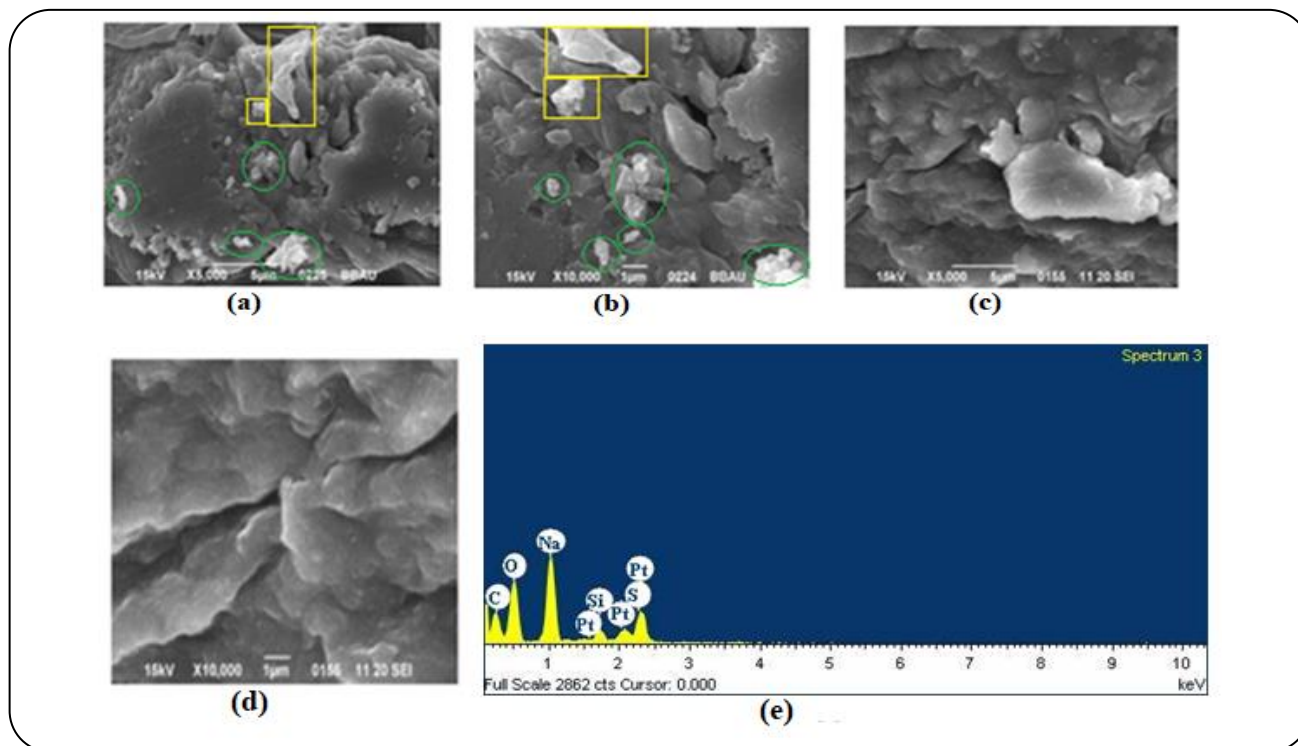
Fig. 6: SEM micrographs of PAAm/CG/FE composite (a) and (b) before adsorption (c) and (d) after adsorption (e) EDS elemental analysis of composite.
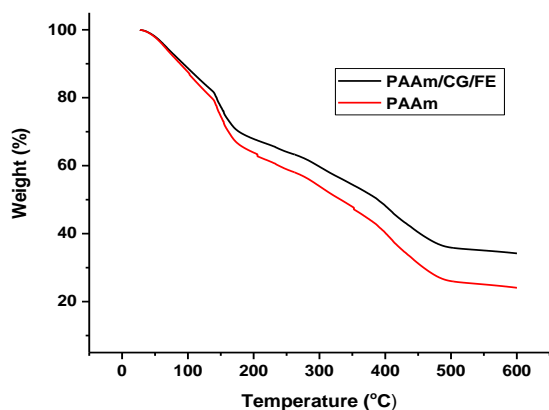

Fig.7: TGA analysis of PAAm and PAAm/CG/FE composite.

Fig.8: Measurement of Zeta potential at different pH value.

PAAm/CG/FE composite is -41.6 mv at pH 10 and beyond this, instability occurs in the surface charge of composite. This is due to the increase in competition for adsorption of OH ions in the basic aqueous medium and MB ions on the surface of the composite. The iso-electric point was not achieved in the full pH range because of insufficient net protonation due to medium to balance the negative charge of composite. Negative charges on composite occurs due to p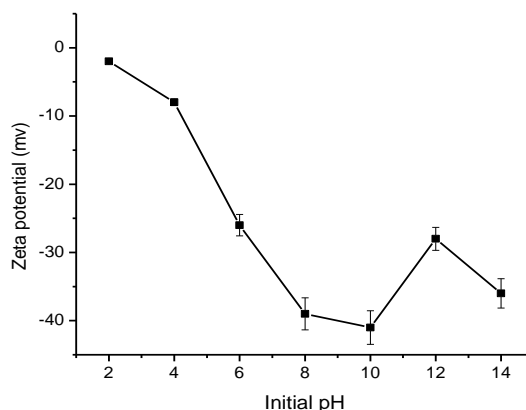rotonation of amide, carbonyl and hydroxyl functional groups present in composite. Therefore, on varying the pH of solution the cationic dye molecules show great impact on adsorption values due to increases in attraction between the negatively charged surface and cationic molecule [54, 55].

ADSORPTION AND KINETICS ANALYSIS
Effect of Contact Time

Study of effect of contact time on adsorption is very important because to determine equilibrium time and rate

kinetics for the MB-composite system in aqueous water. The effect of contact time on MB dye adsorption has been studied for a time range 10-120 min and results are depicted in Fig. 9 (a). The study was done by the setup of 25 *mL* of MB dye solution of concentration 100 mg/L by the addition of 0.05 g of a composite at pH 7 on a magnetic stirrer with 100 rpm stirring rate at room temperature. It is clear from the graph that the 80 minutes of contact time was required to achieve saturation. The rate of adsorption of dye decreases with an increase in time however, the adsorption capacity of MB dye increases with an increase in time [56]. The rate of dye adsorption is fast enough to reach its 80% of maximum value in during the initial 20 minutes, after that it decreases gradually and finally equilibrium is achieved. PAAm and composite removed 80% and 92% MB dye respectively. Hence, results confirmed that composite has a higher affinity for MB dye removal as compared to PAAm.

Effect of pH

Fig. 9 (b) depicts the same trends and follows the zeta potential results, therefore the pH value of the dye solution is an important factor in MB dye adsorption by synthesized composite. The effect of pH on adsorption on composites was shown in Fig. 9 (b). The adsorption of dye on PAAm/CG/FE composite increases from 18 to 92% from pH range 2 to 8 and then becomes constant after the further increase in the pH value upto 12. pH affects strongly the surface charge of composite and also the functional group dissociation of active sites. The H^+ release in the adsorption procedure changes the pH value of the dye solution by a small amount. The groups on the surface of the composite changes with pH variation. The number of deprotonated or negatively charged functional groups such as amide, and hydroxyl groups increase with the increase in pH of dye solution. The hydrolysis of MB dye also increases with pH increase [57]. Hence, the adsorption of MB on the composite was found to increase gradually with the increase in pH from 2 to 8. Most of the functional groups of composites are ionized and interact with the dye molecules with a strong electrostatic attraction which increases the adsorption capacity of the composite.

Effect of MB solution temperature

The effect of temperature on MB dye adsorption on composite was investigated at 30, 40 and 50 °C. The concentration of dye was 100 mg/L taken at pH 7 with 150 rpm. Fig. 9(c) shows the effect of temperature on adsorption capacity by composite. It was found that with the increase in temperature from 30 to 40 °C, the adsorption capacities increase. However, further temperature increases from 40 to 50 °C, the adsorption capacities decrease. This occurs due to the fact that on increasing the temperature from 30 to 40 °C adsorption sites of composite become more active and adsorption increases, but further increase in the temperature increases the mobility of large MB dye ions, resulting in decreased adsorption on the composite [58].

Effect of MB concentration

The effect of initial concentration on MB adsorption was studied in range of 50 to 250 mg/L. The results have been shown in Fig. 9 (d). It can be concluded from the study that the percentage removal of MB from the aqueous solution strongly depends upon the initial concentration of MB dye. Percentage of adsorption is inversely proportional to initial concentration of MB means adsorption percentage decreased with increase in initial concentration of MB. This is due to at lower concentration the number of ions available are less as compared to sites of adsorption present on the composite [59]. However, higher concentration of MB contains high number of ions and adsorption sites on composite become saturated and this results in the decrease in percentage adsorption of MB on the composite surface.

Kinetic study results

The Table 2 shows the rate constant values (k_1 and k_2) for the pseudo first and second order kinetic studies, respectively along with their corresponding correlation coefficient values (R^2 values). These values were determined with the help of linear fitting of the corresponding kinetics model with experimental data for the MB removal using PAAm and PAAm/CG/FE composite. The high correlation value (R^2) is obtained for the pseudo-second order kinetic model than the pseudo first order model, which suggest that the pseudo-second order kinetic model fits better than the pseudo-first order model for the MB removal. Fig. 10 shows the corresponding fitting
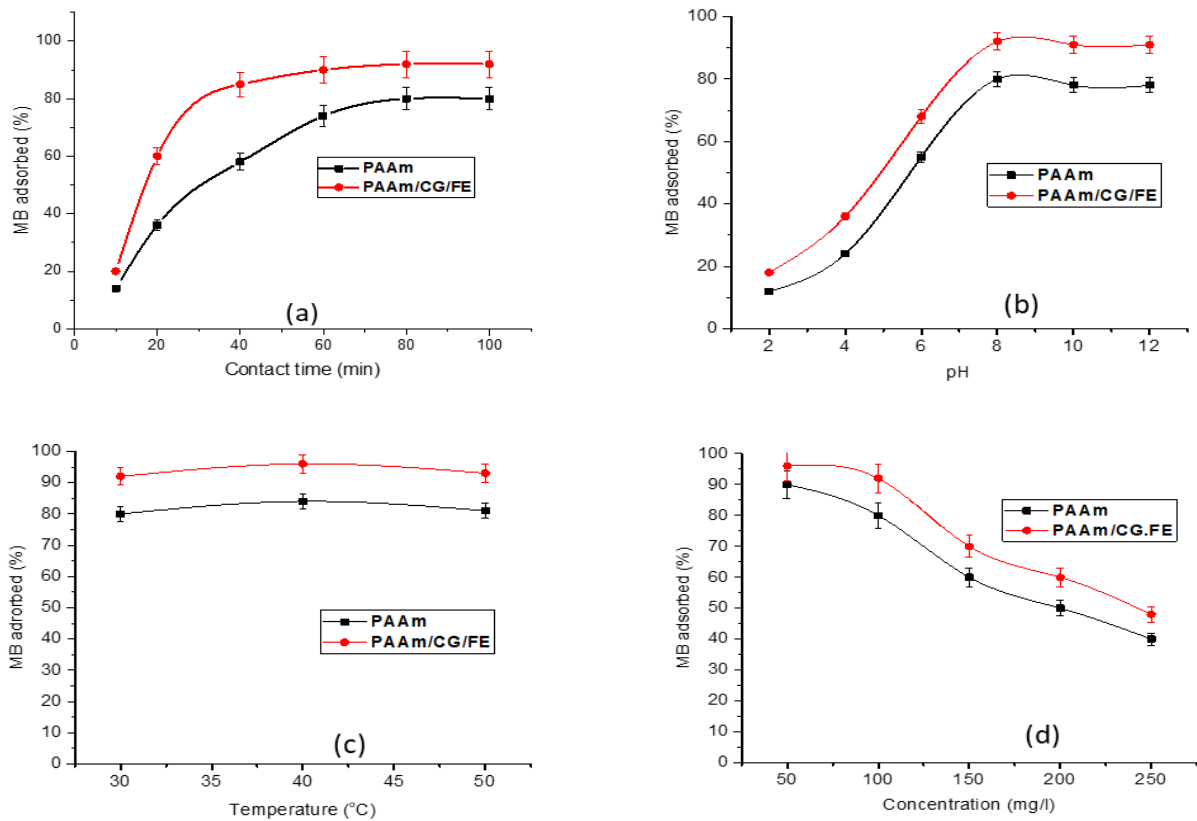
*Fig. 9: Effect on the adsorption capacity of PAAm and PAAm/CG/FE composite by (a) contact time variation;
(b) variation of pH, (c) variation of temperature and (d) variation of MB concentration (dose:0.05 g, vol.: 25 mL).*
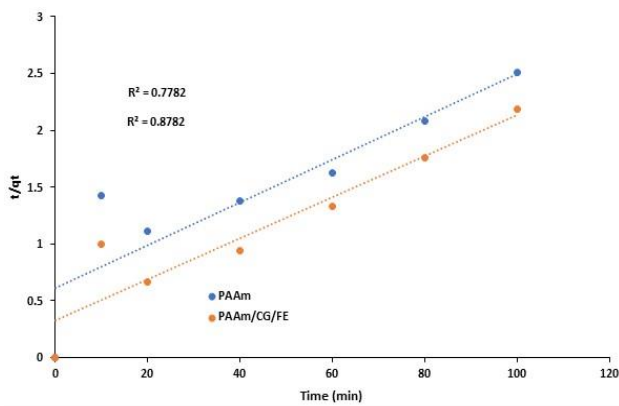

Fig.10: Kinetic model of Pseudo second order for removal of MB with PAAm and second order for PAAm/CG/FE composite.

of pseudo second order kinetic model with experimental data for PAAm and PAAm/CG/FE composite.

Adsorption isotherm analysis

In adsorption isotherm studies the best fitted data has

been found for the Langmuir adsorption isotherm model. The values of R^2 (nonlinear) for PAAm/CG/FE in the Langmuir adsorption isotherm model are higher than that of Freundlich adsorption isotherms (shown in Table 3). This result suggests about monolayer adsorption and presence of finite number of sites of adsorption. Fig. 11(a) represent adsorption isotherm and 11(b) represent Langmuir isotherm fitting of PAAm/CG/FE composite. Freundlich model was also tested with experimental data but based on high ARE % and lower nonlinear correlation values, this model is not best fitted with the experimental MB-composite system as shown in Table 3. Therefore, Langmuir model has been found to be the best fitted model for this experimental study. Thus, it confirms that PAAm/CG/FE can effectively work for MB adsorption for waste water treatment.

Reusability of synthesized composite

The reusability of composite material is a promising aspect which enhances its utility for end application,

Table 2: Parameters of pseudo-first and pseudo-second order constants values R^2.

Adsorbent	Pseudo first order		Pseudo second order	
	k_1 min^{-1}	R^2	k_2/L(mg/min)	R^2
PAAm	0.0536	0.7639	0.6180	0.7782
PAAm/CG/FE	0.0438	0.8616	0.3299	0.8782

Table 3: Parameters of Langmuir and Freundlich adsorption isotherm model for PAAm and PAAm/CG/FE.

	adsorption parameters				R^2 nonlinear	ARE%
PAAm						
Langmuir	Q_m	48.30	b	0.15	0.984	4.51
Freundlich	1/n	0.315	k_f	11.09	0.896	15.10
PAAm/PMC						
Langmuir	Q_m	56.17	b	0.30	0.983	6.85
Freundlich	1/n	0.266	k_f	17.29	0.896	14.02
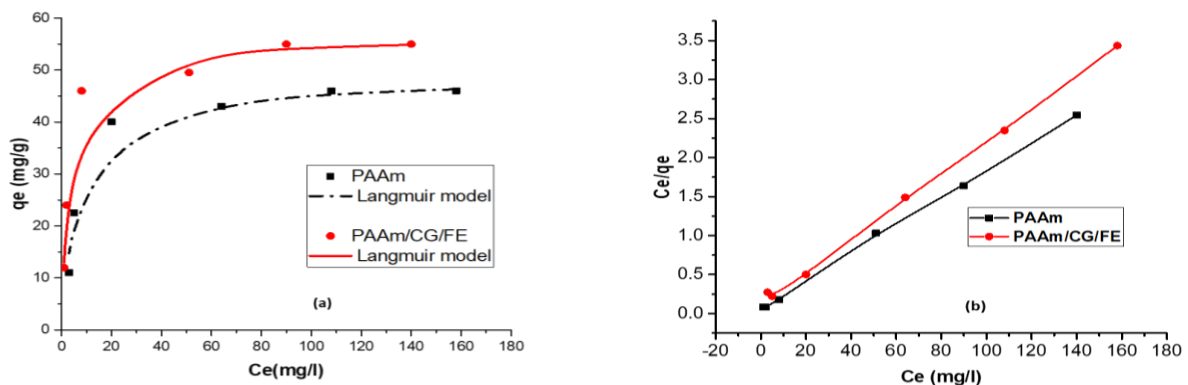
Fig. 11: (a) Adsorption isotherm and (b) Langmuir isotherm fitting of PAAm and PAAm/CG/FE composite.
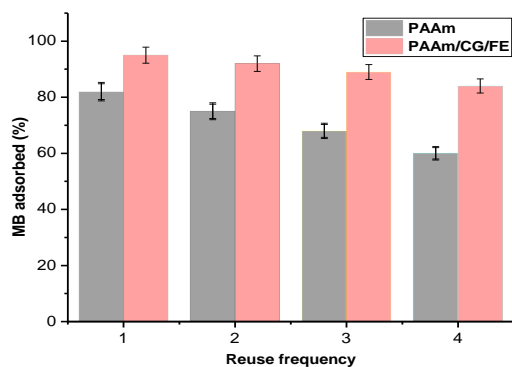
Fig. 12: Relation between the reuse frequency and adsorption capacity of PAAm and PAAm/CG/FE composite.

therefore its adsorption capacity has been determined over the different cycles. Fig. 12 describes the reusability up to four cycles of the adsorption-desorption process. For analysing the reusability of PAAm and PAAm/CG/FE composite, 0.05 g of MB dye adsorbed samples were added in 30 mL of 0.05 M of HCl solution for 120 min at room temperature. Both desorbed samples were removed from HCl solution and centrifuged then washed with distilled water and dried in oven at 80 ºC for 8 h. In comparison to PAAm the composite shows good adsorption capacity even after four times of recycling. The adsorption-desorption shows that adsorption capacity was decreased 30 and 9 % of PAAm and PAAm/CG/FE composite respectively and results are shown in Fig. 12.

Fig.13: Plant Growth Study on wheat plant in MB Wastewater and treated MB wastewater.

Ecological assessment of treated MB wastewater and plant growth study

For testing the eco-toxicological analysis, the untreated and treated MB wastewater was used for the growth of wheat plants to confirm the use of treated wastewater [60]. The growth analysis of the wheat plant was done for 7 days in MB aqueous solution and the treated wastewater (MB dye removed by PAAm/CG/FE composite) and the growth result of plants were shown in Fig.13. Wheat seeds are purchased from the local market of Gorakhpur, Uttar Pradesh, India. Seeds are kept in water overnight. The next day seeds are planted in rice husk in two Petri dishes in equal numbers. One dish was watered by treated and the other was watered with untreated wastewater daily in sufficient amounts. The growth of the wheat plant was analyzed for the next 7 days. The study confirms the high inhibitory effect of MB water in the growth of both root and shoot of wheat plants. The treated wastewater shows good results with healthier growth in comparison to untreated wastewater.

CONCLUSIONS

From this study it can be concluded that, the removal of methylene blue dye can be effectively done in a short period of time by PAAm/CG/FE composite. The adsorption process has been found to be highly dependent on various physico-chemical parameters such as contact time, pH, initial concentration and the temperature of reaction medium. Under identical experimental conditions, the composite has been found to be a better adsorbent than pure PAAm. The FTIR, SEM, EDX and TGA were used for the characterization of the composite. PAAm is water soluble polymer, and due to this it gets dissolved in small amount in water, during the adsorption process and this is responsible for its poor reusability. However, the composite of PAAm can be reused many times, as it is highly stable in aqueous medium and is a low-cost material due to use of waste cotton fibre and fuller's earth clay for its synthesis. The adsorption kinetics has been found to be well described by the pseudo-second order kinetic model and the adsorption process is very well described by the Langmuir adsorption isotherm model. The composite exhibited good maximum monolayer adsorption of 56.17 mg of methylene blue dye per gram of composite. The adsorption capacities were found to decrease only slightly even after four adsorption/ desorption cycles; this demonstrates the high reusability of the composite. The simple synthesis, low cost, biodegradability, high absorptivity, reusability, etc makes it an effective adsorbent for the removal of methylene blue dye from waste-water.

REFERENCES

[1] Jayaswal K., Sahu V., Gurjar B.R., "Water Pollution, Human Health and Remediation. in Water Remediation", Springer, Singapore, 11-27 (2018).

[2] Patwardhan A. D., "Industrial Wastewater Treatment", PHI Learning Pvt. Ltd., New Delhi (2017).

[3] Mittal J., Permissible Synthetic Food Dyes in India, *Resonance – J. Sci. Edu. (JSE),* **25** 567 – 577(2020).

[4] Yagub M.T., Sen T.K., Afroze S., Ang H.M., Dye and its Removal from Aqueous Solution by Adsorption: A Review, *Adv. Colloid Interface Sci. (ACIS)*, **209**: 172-184 (2014).

[5] Tan I.A.W., Ahmad A.L., Hameed B.H., Adsorption of Basic Dye on High-Surface Area Activated Carbon Prepared from Coconut Husk: Equilibrium, Kinetic and Thermodynamic Studies, *J. Hazard. Mater.* (JHM), **154**: 337–346 (2008).

[6] Rafatullah M., Sulaiman O., Hashim R., Ahmad A., Adsorption of Methylene Blue on Low-Cost Adsorbents: A Review, *J. Hazard. Mater. (JHM)*, **177(1-3)**: 70-80 (2010).

[7] Azimi A., Azari A., Rezakazemi M., Ansarpour M., Removal of Heavy Metals from Industrial Wastewaters: A Review, *Chem. Bio. Eng. Reviews (CBER)*, **4(1)**: 37-59 (2017).

[8] Tehrani M.S., Zare-Dorabei R., Highly Efficient Simultaneous Ultrasonic-Assisted Adsorption of Methylene Blue And Rhodamine B Onto Metal Organic Framework MIL-68 (Al): Central Composite Design Optimization, *RSC adv. (RSCA)*, **6(33)**: 27416-27425 (2016).

[9] Marahel F., Mombeni Goodajdar B., Niknam L., Faridnia M., Pournamdari E., Mohammad Doost S., Ultrasonic Assisted Adsorption of Methylene Blue Dye and Neural Network Model For Adsorption of Methylene Blue Dye by Synthesised Mn-Doped Pbs Nanoparticles, *Int. J. Environ. Anal. Chem. (IJEAC)*, 1-22 (2021).

[10] Wang L., Zhang J., Wang, A., Fast Removal of Methylene Blue from Aqueous Solution by Adsorption onto Chitosan-G-Poly (Acrylic Acid)/Attapulgite Composite, *Desalination (D)*, **266(1-3)**: 33-39 (2011).

[11] Zhou C., Wu Q., Lei T., Negulescu I.I., Adsorption Kinetic and Equilibrium Studies for Methylene Blue Dye by Partially Hydrolyzed Polyacrylamide/Cellulose Nanocrystal Nanocomposite Hydrogels, *Chem. Eng. J. (CEJ)*, **251**:17-24 (2014).

[12] Bulut Y., Karaer H., Adsorption of Methylene Blue from Aqueous Solution by Crosslinked Chitosan/Bentonite Composite, *J. Dispers. Sci. Technol. (JDST)*, **36(1)**: 61-67 (2015).

[13] Singh N.B., Nagpal G., Agrawal S., Water Purification by Using Adsorbents: A Review, *Environ. Technol. Innov. (ETI)*, **11**:187-240 (2018).

[14] Gupta V.K., Agarwal S., Ahmad R., Mirza A., Mittal, J., Sequestration of Toxic Congo Red Dye from Aqueous Solution Using Ecofriendly Guar Gum/Activated Carbon Nanocomposite, *Int. J. Biol. Macromol. (IJBM)*, **158**:1310-1318 (2020).

[15] Kumar V., Saharan P., Sharma A.K., Umar A., Kaushal I., Mittal A., Al-Hadeethi Y., Rashad B., Silver Doped Manganese Oxide-Carbon Nanotube Nanocomposite for Enhanced Dye-Sequestration: Isotherm Studies and RSM Modelling Approach, *Ceram. Int. (CI)*, **46(8)**:10309-10319 (2020).

[16] Van Tran V., Park D., Lee Y.C., Hydrogel Applications for Adsorption of Contaminants in Water and Wastewater Treatment, *Environ. Sci. Pollut. Res. (ESPR)*, **25(25)**: 24569-24599 (2018).

[17] Liu B. Wang D. Yu G. Meng X., Adsorption of Heavy Metal Ions, Dyes and Proteins by Chitosan Composites and Derivatives—A Review, *J. Ocean Univ.China (JOUC)*, **12(3)**: 500-508 (2013).

[18] Kausar A., Iqbal M., Javed A., Aftab K., Bhatti H.N., Nouren S., Dyes Adsorption Using Clay and Modified Clay: A Review, *J. Mol. Liq. (JML)*, **256**: 395-407 (2018).

[19] Ramezani F., Zare-Dorabei R., Simultaneous Ultrasonic-Assisted Removal of Malachite Green and Methylene Blue from Aqueous Solution by Zr-SBA-15, *Polyhedron (P)*, **166**: 153-161 (2019).

[20] Anastopoulos I., Pashalidis I., Orfanos A.G., Manariotis I.D., Tatarchuk T., Sellaoui L., Bonilla-Petriciolet A., Mittal A., Núñez-Delgado, A., Removal of Caffeine, Nicotine and Amoxicillin From (Waste) Waters by Various Adsorbents. A Review, *J. Environ. Manage. (JEM)*, **261**: 10236 (2020)

[21] Kiani A., Haratipour P., Ahmadi M., Zare-Dorabei R., Mahmoodi A., Efficient Removal of Some Anionic Dyes from Aqueous Solution Using A Polymer-Coated Magnetic Nano-Adsorbent, *J. Water Supply Res. T. (JWSRT)*, **66(4)**: 239-248 (2017).

[22] Joseph L., Jun B.M., Jang M., Park C.M., Muñoz-Senmache J.C., Hernández-Maldonado A.J., Heyden A., Yu M., Yoon Y., Removal of Contaminants of Emerging Concern by Metal-Organic Framework Nanoadsorbents: A Review, *Chem. Eng. J. (CEJ)*, **369**: 928-946 (2019).

[23] Arora C., Soni S., Sahu S., Mittal J., Kumar P., Bajpai P.K., Iron Based Metal Organic Framework for Efficient Removal of Methylene Blue Dye from Industrial Waste, *J. Mol. Liq. (JML)*, **284**:343-352 (2019).

[24] Soni S., Bajpai P.K., Mittal J., Arora C., Utilisation of Cobalt Doped Iron Based MOF for Enhanced Removal and Recovery of Methylene Blue Dye from Waste Water, *J. Mol. Liq. (JML)*, **314**:113642 (2020).

[25] Bagotia N., Sharma A.K., Kumar S., A Review on Modified Sugarcane Bagasse Biosorbent for Removal of Dyes, *Chemosphere (C)*, 129309 (2020).

[26] Mittal A., Mittal J., Hen Feather: A Remarkable Adsorbent for Dye Removal, "Green Chemistry for Dyes Removal from Wastewater", Scrivener Publishing (Wiley), 409 (2015).

[27] Guiza S., Bagane M., Al-Soudani A. H., Amore H. B., Adsorption of Basic Dyes onto Natural Clay, *Adsorp. Sci. Technol. (AST)*, **22(3)**: 245-255 (2004).

[28] Anastopoulos I., Mittal A., Usman M., Mittal J., Yu G., Núñez-Delgado A., Kornaros M., A Review on Halloysite-Based Adsorbents To Remove Pollutants in Water and Wastewater, *J. Mol. Liq. (JML)*, **269**:855-868 (2018).

[29] Adeyemo A.A., Adeoye I.O., Bello O.S., Adsorption of Dyes Using Different Types of Clay: A Review, *Appl. Water Sci. (AWS)*, **7(2)**:543-568 (2017).

[30] Jameel M., Khan S.A., Afzal A., Adsorption Studies of Fullers Earth Nanocomposites for the Removal of Copper and Reactive Yellow 18, *Dig. J. Nanomater. Bios. (DJNB)*, **16(1)**: 261-270 (2021).

[31] Jamshaid A., Hamid A., Muhammad N., Naseer A., Ghauri M., Iqbal J., Rafiq S., Shah N.S., Cellulose-Based Materials for the Removal of Heavy Metals from Wastewater–An Overview, *Chem. Bio. Eng. Reviews (CBER)*, **4(4)**:240-256 (2017).

[32] Liu R., Ma W., Jia C.Y., Wang L., Li H.Y., Effect of pH on Biosorption of Boron onto Cotton Cellulose, *Desalination (D)*, **207(1-3)**: 257-267 (2007).

[33] Wanassi B., Hariz I.B., Ghimbeu C.M., Vaulot C., Jeguirim, M., Green Carbon Composite-Derived Polymer Resin and Waste Cotton Fibers for the Removal of Alizarin Red S Dye, *Energies (E)*, **10(9)**:1321 (2017).

[34] Jabli M., Baouab M.H.V., Roudesli M.S., Bartegi, A., Adsorption of Acid Dyes from Aqueous Solution on a Chitosan-Cotton Composite Material Prepared by a New Pad-Dry Process, *J. Eng. Fibers. Fabr. (JEFF)*, **6(3)**:155892501100600301 (2011).

[35] Niu Y., Hu W., Guo M., Wang Y., Jia J., Hu Z., Preparation of Cotton-Based Fibrous Adsorbents for the Removal of Heavy Metal Ions, *Carbohydr. Polym. (CP)*, **225**:115218 (2019).

[36] Yang A., Wang Z., Zhu, Y., Facile Preparation and Adsorption Performance of Low-Cost MOF@ Cotton Fibre Composite for Uranium Removal, *Sci. Rep. (SR)*, **10(1)**:1-10 (2020).

[37] Peng B., Yao Z., Wang X., Crombeen M., Sweeney D.G., Tam K.C., Cellulose-Based Materials in Wastewater Treatment Of Petroleum Industry, *Green Energy Environ. (GEE)*, **5(1)**: 37-49 (2020).

[38] Ren H., Gao Z., Wu D., Jiang J., Sun Y., Luo, C., Efficient Pb (II) Removal Using Sodium Alginate–Carboxymethyl Cellulose Gel Beads: Preparation, Characterization, and Adsorption Mechanism, *Carbohydr. Polym. (CP)*, **137**: 402-409 (2016).

[39] Wertz J.L., Mercier J.P., Bedue O., *Cellulose Science and Technology*, EPFL press. (2019).

[40] Tangri A., Polyacrylamide Based Hydrogels: Synthesis, Characterization and Applications, *Int. J. Pharm. Chem. Biol. Sci. (IJPCBS)*, **4(4)** (2014).

[41] Shalla A. H., Yaseen Z., Bhat M. A., Rangreez T. A., Maswal M., Recent Review for Removal of Metal Ions by Hydrogels, *Sep. Sci. Technol. (SST)*, **54(1)**: 89-100 (2019).

[42] Abu-Danso E., Srivastava V., Sillanpaa M., Bhatnagar A., Pretreatment Assisted Synthesis and Characterization of Cellulose Nanocrystals and Cellulose Nanofibers from Absorbent Cotton, *Int. J. Biol. Macromol.* (IJBM), **102**: 248–257 (2017).

[43] Avşar A., Gokbulut Y., Ay B., Serin S., A Novel Catalyst System for the Synthesis of N, N′-Methylenebisacrylamide from acrylamide, *Des. Monomers Polym. (DMP)*, **20(1)**: 434-440 (2017).

[44] Jang S.H., Jeong Y.G., Min B.G., Lyoo W.S., Lee S.C., Preparation and Lead Ion Removal Property of Hydroxyapatite/Polyacrylamide Composite Hydrogels, *J. Hazard. Mater. (JHM)*, **159(2-3)**: 294-299 (2008).

[45] Zhao G., Zhang H., Fan Q., Ren X., Li J., Chen Y., Wang X., Sorption of Copper (II) Onto Super-Adsorbent of Bentonite–Polyacrylamide Composites, *J. Hazard. Mater. (JHM)*, **173(1-3)**:661-668 (2010)

[46] Srivastava A., Singh M., Karsauliya K., Mondal D.P., Khare P., Singh S., Singh S.P., Effective Elimination Of Endocrine Disrupting Bisphenol A and S From Drinking Water Using Phenolic Resin-Based Activated Carbon Fiber: Adsorption, Thermodynamic and Kinetic Studies, *Environ. Nanotechnol., Monit. Manag. (ENMM)*, **14**:100316 (2020).

[47] Ji L., Chen W., Zheng S., Xu Z., Zhu D., Adsorption of Sulfonamide Antibiotics to Multiwalled Carbon Nanotubes, *Langmuir (L)*, **25(19)**: 11608-11613 (2009).

[48] Dos Santos A., Viante M.F., Pochapski D.J., Downs A.J., Almeida C.A.P., Enhanced Removal of P-Nitrophenol from Aqueous Media by Montmorillonite Clay Modified with a Cationic Surfactant, *J. Hazard. Mater. (JHM)*, **355**: 136-144 (2018).

[49] Mondal S., Majumder S.K., Honeycomb-Like Porous Activated Carbon for Efficient Copper (II) Adsorption Synthesized from Natural Source: Kinetic Study And Equilibrium Isotherm Analysis, *J. Environ. Chem. Eng. (JECE)*, 7(4):103236 (2019).

[50] Jayaramudu T., Ko H.U., Kim H.C., Kim J.W., Kim J., Swelling Behavior Of Polyacrylamide–Cellulose Nanocrystal Hydrogels: Swelling Kinetics, Temperature, and pH Effects, *Materials (M)*, **12(13)**: 2080 (2019).

[51] Nayak P.S., Singh B.K., Instrumental Characterization of clay by XRF, XRD and FTIR, *Bull. Mater. Sci. (BMS)*, **30(3)**: 235-238 (2007).

[52] Chen Y., Zhao Y., Zhou S., Chu X., Yang L., Xing W., Preparation and Characterization of Polyacrylamide/ Palygorskite, *Appl. Clay Sci. (ACS)*, **46(2)**: 148-152 (2009).

[53] Ibrahim A.G., Sayed A.Z., El-Wahab H.A., Sayah M.M., Synthesis of Poly (acrylamide-graft-chitosan) Hydrogel: Optimization of the Grafting Parameters and Swelling Studies, *Am. J. Polym. Sci. Technol. (AJPST)*, **5**: 55-62 (2019).

[54] Abu-Danso E., Peraniemi S., Leiviska T., Kim T., Tripathi K.M., Bhatnagar A., Synthesis of Clay-Cellulose Biocomposite for the Removal of Toxic Metal Ions from Aqueous Medium, *J. Hazard. Mater. (JHM)*, **381**: 120871 (2020).

[55] Teli M.D., Kale R.D., Bhatt L., Effect of Nano Clay Loading on Zeta Potential of Polyester Nanocomposite Fibre, *Indian J. Fibre Text. (IJFTR)*, **42(2)**: 125-131 (2017).

[56] Tang Y., Ma D., Zhu L., Sorption Behavior of Methyl Violet onto Poly (acrylic acid-co-acrylamide)/Kaolin Hydrogel Composite, *Polym. Plast. Technol. Eng. (PPTE)*, **53(8)**:851-857 (2014).

[57] Liu Y., Zheng Y., Wang A., Enhanced Adsorption of Methylene Blue from Aqueous Solution by Chitosan-G-Poly (Acrylic Acid)/Vermiculite Hydrogel Composites, *J. Environ. Sci. (JES)*, **22(4)**: 486-493 (2010).

[58] Zou X., Zhang H., Chen T., Li H., Meng C., Xia Y., Guo J., Preparation and Characterization of Polyacrylamide/Sodium Alginate Microspheres and its Adsorption of MB Dye, *Colloids Surf., A Physicochem. Eng. Asp. (CSPEA)*, **567**: 184-192 (2019).

[59] Vaz M.G., Pereira A.G., Fajardo A.R., Azevedo A.C., Rodrigues F.H., Methylene Blue Adsorption on Chitosan-G-Poly (Acrylic Acid)/Rice Husk Ash Superabsorbent Composite: Kinetics, Equilibrium, and Thermodynamics, *Water Air Soil Pollut. (WASP)*, **228(1)**: 1-13 (2017).

[60] Gunture Kaushik J., Garg A.K., Saini D., Khare P., Sonkar S. K., Pollutant Diesel Soot Derived Onion-like Nanocarbons for the Adsorption of Organic Dyes and Environmental Assessment of Treated Wastewater, *Ind. Eng. Chem. Res. (IECR)*, **59(26)**: 12065-12074 (2020).