FINAL TECHNICAL REPORT
ON

SYNTHESIS OF POLYMER NANO HYDROGEL AND DEVELOPMENT OF HYBRID WASTE WATER TREATMENT SYSTEM USING CAVITATION TECHNIQUE AND HYDROGEL

[F. No. 10-1/2010-CT (WM)]

INVESTIGATED BY

Dr. Shirish Sonawane,
Department of Chemical Engineering,
National Institute of Technology, Warangal

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Dr. S. Sridhar, Principal Scientist, CSIR-IICT, Hyderabad - Chairman

Dr. Nitin Labhsetwar, Scientist F, NEERI, Nagpur - Member

Dr. Pramod Borse, Scientist F, ARCI, Hyderbad - Member

Dr. H. Kharkwal, MoEF&CC, New Delhi - Member Secretary

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FORMAT FOR FINAL TECHNICAL REPORT OF RESEARCH PROJECTS FUNDED BY THE MINISTRY OF ENVIRONMENT, FOREST& CLIMATE CHANGE

PART – I

1. Title of the Project: Synthesis of Polymer Nano Hydrogel and Development hybrid wastewater treatment system using Cavitation Technique and Hydrogel.

2. Name of Members of Research Team and their designation

I. Dr. Shirish Sonawane,
   Principal Investigator,
   Associate Professor,
   Chemical Engineering Department

II. Mr. Bhaskar Bethi,
   Junior Research Fellow

3. Number and date of Sanction letter: F. No. 10-1/2010-CT (WM), dated 28/12/2013

4. Duration of the Project: 2 Years 7 Months (Including extended period)

5. Total outlay of the Project: Rs. 34, 29,300/-

6. Date of start of Project: 28/12/2013

7. Date of completion of Project: 31/07/2016

PART - II

1. Abstract of the Project

Synthesis of poly(acrylic acid)-bentonite-FeCo (PAA-B-FeCo) hydrogel nanocomposite via ultrasound assisted in situ emulsion polymerization was carried out. Addition of exfoliated bentonite clay platelets and Fe -Co increased the strength and stability of hydrogel and assisted the adsorption of an organic pollutant. The response of the nanocomposite hydrogel was evaluated using a cationic dye, crystal violet (CV) under different temperature, pH, and cavitation environment. The optimum temperature was found to be 35 ^{0}C and basic pH (optimum at 11) was responsible for the higher adsorption of dye due to dissociation of COO$^-$ ions at higher pH. Bimetallic components form the metal ions in hydrogel which shows repulsion at low pH resulting to lower response. Thermodynamic parameters for adsorption indicated that the dye adsorption onto PAA-B-FeCo hydrogel was spontaneous and endothermic in nature.

Removal of brilliant green dye from water using a poly (acrylic acid) hydrogel composite (PAA-K hydrogel) prepared by incorporation of kaoline clay has been investigated. The composite has been synthesized using ultrasound assisted polymerization process as well as the conventional process, with an objective of showing the better effectiveness of ultrasound assisted synthesis. It has been observed that the hydrogel prepared by ultrasound assisted polymerization process showed better results. The optimum conditions for the removal of dye are pH: 7, temperature: 35 ^{0}C, initial dye concentration is 30 mg/L and hydrogel loading 1 g. The extent of removal of dye increased with an increase in the contact time and initial dye concentration. A pseudo-second-order kinetic model has been developed to explain the adsorption kinetics of dye on the PAA-K hydrogel. Thermodynamic and kinetic parameters indicate that the adsorption process is spontaneous in nature and hence the PAA-K hydrogel prepared by ultrasound process is a promising adsorbent compared to conventional process.

In this project, a first report on combined novel hybrid technique (hydrodynamic cavitation + hydrogels packed bed adsorption) has been studied for dye degradation and subsequent adsorption of dye molecules. A lab scale hybrid system consists of 5 L of capacity have been fabricated in in-house for carrying out the initial experiments. Initially, hydrodynamic cavitation (HC) was employed for the degradation of dye molecules and subsequent adsorption of dye molecules have been carried out by adopting synthesized polymer hydrogels. Polyacrylic acid (PAA)/nanocomposite hydrogels which includes PAA-Bentonite clay nanocomposite and PAA-Greaphe oxide nanocomposite hydrogels have been synthesized via ultrasound assisted emulsion polymerization technique. Synthesized hydrogels have been characterized by XRD and TEM analysis. Operational parameters such as effect of inlet pressure, effect of bentonite clay content in PAA hydrogel, effect of hydrogel quantity loading in packed bed, effect of pH on removal of dye pollutants have been investigated using hybrid technique. Initially the azo type of dyes such as malachite green and crystal violet dye removal have been studied using the lab scale hybrid system. The obtained results revealed that adsorption of CV dye on PAA hydrogel followed the pseudo second order kinetics. Synergetic effect of combined technique was evaluated based on the reaction kinetics obtained. The developed hybrid system has also been tested for the treatment of real industrial textile wastewater to know its effectiveness. Power consumption and cost effectiveness of hybrid system was also evaluated based on the energy consumption for treatment of 1 L of dye wastewater.

2. Introduction

The composites encapsulating nanoparticle in polymer matrix display novel and often enhanced properties compared to the traditional materials [1–4]. In recent years, nanoparticles have been comprehensively investigated due to their special properties such as a high aspect ratio and the small-size effect, higher cation exchange capacity (CEC). Several physical and chemical methods such as ball milling, Sol gel, vapor deposition, microwave technique have been used for getting nanoparticles [1]. Ultrasound assisted synthesis of nanoparticles is one of the important technique. The radicals produced in the interior of the bubble can then diffuse into the bulk solution and reduce metal ions yielding nano-sized metallic particles. Although additional radicals can be produced in the surrounding solution due to the presence of a stabilizer such as a water-soluble polymer, it is realized that these reactions are dominated by the initial formation of radicals in the interior of the collapsing bubble. Ultrasound also reduces the nucleation and crystal growth hence reduction in the induction time during the nanoparticle synthesis [2] In waste water treatment nano Fe_3O_4 [3], Nano clay Betonite [4], Nano metal particles Fe, Ni [5], Nanoparticles which have photo catalytic activity such as TiO_2 [6], ZnO [7,8] are utilized for degradation of waste. Photo Fenton reaction using Fe based nanoparticles along with H_2O_2 and UV rays used for degradation of photo-catalytic compounds. Number of possibilities such as nano Fe_2O_4, Fe-CO nano-oxides is being used for degradation of dyes and commonly known as Fenton catalyst [9-11].

When a liquid is irradiated by ultrasound, microbubbles can appear, grow and oscillate extremely fast, and even collapse violently, if the acoustic pressure is high enough. These collapses, occurring near a solid surface, will generate microjets and shockwaves, resulting in cleaning and erosion of the surface, and fragmentation of the solid which enhances mass transfer rates and solid-liquid interface areas under ultrasound [12]. Cavitational reactors are a novel and promising form of multiphase reactors, based on the principle of release of large magnitude of energy due to the violent collapse of the cavities. Due to generation of hot spots and highly reactive free radicals in the system. H_2O_2 is generated during the collapse of cavities. These peroxide radicals help in reduction of large molecules into the smaller molecules. Presence of additives (solids) in the system might ease the process of cavity generation and hence intensify the cavitational activity in the reactor. Cavitational reactors find a ready application in the area of wastewater treatment. Cavitation has been looked upon as potential treatment method which is capable of converting chemical substrates like chlorinated hydrocarbons, aromatic compounds, textile dyes, phenolic compounds and esters into short chain organic acids, inorganic ions as final products.[13-15]

Due to the scientific and technological progress, contamination by dyes, organic matter, pigment etc created a serious problem. Relatively large group of organic chemicals that are encountered in practically all spheres of our daily life. It is therefore possible that such chemicals have undesirable effects not only on the environment, but also on human being.

Conventional methods of the treatment of dye wastewater include adsorption, chlorination and ozonation, electrochemical process, biological methods and chemical oxidation. Slow degradation rate, poor efficiency of the process, small pore diameter of catalytic material, generation of solid effluent are some of the limitation related to conventional waste water treatment system. Membrane based separation is one of the recent techniques used for waste water but selection of membrane and clogging of membrane pores, applicability in higher loading are limitation associated with these technologies. Recently photo-catalysis has been successfully used to oxidize many organic pollutants and particularly to decolorize and mineralize dyes. Some of the attempts have been carried out to make hybrid system to improve the efficiency of the process. It includes photo-catalytic reaction along with oxidation process. Fenton reaction alongwith with photocatalytic reaction. Sonochemical degradation alongwith the photocatalytic reaction etc.

Polymeric hydrogels play an important role in the treatment of waste water. Over the past several decades, polymeric hydrogels have attracted much scientific interest and have found uses in many fields, such as molecular filters, super absorbents, and contact lenses. Hydrogels are water-swollen crosslinked network of hydrophilic polymers. Due to the hydrophilic groups in their backbone, hydrogels can imbibe large quantities of water and swell. Gel is a three-dimensionally cross-linked polymeric system with various distinctive features which can be of use from practical viewpoints. Among them, the most important one is that gel possibly in a highly swollen state taking up a considerable amount of solvent inside its mesoscopic network structure. Because of this property, gel can be expected as quite a versatile media in engineering fields. The swollen state of gel is suitable for adsorption, retention or separation of various target substances. Because of these characteristics, they are frequently applied to effluent treatment processes.

The smart hydrogels are gaining important advantages in responding to external stimuli such as pH, ionic strength, temperature, and electric current. Functionalized nanoparticles with specific identity such as ionic conductivity and hydrophobicity can be prepared using physical and chemical crosslinking. Ultrasound assisted techniques help in production of these hydrogel nanoparticles into the smaller size. Due to combine effect of ultrasound and micellar structure polymer nanohydrogels have different morphologies and core shell flowers of different structures such as colloidal, ionic, magnetic etc. These nanoparticles of hydrogels can be used for chemical separation and catalysis. Recently, adsorbents with magnetic properties gained much attention due to the easy removal for adsorbed pollutants from aquatic environment as a result of magnetic field creation.

Diffusion processes in swollen cross linked polymer networks (polymer gels) that have direct impact on numerous practical applications such as drug delivery systems and transport across membranes [16].

Recently, some attempts have been made to modify the properties of polymeric hydrogels by the incorporation of nano- or micro-particles of inorganic materials, such as montmorillonite, kaolin, mica, bentonite into the polymer networks. Hydrogels loaded with dispersed clays are a new class of composite materials which combine elasticity and permeability of the gels with high ability of the clays to adsorb different substances. Many hydrogel composites such as polyacrylamide with bentonites or montmorillonites, polyacrylic acid or poly(N-isopropyacrylamide) with montmorillonites etc. The microstructure of a hydrogel can affect solute diffusion. Some of the factors affecting solute diffusion in hydrogels are chain entanglement, chain mobility crosslinking density, equilibrium degree of swelling, degree of crosslinking, and the relaxational characteristics of the gel network. On a molecular level, the solute diffusion rate through swollen gels depends on the relative hydrodynamic radius of the solute, and the network mesh size formed by the macromolecular chains; a larger solute diffuses at a slower rate than a smaller one. [17-20]

3. Objectives

- Synthesis of polymer hydrogel and incorporation of nanoparticles into the polymer matrix.
- Comparative study of cavitation effect and gel adsorption onto model pollutants.
- Development of simplified process for removal of these textile dye compounds. Testing effectiveness of developed system for industrial waste water treatment.

4. Detailed report of work done on the Project including Methodology

4.1 A case study on ultrasound assisted preparation of nanoclay Bentonite-FeCo nanocomposite hybrid hydrogel for removal of organic pollutant from water

4.1.1 Materials

Acrylic acid (AA), ammonium persulphate (APS), sodium dodecyl sulfate (SDS) and crystal violet dye (CV) were of analytical grade and procured from M/s CDH, India. Natural Bentonite clay was obtained from MD Chemicals, Pune, India. Millipore deionized water was used for all experiments. N-acetyl-N,N,N-trimethyl ammonium bromide (CTAB), ferric chloride, cobalt chloride and sodium borohydride ($NaBH_4$) were procured from Sigma Aldrich.

4.1.2 Synthesis of pure poly(acrylic acid) and PAA-B-FeCo hydrogel

Initially, pristine bentonite clay was washed 3–4 times with demineralised water. Impurities such as silica and iron oxides were removed by a differential sedimentation technique. The mixture was stirred for 1 h and kept undisturbed overnight. After filtration, the solid was exposed to slow evaporation, till the desired dryness was obtained. Modification of bentonite was carried out by ion exchange reaction. The following procedure was used to carry out ion exchange reaction so as to obtain modified bentonite nanoclay. 10 g bentonite clay (calculated on the basis of CEC of bentonite used) was mixed in 100 mL water containing 2 mL of hydrochloric acid and then solution was heated to 70 ^{0}C. HCl was added into clay solution as acidic environment facilitates the distribution of quaternary ammonium salts inside the gallery spacing of clay. CTAB solution (0.05 M) was dispersed into bentonite containing aqueous solution. The dispersion was stirred vigorously for 12 h at 70 ^{0}C. Unreacted amines were removed by continuous washing of precipitate using hot water. The final precipitate was thoroughly dried in an oven at 80 ^{0}C for 24 h to obtain the modified bentonite nanoclay. A detailed procedure for synthesis of nanoclay bentonite using sonochemical technique has been reported by Sonawane et al [21-22].

The synthesis of inorganic metal nanocomposite was carried out as follows: An aqueous solution containing ferric chloride (0.05 M, 100 mL) and cobalt chloride (0.05 M 100 mL) was sonicated for 10 minutes in an ultrasonic probe reactor (Dakshin, Mumbai India, probe diameter 22 mm). The solution was then added to 10 g of prepared nanoclay bentonite aqueous slurry. The amount of addition of precursors was decided based on the cation exchange capacity (CEC) of the bentonite clay which was 72 meq/g of clay. The mixture was sonicated for 30 minutes in order to disperse the chloride solution into the gallery spacing. Further, ultrasonic irradiation was carried out for 2 hours using ultrasonic probe reactor with 22.5 KHz frequency and a nominal power (120 W). After 30 minutes, sodium borohydride (0.1 M) was added drop wise to the solution containing bentonite, $FeCl_2$ and $CoCl_2$. Different procedure was followed for the preparation of Fe-Co as compared to that reported in literature. In our case we used a simple precipitation reduction route using sonochemical approach for formation of B- Fe Co nanocomposite [23].

The synthesis of insitu emulsion nanocomposite hydrogel using cavitation technique was carried out as follows: Water (69 g) containing SDS (0.54 g) was added to the reaction mixture and the entire solution was thoroughly deoxygenated by bubbling with argon for 45 min at room temperature. Initially 36 g of AA was added and the solution was irradiated for 10 minutes in the ultrasound reactor to form uniform monomer droplets. The temperature of the reaction mixture was maintained at 60 ^{0}C using a water bath. The liquid mixture was then subjected to sonication. 2.3 g of ammonium persulphate (APS) initiator in 5 mL distilled water was added dropwise into the reaction mixture. The polymerization reaction was completed within 40 minutes. Within the initial 15 minutes of sonication, a viscous mass was formed indicating the formation of pure poly(acrylic acid) hydrogel. The resulting polymerized hydrogel was then dried in an oven for 48 h at 85°C.

PAA-B-FeCo hydrogel was prepared in a similar manner, except for the addition of 1 g of modified B-FeCo nanoparticles to acrylic acid during polymerization. During the studies done by different researchers on the hydrogels loaded with clays, different amounts of clays are added to the hydrogels ranging from 0.5 g clay to 2 g clay by taking basis of quantities of monomer, initiator and solvent. In the present investigation bentonite-FeCo nanoparticles were added on the weight percent basis of monomer acrylic acid. Here we have added 1 g of bentonite-FeCo nanoparticles which corresponds to 2.77% (Wt %) of acrylic acid. The addition was very small to act as crosslinking agent during polymerization as it contains the clay platelets. During the sonication of this reaction mixture, the formation of thick brown solution was initially observed which was then converted into a gel. This hydrogel was dried in an oven for 48 hr at 85° C.

4.1.3 Sample characterization

UV–vis spectrophotometer (SHIMADZU 160A model) was used to determine the concentration of CV dye. The wavelength of maximum absorbance (λ_{max}) of CV dye was found to be 590 nm. Demineralized water was used as a reference. FTIR spectra of the hydrogel samples were recorded on a Perkin Elmer FTIR spectrometer (Paragon 1000 PC) in the wave number range of 500-4000 cm^{-1} with resolution of 1 cm^{-1}.

4.1.4 Swelling behavior of PAA and nanocomposite hydrogel

The swelling behavior of pure PAA and PAA-B-FeCo hydrogels was studied at 25 ^{0}C in deionized water using a gravimetric procedure [24]. Pre-weighed PAA and PAA-B-FeCo hydrogels were kept in distilled water. After regular intervals of time, weight of swollen pieces of hydrogels was measured. The weight measurement of swollen hydrogel was continued till equilibrium was reached. The swelling ratio, S was then calculated using Equation (1)

$$S = (W_s - W_d)/W_d \qquad (1)$$

Where W_s and W_d were the swollen and dry weights of the hydrogel, respectively.

4.1.5 Adsorption of CV dye

To study the effects of different experimental parameters such as, pH, temperature, concentration, quantity of hydrogel and cavitation environment in batch mode on the adsorption kinetics of CV dye onto PAA-B-FeCo hydrogel, the following procedure was carried out.

During the experiment, 100 mL of the dye solution of desired concentration with 1 g hydrogel was taken in a 200 mL beaker. The desired pH value of dye solution was adjusted using a buffer solution. The effect of initial dye concentration was studied by taking different concentrations of the dye ranging from 10 to 50 mg/L. To study the effect of hydrogel loading, different quantities of PAA-B-FeCo hydrogel (0.5– 2.0g) were used by keeping all other parameters constant. A constant temperature was maintained throughout experimentation using water bath. The percentage dye removal and dye adsorbed per mg of adsorbent (q_t) were calculated using the following equations:

$$\text{Percentage removal} = (C_o - C_e)/ C_o \times 100 \qquad (2)$$

Where, C_o and C_e are the initial and equilibrium concentrations of CV dye (mg/L), respectively.

The amount of dye adsorbed per unit mass of hydrogel can be determined using following equation,

$$q_t = (C_0\text{-}C_t)\ V/M \qquad (3)$$

V is volume of the dye solution in L and M is the mass of dry hydrogel in g.

4.1.6 Results obtained

Nanoclay supported Fe and Co particles were initially incorporated into the gallery spacing of bentonite clay by reducing Fe and Co ions inside the clay. To facilitate the incorporation of these metal particles, initially natural bentonite clay was intercalated using quaternary ammonium salts. The long chain of CTAB molecules (C_{16}-C_{18}) of the quaternary ammonium salt increases the cation exchange capacity of bentonite clay from 96 to 120 meq/g of clay. The acoustic cavitation generated physical forces increase the diffusion of precursors inside the gallery spacing. These nanoparticles remain attached to the clay platelets because of presence of CTAB in the platelets. Exfoliation of the platelets takes place during polymerization, because of the shearing effect of acoustic cavitation and hence the platelets exfoliate into the polymer. The details of the procedure and increase in d spacing are described in the literature [21-22]. A diagrammatic representation of formation of nanocomposite hydrogel is shown in **Figure 1**.

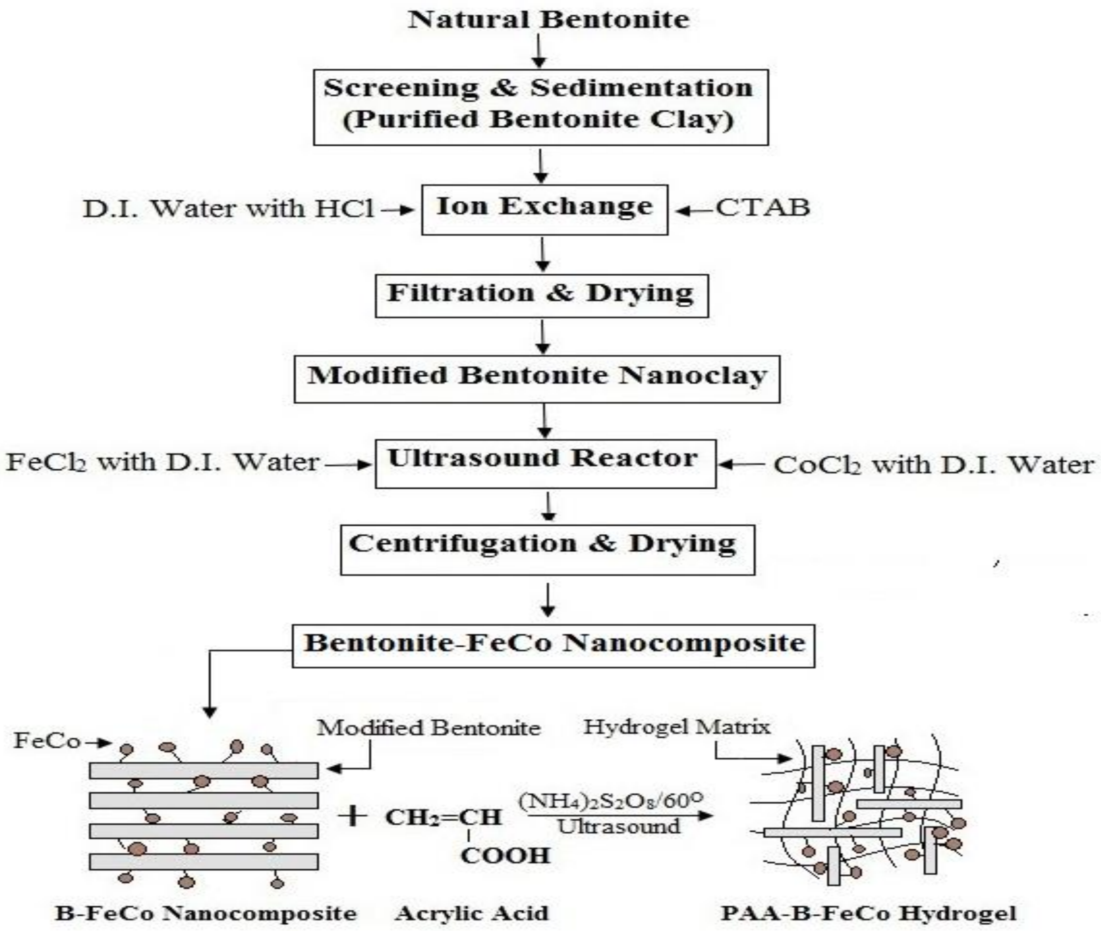
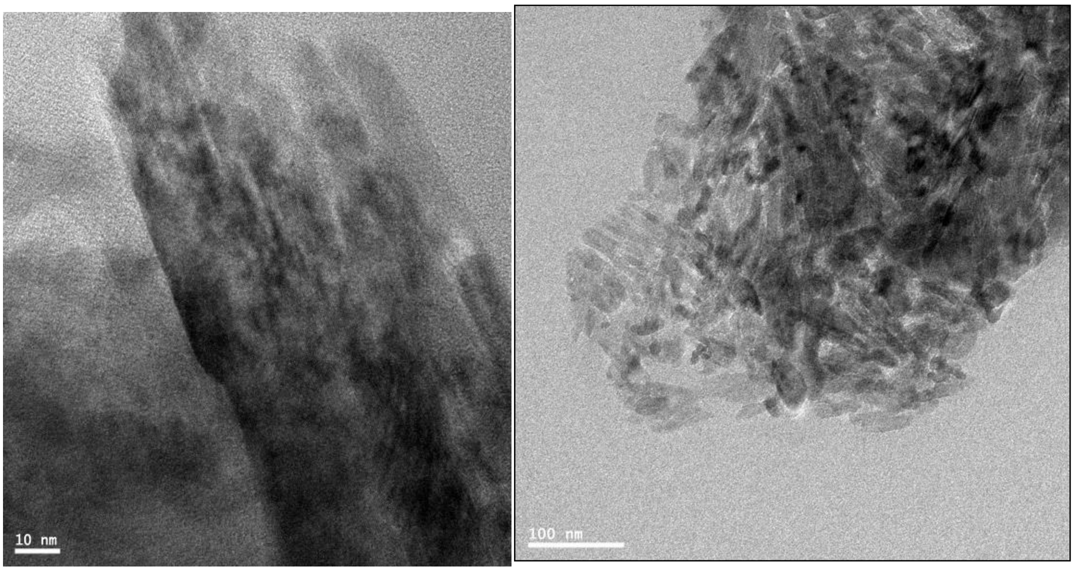


Fig. 1. Ultrasound assisted synthesis of nanoclay B- FeCo nanocomposite hydrogel

Figure 2 shows the TEM images of B-FeCo nanoparticles dispersed in the PAA hydrogel matrix. **Figure 2a** shows that the nanoparticles are uniformly distributed in the hydrogel matrix. The particle size of B-FeCo was found to be about 50 nm. **Figure 2b** shows that the particles of Fe-Co are spherical in nature. TEM images indicate that the nanoparticles are uniformly dispersed in the hydrogel matrix.



(A) (B)

Fig. 2. TEM image of (A) B-FeCo hydrogel nanocomposite, B) Fe Co particle into present in hydrogel nanocomposite

When the pure poly(acrylic acid) hydrogel was put into the dye solution it was dissolved, therefore bentonite and Fe-Co was added to the hydrogel to give it mechanical strength to prevent the collapse of hydrogel matrix. The addition of B-Fe served the dual purpose of providing the mechanical strength to the hydrogel as well as increased the adsorption capacity due to improvement in the electrostatic interaction.

As discussed in experimental section Fe-Co nanoparticles were surrounded with COOH groups of polyacrylic acid. It is important to note that bare magnetic particles in water based system are susceptible to oxidation and particles are aggregated which reduce the efficiency of separation and adsorption; hence the presence of COOH groups in the hydrogel offer improvement in the efficiency of the Fe-Co nanoparticles.

4.1.7 Swelling behavior of hydrogel

When pre-weighed samples of PAA-B-FeCo hydrogel (1 g) were kept for more than 12 h in water, the compact (dry) network structure of the polymer matrix relaxed and swollen due to the diffusion of water molecules inside the matrix, untill an equilibrium was reached. At this stage, pressure inside the hydrogel matrix increased due to the presence of large amount of water molecules. The dissolution of the hydrogel did not occur due to the presence of cross linker as against pure PAA hydrogel which dissolved in water. Hence, the mechanical strength and dissolution properties could be changed by the addition of cross linker and nanoparticles of Fe-Co during the polymerization. In this work, we have used B-FeCo as the cross linker as well as adsorbent. The B-FeCo nanocomposite hydrogel shows enhanced swelling behavior due to formation of network structure between PAA and B-FeCo.

The time dependent swelling behavior of the hydrogel is calculated by equation 4 [25].

$$F= M_t/M_s= Kt^n \qquad (4)$$

Where, 'F' is the fractional uptake at time 't', K is the diffusion constant; 'M_t' and 'M_s' are the masses of water uptake at time't' and equilibrium, respectively. Characteristic exponent 'n' is related to the transport mode of the penetrating molecule. Equation (4) is valid for the first 60 % of the fractional uptake of water. The value of 'n' for case of Fickian diffusion (rate of diffusion is slow compared to relaxation rate of hydrogel) is 0.5 and is 1 when rate of diffusion is fast compared to relaxation rate. Value of 'n' for Non-Fickian diffusion is between $0.5<n<1$ [45]. A graph of $\ln(M_t/M_s)$ against ln 't' can be used to evaluate 'n' as shown in **Figure 3**. The value of n is found to be 0.56 indicating that the transport mode of water in the gel is non-Fickian diffusion. The diffusion constant 'K' can be calculated from the intercept of the line, which is 0.13.

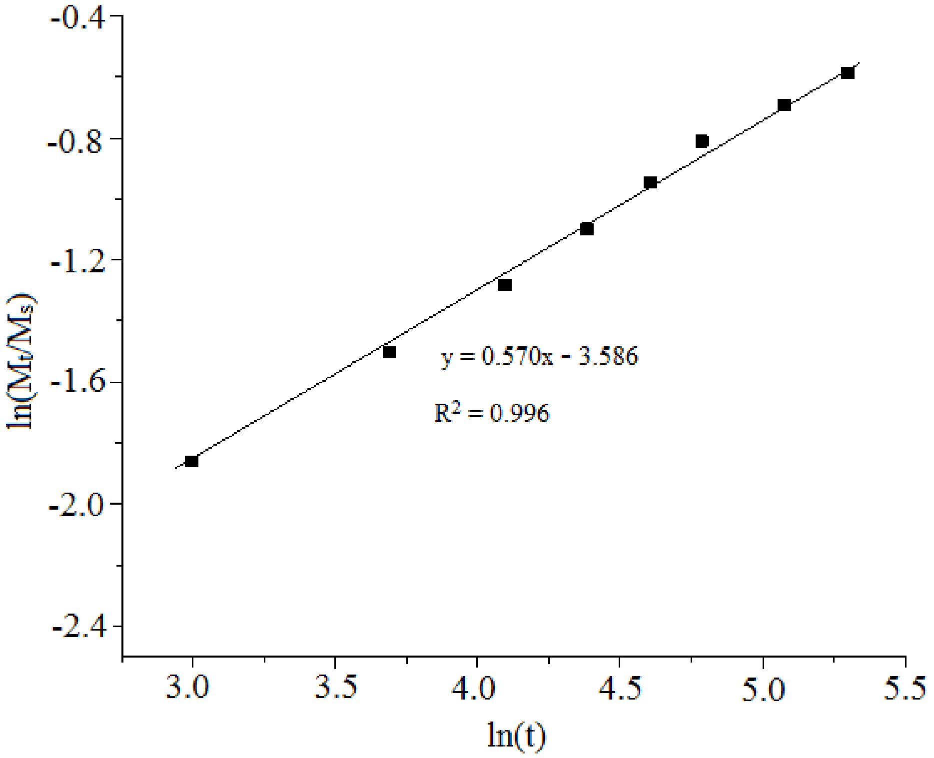


Fig. 3. Plot of ln(Mt/Ms) against ln(t) of water in PAA-B-FeCo hydrogel

4.1.8 Effect of pH on dye adsorption

The pH of the solution is an important parameter, which affects the adsorption process. The effect of solution pH depends on the ions present in the reaction mixture and electrostatic interactions at the adsorption surface. To determine the effect of different pH on CV dye removal, experiments were carried out by adjusting the pH value to 4, 9 and 11 using acid/base buffer solutions. The natural pH of the solution was 6.5. **Figure 4a** shows the effect of pH on the dye adsorption at an initial concentration of 30 mg/L in presence of 1 g of hydrogel nanocomposite. The maximum dye removal was observed (above 75 %) in the pH range of 9 to 11. At higher pH, the COOH functional groups of acrylic acid present in the hydrogel matrix dissociates to form COO^- ions, which is responsible for higher adsorption of dye in basic pH. The electrostatic attraction between the positively charged dye and negatively charged COO^- ions, results into the formation of ionic complex which increases the dye removal. Hence for further experiments, pH 11 was used as the solution pH. **Figure 4b** shows plausible responsive mechanism of adsorption of CV molecules towards hydrogel at different pH conditions.

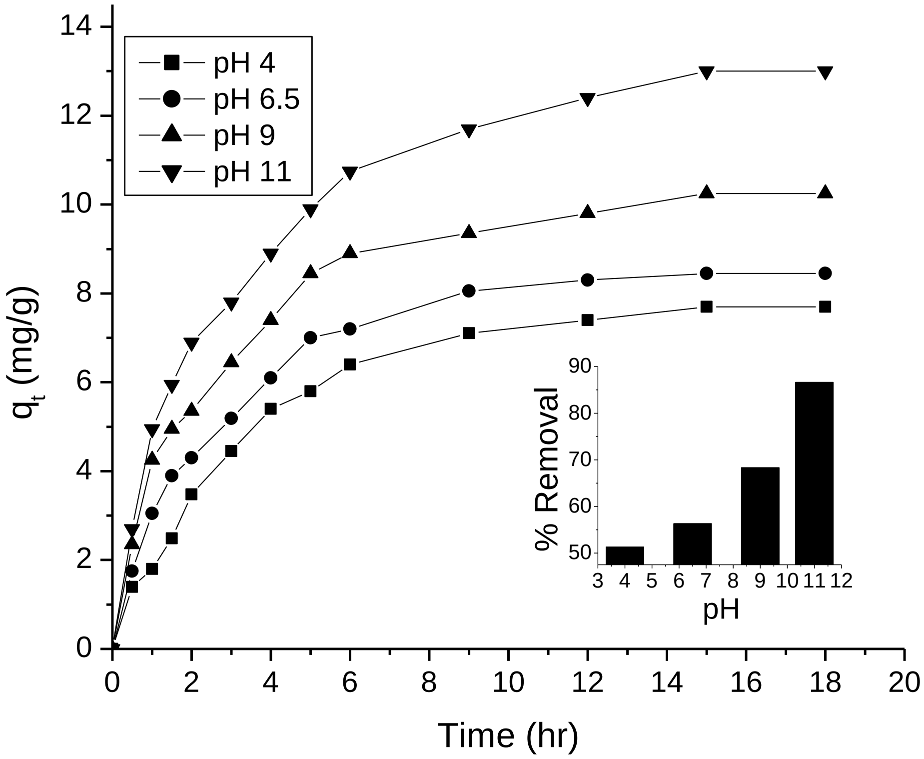


Fig. 4a. Time Vs amount of CV dye adsorbed onto PAA-B-FeCo hydrogel at 35^o C and different pH

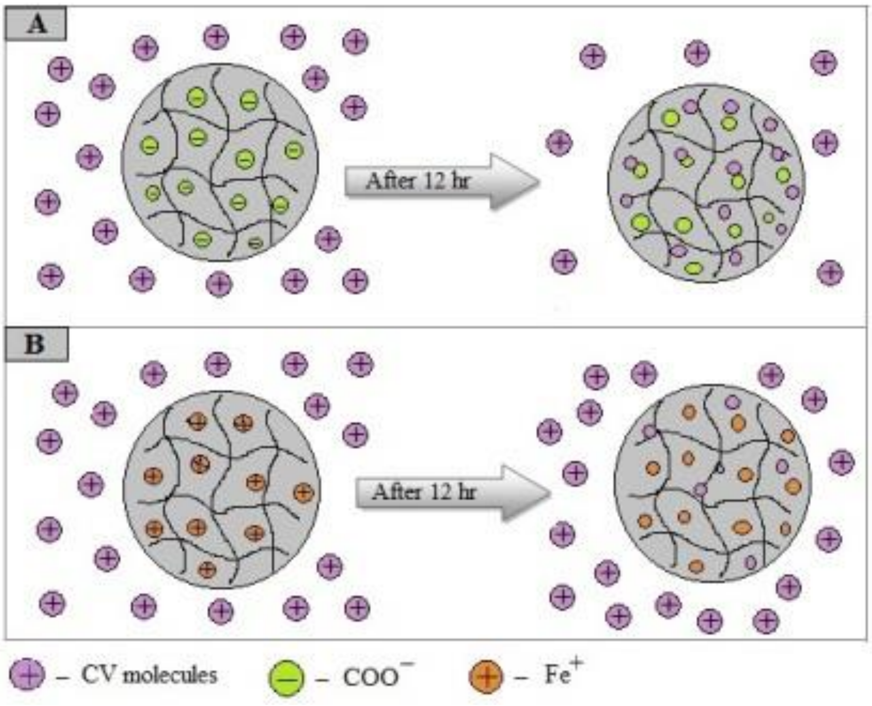
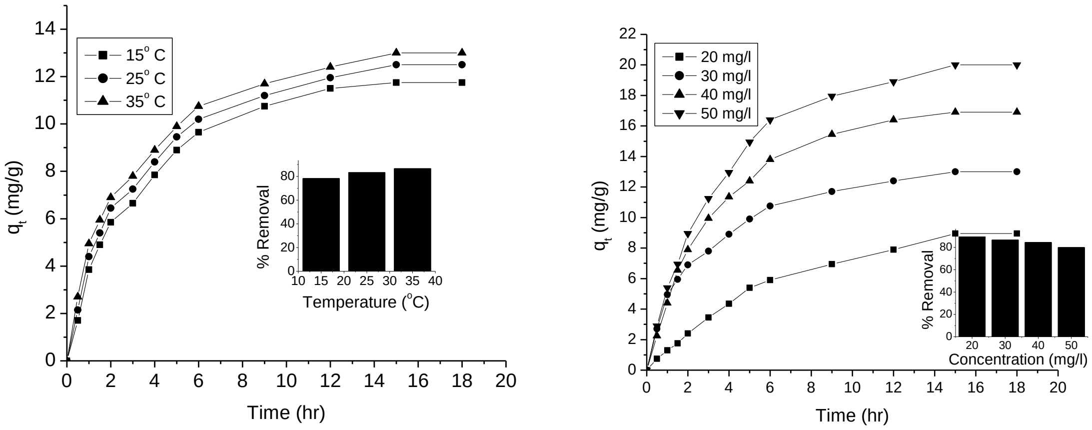


Fig. 4b. Adsorption mechanism of CV dye in PAA-B-FeCo hydrogel (A) pH 11 (B) pH 4

4.1.9 Effect of temperature

The effect of temperature on the adsorption of CV was evaluated for 1 g hydrogel with 30 mg/L dye solution at three different temperature conditions (15, 25 and 35 ^{o}C) at 11 pH value. The initial concentration was fixed but the temperature was varied. The adsorption of the dye increases with increase in temperature as shown in **Figure 5a**. This is because at higher temperature the hydrogel network gets relaxed and dye molecules can easily diffuse through the matrix resulting into more adsorption. A maximum of about 87 % removal was obtained at 35 ^{0}C, hence remaining experiments were carried out at 35 ^{0}C.



(a) (b)

Fig. 5. a) Time Vs amount of CV dye adsorbed onto PAA-B-FeCo hydrogel at different temperatures and 11 pH, (b) Time Vs amount of CV dye adsorbed onto PAA-B-FeCo hydrogel at different initial concentrations at 11 pH and 35° C

4.2.0 Effect of initial dye concentration

The adsorption capacity of hydrogel was determined by equilibrium adsorption studies, at different concentrations of CV dye ranging from 20-50 mg/L; with 1 g of PAA-B-FeCo hydrogel at pH 11 and 35° C. Results indicated that the dye uptake by hydrogel increases sharply with increasing initial dye concentration as shown in **Figure 5b**. This is because at higher initial concentration of the dye, the availability of the number of dye molecules is more, which can easily penetrate through hydrogel. However, the removal efficiency was reduced at high concentrations, because the hydrogel gets saturated.

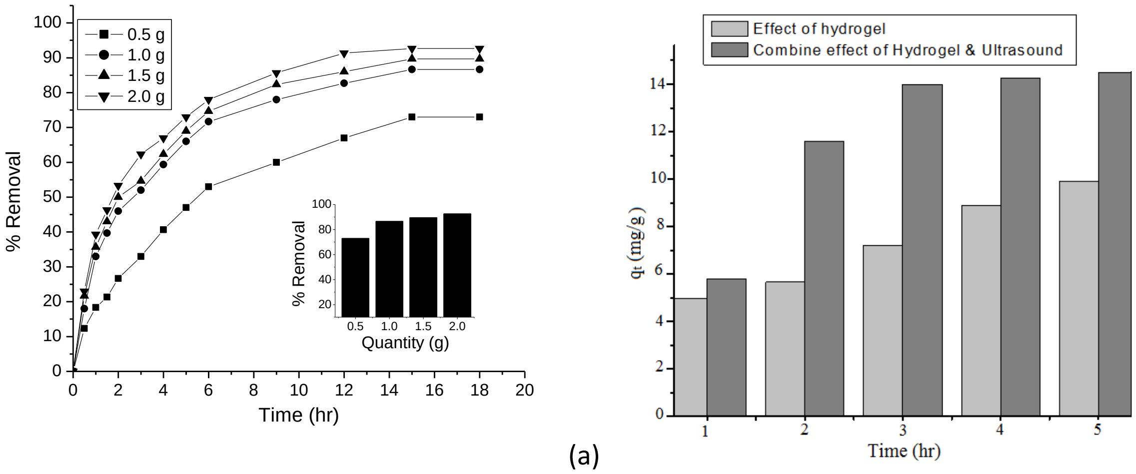
Compared to the previous research performed by Zhang et al. [26] for adsorption of CV on composite hydrogel (adsorption capacity = 0.3 mg/g), the PAA-B-FeCo hydrogel prepared in the present investigation shows far better results (adsorption capacity = 13 mg/g). The results are also superior in comparison with the use of wollastonite as an adsorbent (adsorption capacity = 0.88 mg/g) [27]. These results may be attributed to the fact that there may be large number of charge groups on the clay surface and absence of organic cross-linker in the composites leads to flexible polymer chains so that the cationic dye molecules can easily enter into the hydrogel network and interact with the clay.

4.2.1 Effect of quantity of hydrogel

The effect of hydrogel quantity on adsorption was studied by using different amounts of hydrogel (0.5, 1, 1.5, 2 g) in 30 mg/L concentration of 100 mL CV dye solution. **Figure 6a** shows that the percent removal of the dye increases with an increase in the quantity of hydrogel. About 95 % of dye was removed, when 2 g of hydrogel sample was kept in the solution. This indicates that the presence of higher quantity of hydrogel provides large number of negatively charged ions to adsorb more amount of CV dye due to electrostatic force.

4.2.2 Effect of ultrasound in dye removal

In this experiment, combined effect of ultrasound and hydrogel adsorption was evaluated and compared. In both the experiments 100 mL solution of 30 mg/l concentration and 1 g of hydrogel was used. The removal efficiencies for hydrogel alone and the combined effect of ultrasound and hydrogel are shown in **Figure 6b**, which indicates that combination of hydrogel and ultrasound gives higher dye removal as compared to hydrogel adsorption alone. With hydrogel alone, 87 % removal was achieved in 15 h and with combination of ultrasound 97 % removal was achieved in only 5 h. This enhancement could be due to the mechanical agitation generated by the physical forces generated by acoustic cavitation.



(a)

(b)

Fig. 6. (a) Time vs percentage removal of CV dye at different initial quantity of PAA-B-FeCo hydrogel at 11 pH and 35° C (b) Time Vs quantity of CV dye adsorbed using hydrogel & hydrogel with ultrasound at pH 11 and temperature 35° C

4.2.3 FTIR Study

Figure 7 shows FTIR spectra of pure PAA, PAA-B-FeCo hydrogel, before and after adsorption of the dye respectively. The FTIR spectra of the pure PAA and PAA-B-FeCo hydrogel show the peak at 1700 cm^{-1}, which is characteristic peak of the C = O stretching due to presence of carboxyl groups in poly(acrylic acid). After the adsorption of the dye, this band is shifted to 1690 cm^{-1} . The FTIR spectra of PAA-B-FeCo hydrogel after the adsorption of CV dye shows a peak at 3500 cm^{-1} which originates due to the formation of hydrogen bond between hydogel and the dye. The presence of band at 3610 cm^{-1} indicates the OH stretching vibration of bentonite clay. There are small bands originating at 1539 and 1400 cm^{-1} which are due to the stretching of –COOH and –COO$^-$ groups at higher pH value.

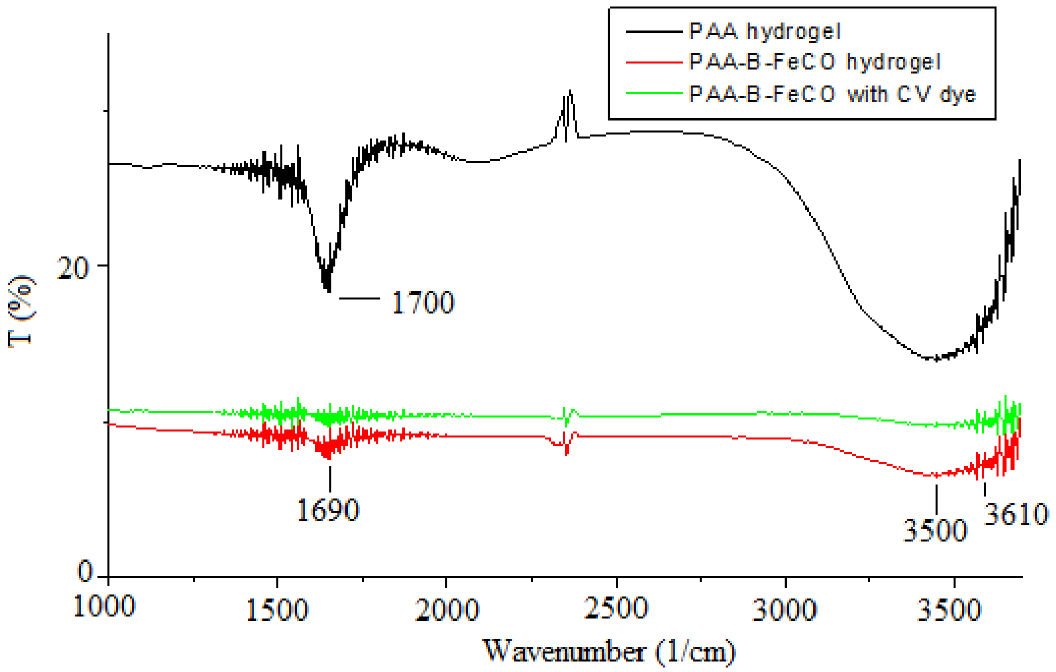


Fig. 7. FTIR spectra of pure PAA hydrogel, PAA-B-FeCo hydrogel before and after adsorption of CV

4.2.4 Adsorption isotherm model

Equilibrium data in terms of adsorption isotherm is a basic requirement for the design of adsorption systems. The equilibrium removal of dyes was mathematically expressed in terms of Langmuir and Freundlich adsorption isotherms. The Langmuir equation is based on the assumption that maximum adsorption corresponds to saturated monolayer of the adsorbate molecule on the adsorbent surface. In Langmuir equation,

$$C_e/q_e = 1/(\alpha Q_m) + C_e/Q_m \quad (5)$$

the constant α is related to the energy of adsorption, C_e (mg/L) is the equilibrium concentration of the dye in solution, q_e (mg/g) is the amount of adsorbed dye on the adsorbent surface and the constant Q_m represents the maximum binding at the complete saturation of adsorbent binding sites. Q_m and α values can be obtained from slope and intercept of the linear plot of C_e/q_e vs C_e (**Figure 8a**), respectively. The values of Q_m and α are given in **Table 1a**. It can be seen that the adsorption of the dye on PAA-B-FeCo hydrogel followed the Langmuir model.

The Freundlich isotherm model suggests that sorption energy exponentially decreases on completion of the sorptional sites of adsorbent. This isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich isotherm is described by equation

$$q_e = K_F \times \log C_e^{(1/n)} \qquad (6)$$

Taking log on both sides,

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (7)$$

Where, K_F and n are the physical constants of the Freundlich isotherm. The slope and intercept of the linear plot of log q_e vs log C_e (**Figure 8b**) give the values of n and K_F. Values 1/n indicate the type of isotherm to be irreversible ($1/n=0$), favorable ($0<1/n<1$) or unfavorable ($1/n>1$). The results showed that besides the Langmuir isotherm, Freundlich isotherm is also suitable for describing the adsorption of CV dye on PAA-B-FeCo hydrogel. The Freundlich constants are given in **Table 1a**.

4.2.5 Thermodynamic parameters

The thermodynamic parameters ΔG^o, ΔS^o and ΔH^o for this adsorption process are determined by using following equations [28,29].

$$\Delta G^o = -RT \ln K \qquad (8)$$

where K is the thermodynamic equilibrium constant. The effect of temperature on thermodynamic constant is determined by

$$d \ln K/dt = \Delta H^o/RT^2 \qquad (9)$$

Integrating & rearranging equation (9)

$$\ln K = - (\Delta H^o/RT) + \Delta S^o/R \qquad (10)$$

and Gibbs free energy is given by

$$\Delta G^o = \Delta H^o – T \Delta S^o \qquad (11)$$

Where ΔG^o is the free energy change (J/mol); R is the universal constant (8.314 J/mol K) and T the absolute temperature (K).

The values of K can be determined by plotting $\ln(q_e/C_e)$ against q_e and extrapolating to zero (**Figure 8c**). The ΔH^o and ΔS^o values were calculated from slope and intercept of the linear plot, of lnK vs 1/T as shown in **Figure 8d.** The corresponding values of thermodynamic parameters are presented in **Table 1b**. The negative values of ΔG^o indicates that the dye adsorption process is spontaneous and feasible. The positive value of ΔH^o shows the adsorption process is endothermic in nature.

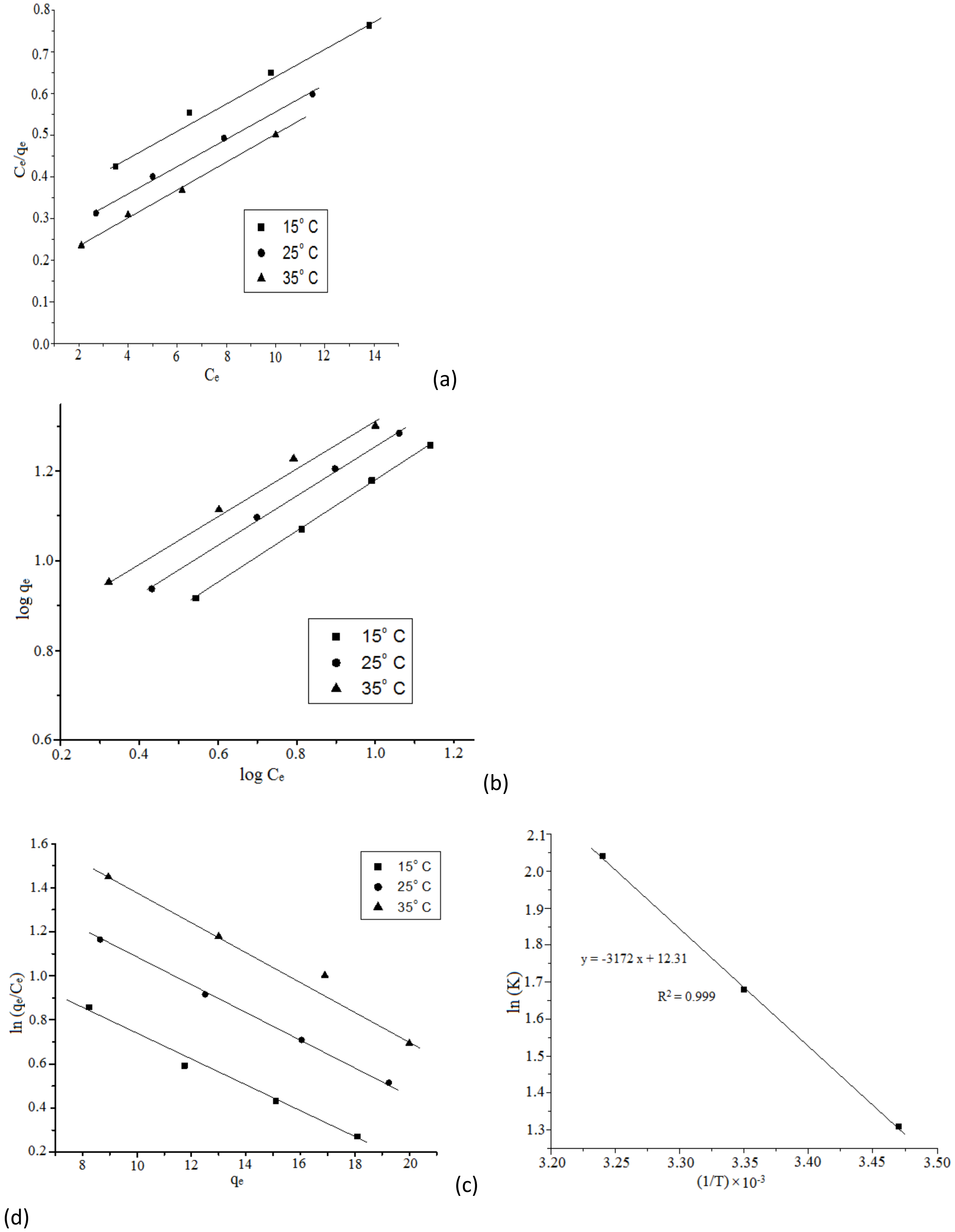


Fig. 8. Plot of (a) C_e/q_e vs C_e for Langmuir isotherm, (b) log qe vs log Ce for Freundlich isotherm, (c) ln (q_e/C_e) vs q_e for K values at different temperatures and (d) Plot of ln K vs 1/T

Table. 1a. Langmuir and Freundlich isotherm constants

Temperature (K)	**Langmuir constants**		
	Q_m (mg/gm)	α	R^2
288	30.30	0.098	0.989
298	31.15	0.138	0.996
308	31.25	0.197	0.997
Temperature (K)	**Freundlich constants**		
	K_F	n	R^2
288	3.98	1.754	0.999
298	5.01	1.818	0.998
308	6.16	1.923	0.988

Table. 1b. Thermodynamic parameters of adsorption of dye onto nanocomposite hydrogel

Temperature (K)	**lnK**	**ΔG^o (J/mol)**	**ΔH^o (J/mol)**	**ΔS^o (J/(mol K))**
298	1.31	-3358.86	26372	99.77
308	1.68	- 4354.08		
318	2.04	- 5351.68		

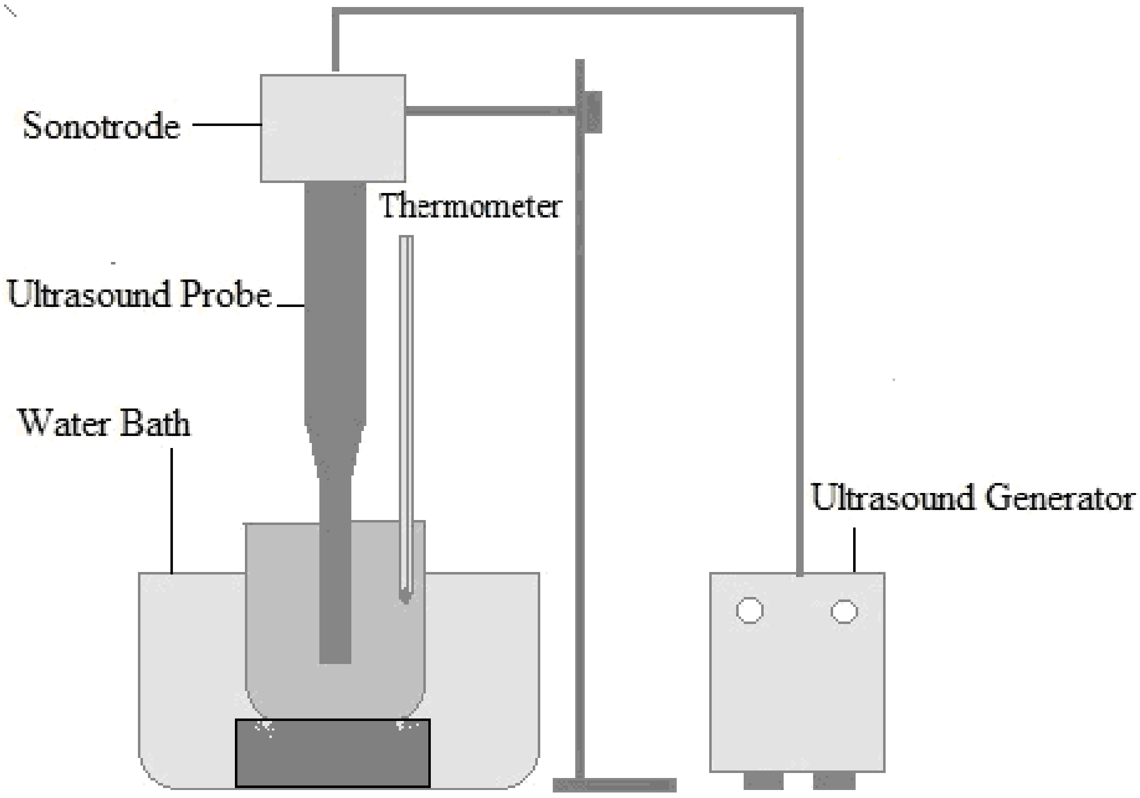
4.3 A case study on removal of brilliant green from wastewater using conventional and ultrasonically prepared Poly(acrylic acid) hydrogel loaded with Kaolin clay

4.3.1 Materials

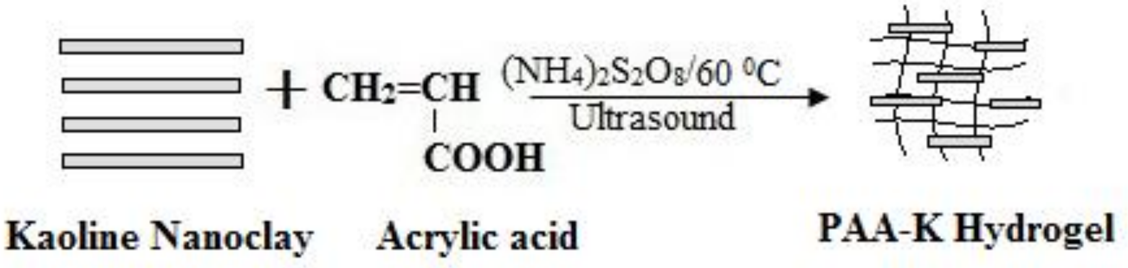
Acrylic acid (AA), Ammonium persulphate (APS), Sodium dodecyl sulfate (SDS) and Brilliant green dye (BG) were of analytical grade and procured from M/s CDH, India. Kaolin (China clay) clay was obtained from MD chemicals Pune, India and used without any further purification. Deionized water was used for dilution in all the experiments.

4.3.2 Synthesis of poly(acrylic acid)-Kaolin (PAA-K) hydrogel using insitu ultrasound assisted emulsion polymerization and conventional process.

PAA-K hydrogel has been synthesized from acrylic acid (monomer), APS (initiator), and SDS (surfactant). Initially, the reactor was flushed using argon to maintain inert atmosphere. In the actual synthesis process, 36 g of acrylic acid with 100 mL water was loaded into the ultrasound polymerization reactor. In other beaker, SDS - kaolin solution was prepared using 0.5 g of SDS and 0.36 g kaolin in 20 mL water (corresponding to 1.0 % (wt %) of acrylic acid). The mixture was then homogeneously mixed using ultrasound bath and added into a polymerization reactor. Then the solution was irradiated for 5 minutes using ultrasonic horn (Dakshin make, 22 mm probe diameter) operating at 22.5 kHz frequency and rated power of 120 W. The total acoustic power dissipated into the sample was calculated using calorimetric method. The total power dissipated into polymerization reactor was 12.5 W/m^3. The objective of using the ultrasonic irradiation was to form uniform small size emulsion droplets which will remain stable and hence, will give uniform final polymer particle size. APS solution was prepared by mixing 0.1 g of APS in 10 mL water and it was added into the reactor as initiator. Reactor temperature was maintained at 60 ^{o} C for 30 minutes. Argon gas was used for blanketing of the polymerization reactor to avoid the contact with atmosphere. The presence of ultrasonic environment in the polymerization reactor assisted the uniform distribution of kaolin platelets through hydrogel network. Another hydrogel containing 2 % (wt %) kaolin was also prepared to study the effect of kaolin loading. **Figure 9 a** shows the experimental setup for the synthesis of hydrogel by ultrasound assisted method and **Figure 9 b** shows the schematic representation of the process of the formation of PAA-K hydrogel. Similar procedure was used for conventional synthesis in which the temperature of the polymerization reactor was maintained at 60° C and the reaction was carried out for 60 min under mechanical stirring instead of using ultrasound probe. In both the preparation methods, the formation of thick solution was initially observed which was then transferred into a sticky suspension. However during the ultrasonic synthesis less time was required for the formation of the gel. The reduction in time compared to conventional synthesis is due to the cavitational effect. Further, the rapid micromixing and implosive collapse of bubbles in a liquid solution could have resulted in extremely high temperature which may have accelerated the reaction.



(a)



(b)

Fig. 9. (a) Experimental set up for synthesis of hydrogel by ultrasound assisted method, (b) Schematic representation of the formation of hydrogel

4.3.3 Water uptake of hydrogel

To confirm the swelling behavior of synthesized hydrogel, 1 g of PAA-K hydrogel was allowed to swell in 100 mL of deionized water at 30 °C for 3 h. At predetermined time intervals, the hydrogel was taken, wiped with filter paper to remove excess water and was weighed to find the water content. The swelling ratio, *S*, was calculated using equation (1)

$$S = \frac{W_s - W_d}{W_d}$$

Where W_s and W_d are the swollen and dry weights of the hydrogel respectively.

4.3.4 Adsorption of BG dye

The adsorption experiments were carried out in a batch mode to study the effect of different parameters like pH, temperature, initial dye concentration, quantity of hydrogel and clay content on the extent of adsorption. PAA-K hydrogel (1 g) was added to 100 mL of aqueous dye solution of known concentration and pH of the solution was adjusted using buffer solution. The effect of initial BG concentration was investigated over the concentration range of 10 to 50 mg/L. The effect of hydrogel loading was investigated using different quantities of PAA- K hydrogel over the range 0.5 to 2 g. Temperature was maintained constant throughout the duration of experiments using water bath. The percentage dye removal has been calculated using the following equation (2):

Percentage removal = $(C_o-C_e)/C_o \times 100$

where, C_o and C_e are the initial and equilibrium concentrations of BG dye (mg/L).

Amount of dye adsorbed per unit mass of hydrogel (mg/g) has been determined using following equation (3).

$q_t = (C_0-C_t)\ V/M$

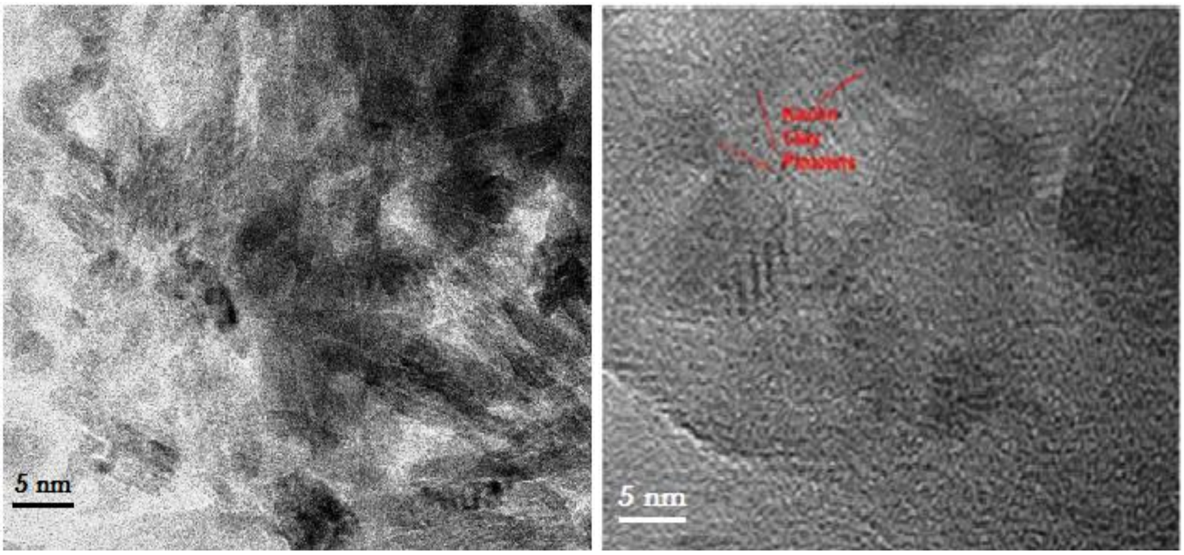
Where V is volume of the dye solution in L and M is the mass of dry hydrogel in gm.

4.3.5 Analysis and Characterization

The concentration of Brilliant Green (BG) was measured using UV–vis spectrophotometer (SHIMADZU 160A model). The wavelength of maximum absorbance (λ_{max}) of BG was found to be 624 nm. Deionized water was used as a reference. FTIR Spectra of the hydrogel samples were recorded on Perkin Elmer FTIR spectrometer (Paragon 1000 PC) in the wave number range of 500-4000 cm^{-1} with resolution of 1 cm^{-1}. FTIR of the sample was taken after partially drying the hydrogel in an oven at 60 ^{o}C for 180 min. Transmission electron microscopy (TEM, magnification 7,50,000 X) image was taken on a Philips Tecnai 20 model.

4.3.6 Morphology of polyacrylic acid and nanocomposite hydrogel

With an objective of investigating the efficacy of dispersion of kaolin clay in the PAA hydrogel matrix, Transmission Electron Microscope (TEM) images of the dried PAA-K hydrogel (0.36 g clay) prepared by conventional as well as ultrasound method have been obtained and shown in the **Figure 10**. **Figure 10a** shows the TEM image of polycyclic acid hydrogel with kaolin prepared by conventional method whereas Figure 2b gives the image for the ultrasonically prepared hydrogel. The presence of dark-spots in both the figures confirms the occurrence of kaolin clay in the hydrogel matrix however it can be observed in the case of **Figure 10a** that the kaolin particles are not uniformly distributed through the hydrogel matrix and aggregation of kaolin particles can be seen at different locations. In contrast, it can be clearly established from the depicted image for the ultrasound assisted synthesis **(Figure 10b)** that the clay platelets are substantially exfoliated and dispersed homogeneously throughout the polymer matrix. Thus, fine and homogeneous clay dispersion was achieved in the hydrogel matrix due to the presence of ultrasound. The complete exfoliation of clay platelets and insertion of polyacrylic acid chains into the gallery spacing of clay is due to the shear and turbulence effects of the cavitation phenomena occurring during the emulsion polymerization. The particle size of kaolin clay was measured from the TEM images, the black spots in **Figure 10b** indicates the presence of clay. The particle size of the kaolin clay was found to be in the range of 20-50 nm.



(a) (b)

Fig. 10. Transmission electron microscopic images of PAA-K nanocomposite hydrogel (a) conventional method, (b) ultrasound assisted method

4.3.7 Swelling behavior of PAA-K hydrogel

The time dependent swelling behavior of hydrogels has been described by a power-law function as shown in the equation (4).

$F = M_t/M_s = Kt^n$

where, F is the fractional uptake at time t, K is a constant depending on the type of the diffusion system, and ‘n’ is related to the transport mode of the penetrate. M_t and M_s are the mass uptake of water at time t and equilibrium respectively. Equation (4) is valid for the initial 60 % of the fractional uptake. The plot of ln (M_t/M_s) against ln (t) depicting the swelling behavior of PAA-K hydrogel synthesized using conventional method and ultrasound assisted method has been shown in **Figure 11**. For the diffusion of water in the hydrogel, value of ‘n’ in equation (4) has been found to be 0.39 for hydrogel prepared by conventional method as against 0.87 for the ultrasound assisted method. The diffusion of solvent into a polymer is a combination of two different processes: the diffusion of the solvent into the swollen matrix, and the advancement of the swollen–unswollen boundary as a result of the stress induced in the polymer. When the first mechanism is the rate determining step there is a linear dependency between the solvent uptake and time and the system exhibits Fickian behavior. Also the value of n is a characteristic exponent of the mode of transport of the penetrating molecule and it actually indicates the type of diffusion inside the hydrogel. The values of n for Fickian diffusion and case II transport are 0.5 and 1, respectively whereas for the n value between 0.5 to 1, it is usually described as the non-Fickian diffusion, which is considered the intermediate between Fickian diffusion and case II transport. In the present investigation, from the obtained values of n, we can conclude that for conventionally synthesized hydrogel the Fickian behavior was observed while for ultrasonically synthesized hydrogel non fickian behavior was observed indicating that the advancement of the swollen–unswollen boundary was slower than the diffusion of the solvent in the swollen polymer indicative of zero-order kinetics. As a result, the water uptake increased linearly with the sorption time. The value of n varied significantly as a result of change in the method of preparation and therefore different diffusion behaviors are expected.

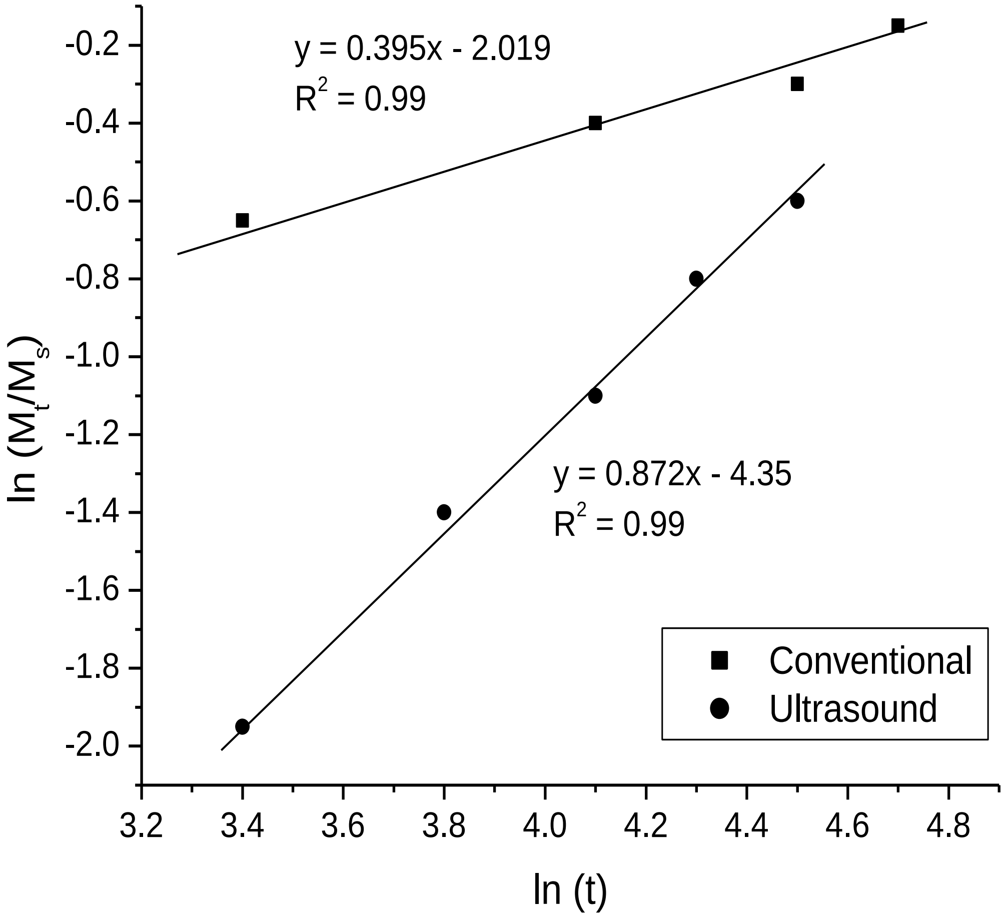


Fig. 11. Plot of ln(Mt/Ms) against ln(t) of water in PAA-K hydrogel

4.3.8 Effect of pH on the responsive adsorption of BG dye

The initial pH of the dye solution is an important parameter, which controls the adsorption process, especially the adsorption capacity. The operating pH of the solution changes the surface charge of the adsorbent, the degree of ionization of the adsorbate molecule and the extent of dissociation of functional groups on the active sites of the adsorbent. The influence of solution pH on the extent of removal of the dye was investigated over the pH range of 4–9 using acidic and basic buffer solutions. The percentage dye removal for the initial dye concentration of 30 mg/L and 1g hydrogel at different operating pH has been shown in **Figure 12.** For both preparation methods it has been observed that the maximum adsorption takes place at pH value of 7. The extent of removal of dye increases with an increase in the pH till an optimum value of 7, beyond which it gradually decreases. The observed results can be attributed to the fact that the pH value affects the structural stability of Brilliant Green molecules. For kaolin, the point of zero charge (ZPC) is 7.0. Below this range, the kaolin surface acquires positive charge and there would be an electrostatic repulsion between cationic dye molecules and kaolin. Above a pH of 7, the kaolin particle acquires a negative surface charge. This should lead to higher cationic dye adsorption, however, this behavior has not been observed in the present investigation as seen in **Figure 12**. The observed trends can be attributed to the chemical structure of a dye molecule and its behavior under alkaline conditions.

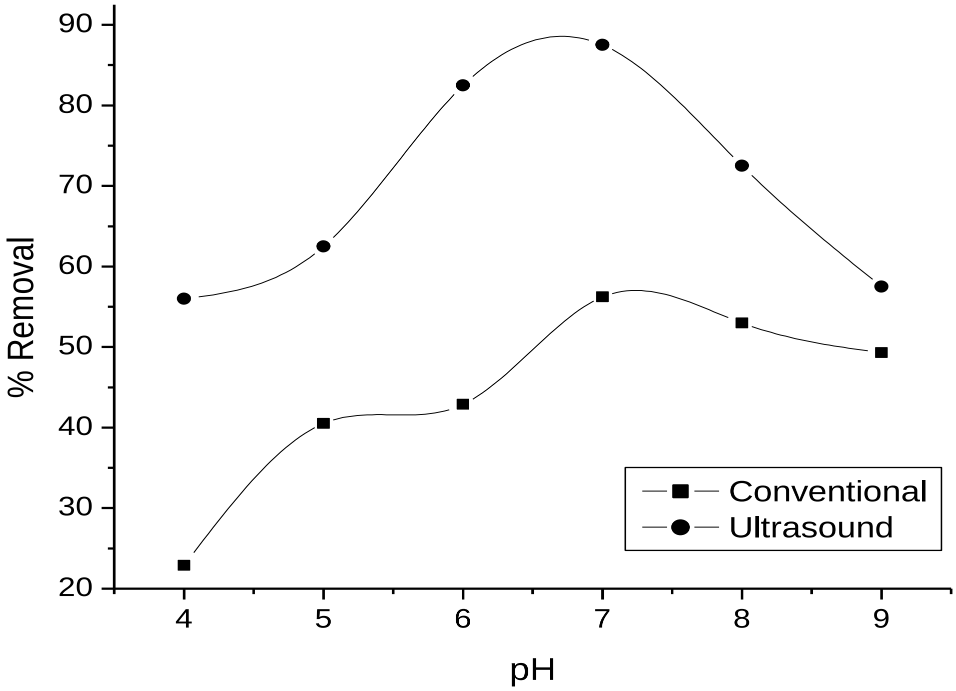


Fig. 12. Effect of pH on adsorption of BG dye on PAA-K hydrogel at 35 °C

4.3.9 Effect of operating temperature on the responsive adsorption of dye

The influence of operating temperature on the adsorption process has been studied at three different temperatures as 15, 25 and 35 °C and the obtained results have been shown in

Figure 13. It can be seen from the figure that the adsorption of the dye increased with an increase in the operating temperature. The maximum extent of removal obtained at 35 ^{0}C was 56.24 % for the conventional method and 88.3 % for ultrasonic method **(Figure 13)**. The observed results can be attributed to the relaxing of the hydrogel network at higher temperatures, due to which the dye molecules can diffuse more easily through the matrix resulting into more adsorption. However it should be noted that the temperature cannot be increased indefinitely as collapse of hydrogel matrix may take place due to heat effects. It has been demonstrated that many hydrogel show continuous volume transition with change in the temperature and highly swollen gel network can collapse at high temperatures. Based on these results and related discussion, the operating temperature was fixed at 35 ^{0}C for all the further experiments.

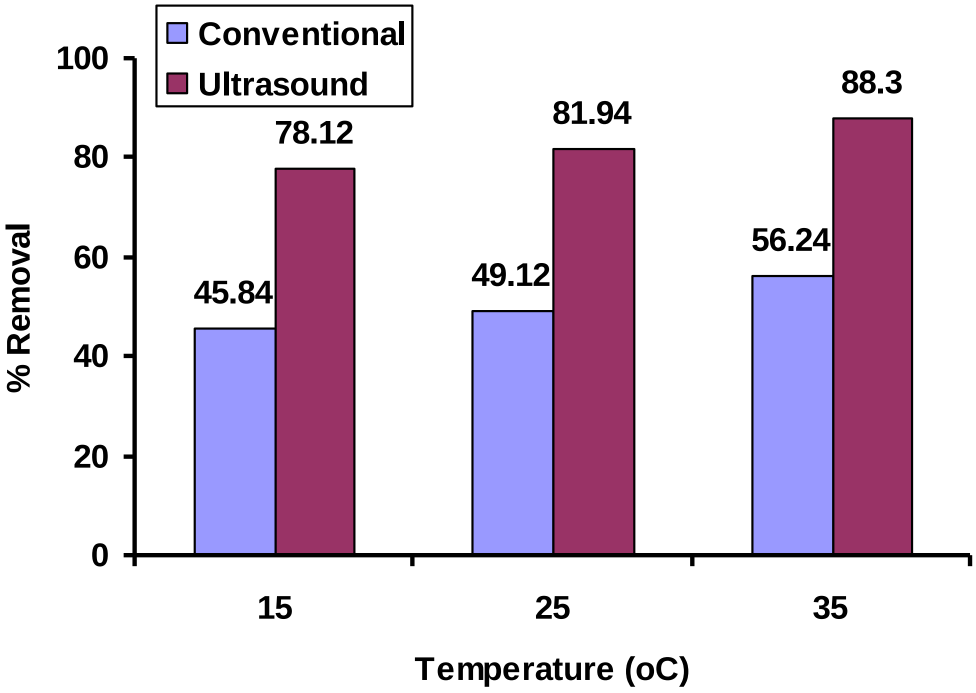
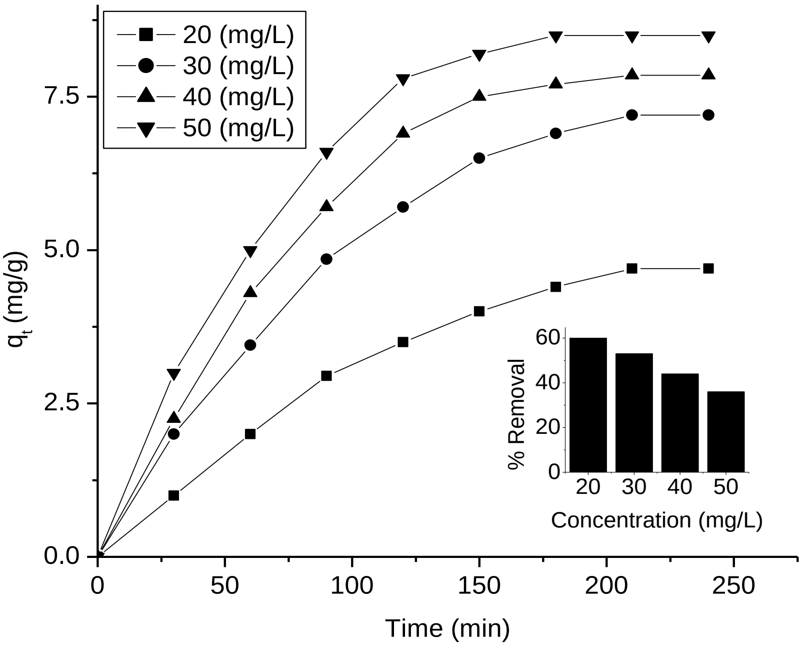


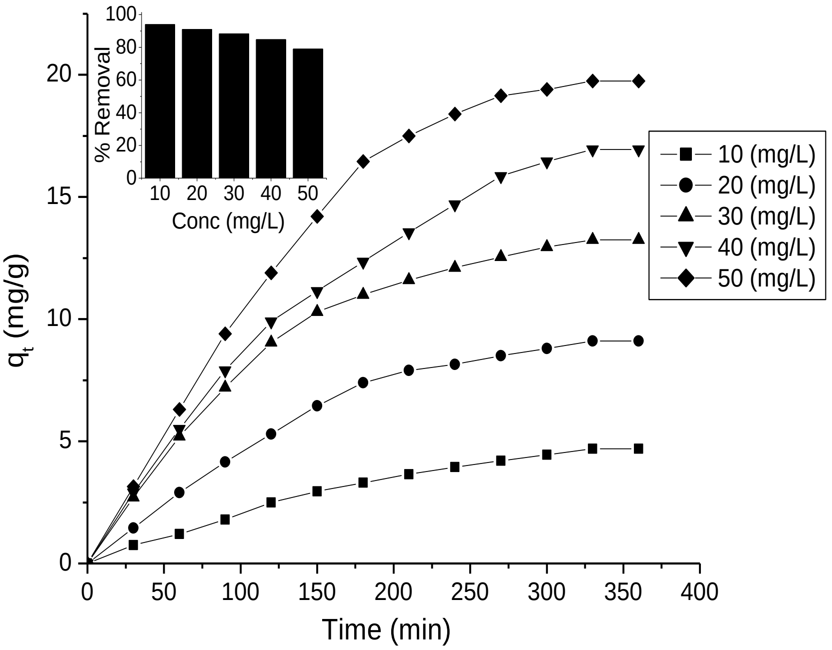
Fig. 13. Effect of temperature on adsorption of BG dye in PAA-K hydrogel at pH 7 for conventional method and ultrasound assisted method

4.4.0 Effect of initial concentration of dye

The effect of initial concentration of dye on the extent of removal has been investigated by varying the initial concentration of BG dye over the range 10-50 mg/L. The solution of dye was mixed with 1 g of PAA-K hydrogel at pH 7 and 35°C temperature and then equilibrated for 5 h. The obtained results indicate that the dye uptake by hydrogel increases sharply with an increase in the initial dye concentration for both the preparation methods as shown in the **Figure 14**. The obtained trends can be attributed to the fact that with increasing concentration of BG in the initial solution, higher concentration gradient at the hydrogel–solvent interface exists resulting in an enhancement of the BG removal rate. It is also seen that for the hydrogel prepared by ultrasonic method the extent of removal was increased by almost 30 % as compared to conventional method. This may be attributed to the cavitational effects such as formation of micro-jets and turbulence during polymerization resulting in uniform distribution of kaolin clay throughout the hydrogel matrix. The change in color of both the hydrogel and dye solution before and after the adsorption has been shown in **Figure 15**.



(a)



(b)

Fig. 14. Effect of initial concentration on adsorption of BG dye in PAA-K hydrogel at pH 7 and 35°C (a) conventional method, (b) ultrasound assisted method

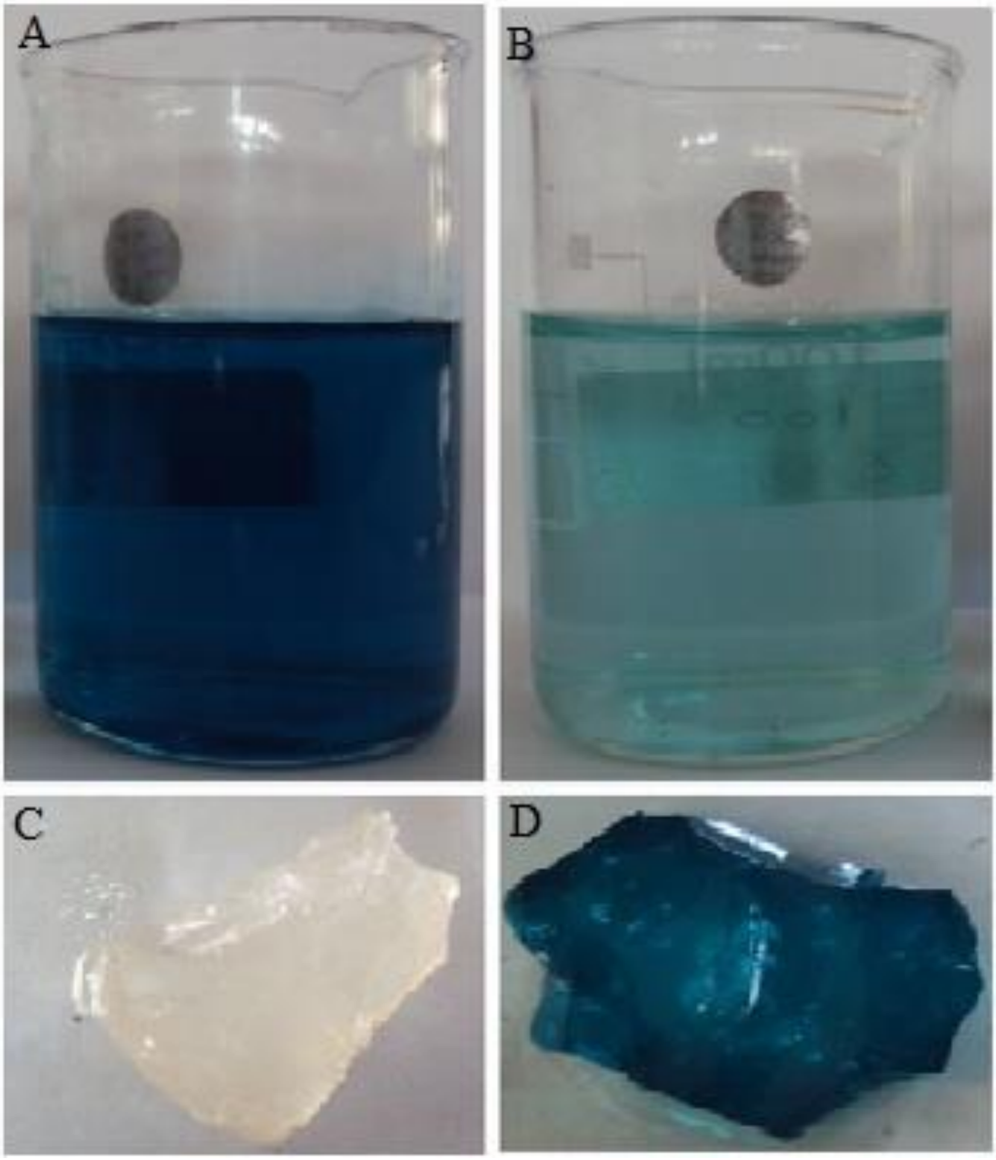


Fig. 15. Colour changes of BG dye and hydrogel before (A), (C) and after adsorption (B), (D) respectively

4.4.1 Effect of quantity of hydrogel and kaolin loading

The effect of hydrogel loading on the extent of removal of dye was studied by using different amounts of hydrogel (0.5, 1, 1.5, 2 g) in 100 mL of fixed concentration (30 mg/L) BG dye solution. **Figure 16** shows that the percent removal of the dye increases with an increase in the quantity of hydrogel. The higher dye removal, close to 100%, was reached when 2 g of ultrasonically synthesized hydrogel was used. This indicates that the presence of higher quantity of hydrogel provides large number of active adsorbent sites to enhanced quantum of the pollutant. At the same time when the conventionally synthesized hydrogel was used, 2 g hydrogel was able to remove only 63 % dye.

Effect of the clay content on BG adsorption was investigated for PAA-K hydrogel prepared by both methods. For this purpose, PAA-K hydrogel was loaded with two different amounts viz. 0.36 g (1 wt% of monomer) and 0.72 g (2 wt% of monomer) of the kaolin clay. The PAA-K hydrogels containing different amounts of kaolin were added to 100 mL solutions of BG dye with different concentrations (10-50 mg/L) at 35 ^{0}C in a water bath. The removal efficiency (RE %) of the dye by the PAA-K hydrogel containing different amounts of clay has been shown in **Figure 17**. **Figure 17a** shows the dye removal for conventional method and **Figure 17b** shows the same for ultrasound assisted synthesis method. It can be seen from both the figures that the dye uptake increases with increasing clay content. The obtained results can be explained on the basis of the fact that enhanced adsorbent active sites are available with an increase in the kaolin content. However there was not a major enhancement in the removal efficiency with the increase in the quantity of kaolin from 1 % to 2 % (wt % monomer).

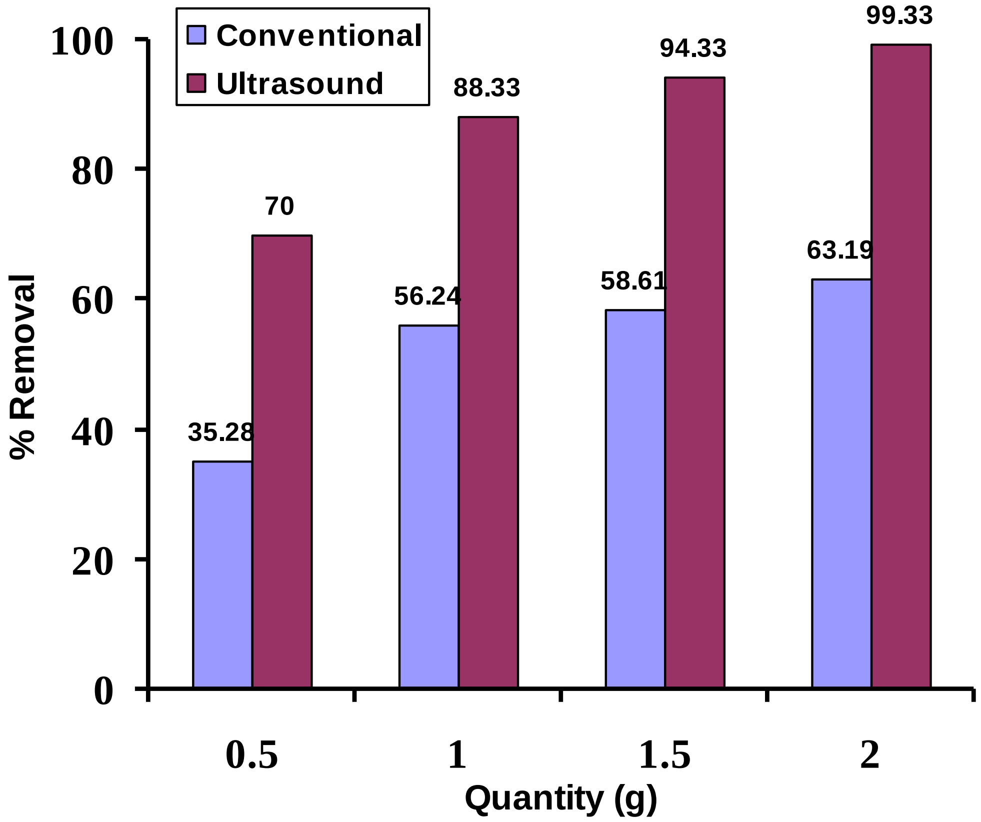


Fig. 16. Effect of initial quantity of PAA-K hydrogel on removal of BG at pH 7 and 35 ^{o}C

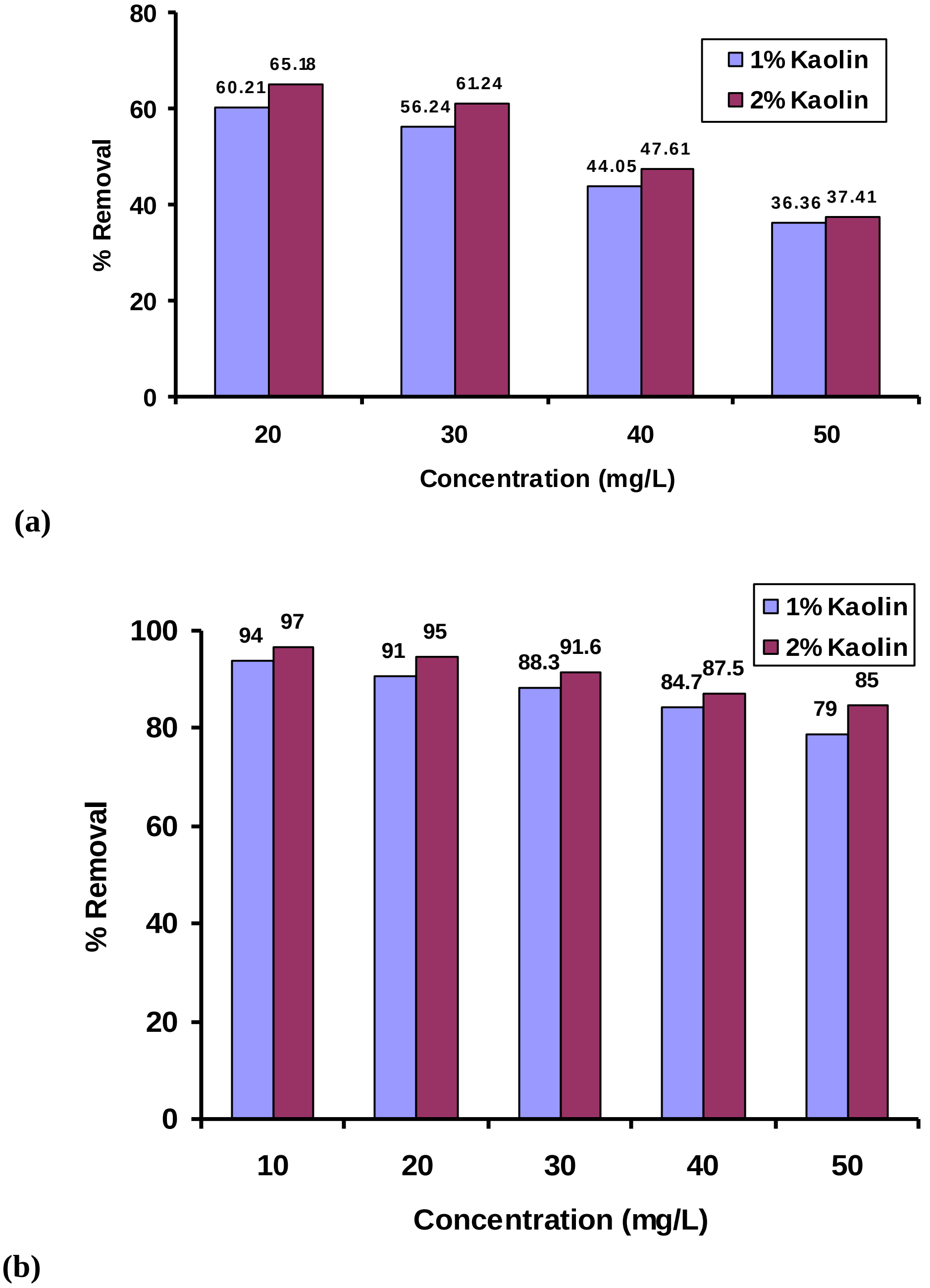


Fig. 17. Effect of clay loading in PAA-K hydrogel for the adsorption of BG dye at pH 7 and 35^{o}C (a) conventional method, (b) ultrasound assisted method

4.4.2 FTIR Study of hydrogel nanocomposite before and after adsorption

The characterization of hydrogel was obtained using FTIR analysis to study the interaction between the dye molecules and the PAA-K hydrogel and to confirm the presence of carboxyl group of acrylic acid. **Figure 18** shows FTIR spectra of PAA-K hydrogel (synthesized by ultrasonic method), before and after adsorption of the dye. It can be seen from the spectra that before adsorption, the FTIR spectra of the PAA-K hydrogel shows a peak at 1700 cm^{-1}, which is characteristic peak of the C = O stretching due to the presence of carboxyl groups in poly(acrylic acid). After the adsorption of the dye, the band is shifted to 1625 cm^{-1}. Also, after the adsorption of dye, the FTIR spectra shows a peak at 3350 cm^{-1} which originates due to the formation of hydrogen bond between hydogel and the dye. The presence of band at 1010 cm^{-1} indicates the Si-O stretching vibration of kaolin clay. The presence of band at 3500 cm^{-1} is due to some quantity of moisture in the hydrogel. There are small bands originating at 2850 and 2950 cm^{-1} which are due to the – CH_3 groups of the dye molecules.

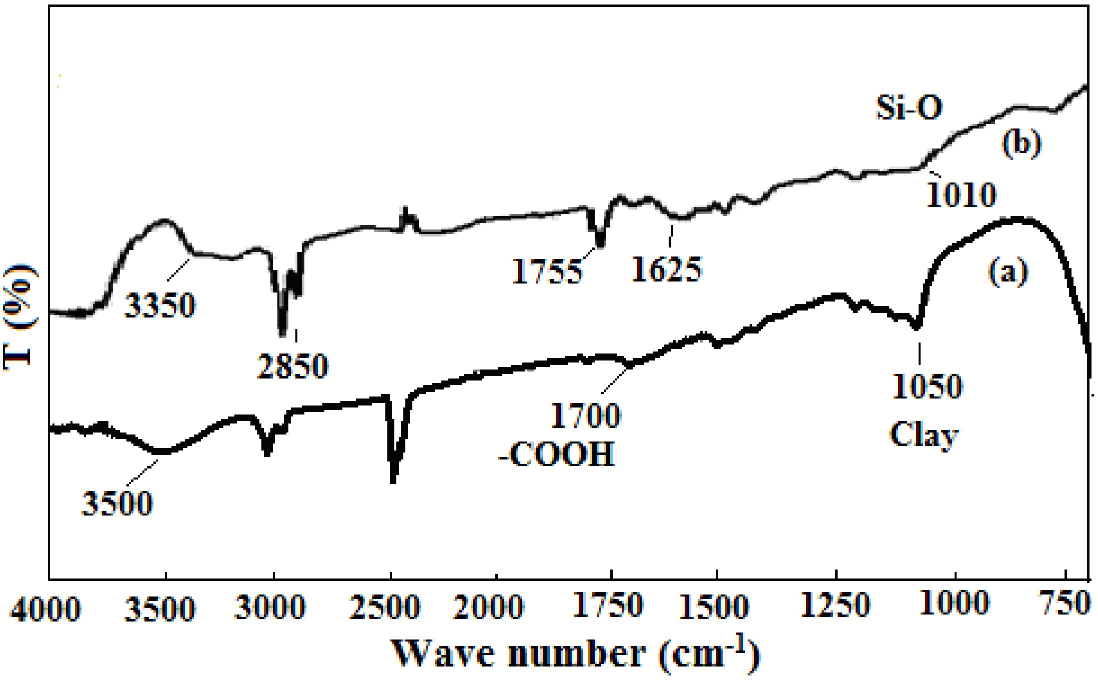


Fig. 18. FTIR spectra of pure PAA-K hydrogel a) before adsorption, b) after adsorption of BG dye (ultrasound assisted method)

4.4.3 Adsorption kinetics and adsorption isotherm models

After studying the effect of different operating parameters on the adsorption of BG dye by hydrogel prepared by both the methods it was observed that the hydrogel prepared by ultrasound assisted polymerization process proved to be superior to the hydrogel prepared by conventional method. Therefore for studying the adsorption kinetics the results obtained with hydrogel prepared by ultrasound assisted polymerization process were analyzed in greater details.

In order to find out the rate-controlling step of the adsorption process, it is necessary to establish well defined kinetic models. Pseudo-second-order kinetic model was used to fit the experimental data at different initial concentrations and temperatures. The kinetic rate equation is expressed as follows [30-31]

$$dq/dt = K_2(q_e - q)^2 \qquad (5)$$

where, K_2 (g/mg.min) is the pseudo second-order rate constant of adsorption. After integrating equation (5), the following equation is obtained:

$$t/q = 1/(K_2 q_e^2) + t/q_e \qquad (6)$$

The plot of t/q against t for the different temperatures gives a characteristic straight line fit as shown in **Figure 19**. The obtained values of second-order rate constants K_2 and q_e values are reported in **Table 3**. The results indicate that the correlation coefficients for the second-order kinetic model were close to 1.0 for all the cases indicating a good fit of the models to the experimental data sets. Therefore, the adsorption of BG dye by the PAA-K hydrogel can be approximated more favorably by the pseudo-second-order model.

There are several isotherm models available for analyzing the experimental data and for describing the equilibrium of adsorption. The more commonly used Langmuir and Freundlich isotherm have been used in this work to determine equilibrium relationships between sorbent and sorbate. The Langmuir equation is given as [31-32]

$$C_e/q_e = 1/(\alpha Q_m) + C_e/Q_m \qquad (12)$$

where, C_e (mg/L) is the concentration of the dye solution at equilibrium, q_e (mg/g) is the amount of dye adsorbed at equilibrium, Q_m is the maximum adsorption capacity and α is the

Langmuir constant. Q_m and α values were obtained from slope and intercept of the linear plot of C_e/q_e vs C_e (**Figure 20**) respectively. The values of Q_m and α are given in the **Table 2a**.

Freundlich isotherm is an empirical equation employed to describe heterogeneous systems [31-32]. The Freundlich isotherm is described by equation

$$q_e = K_F \times \log C_e^{\,(1/n)} \qquad (13)$$

Taking log of equation (8)

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (14)$$

where, K_F and n are the physical constants of the Freundlich adsorption isotherm indicating sorption capacity (mg/g) and intensity respectively. The slope and intercept of the linear plot of log q_e vs log C_e gives the values of n and K_F (**Figure 21**). The Freundlich constants are given in the **Table 2b**. Values 1/n indicate the type of isotherm to be irreversible (1/n=0), favorable (0<1/n<1) or unfavorable (1/n>1). Results showed that n was greater than unity, indicating the dye was adsorbed favorably by the hydrogel at all the temperatures studied. The regression correlation coefficients of both the models were close to 1.0 suggesting that both the isotherms could satisfactorily explain the adsorption of the dye molecules on the hydrogel.

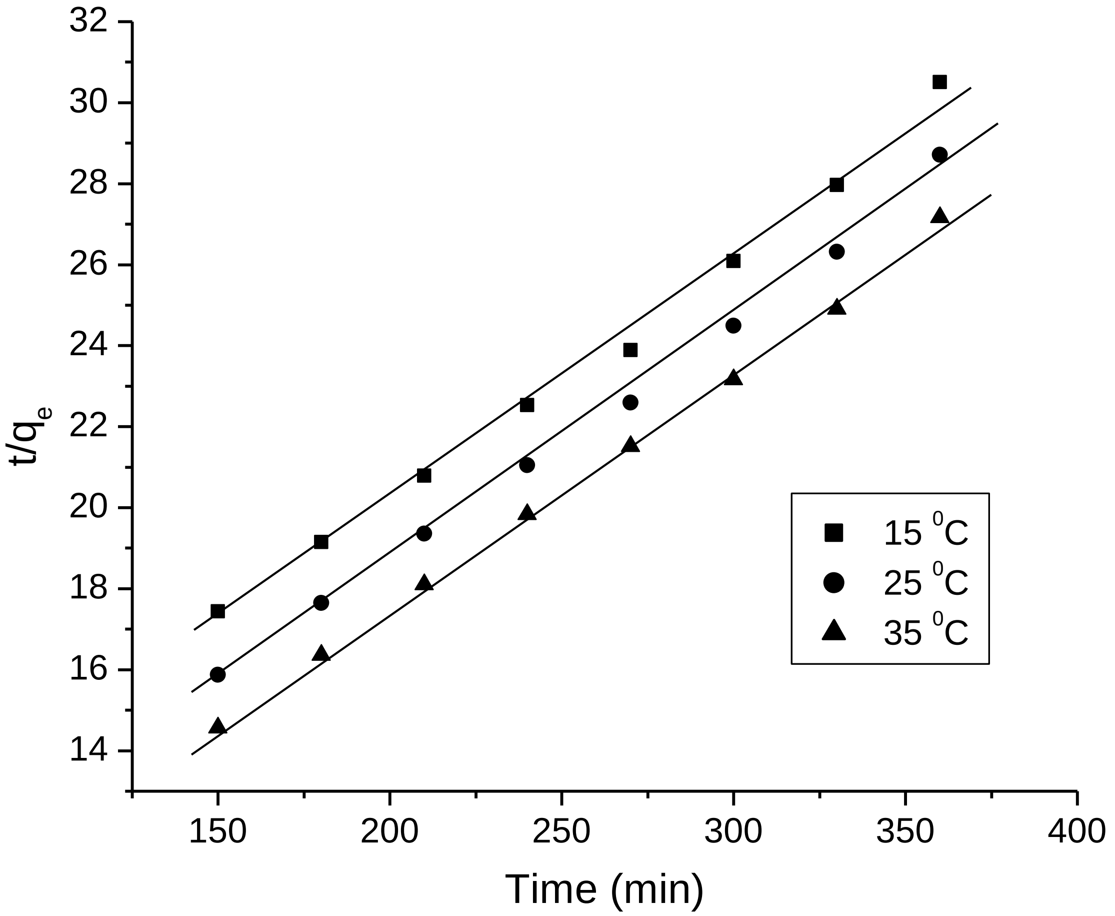


Fig. 19. Adsorption kinetics of BG dye at different temperatures for pseudo-second-order kinetic model

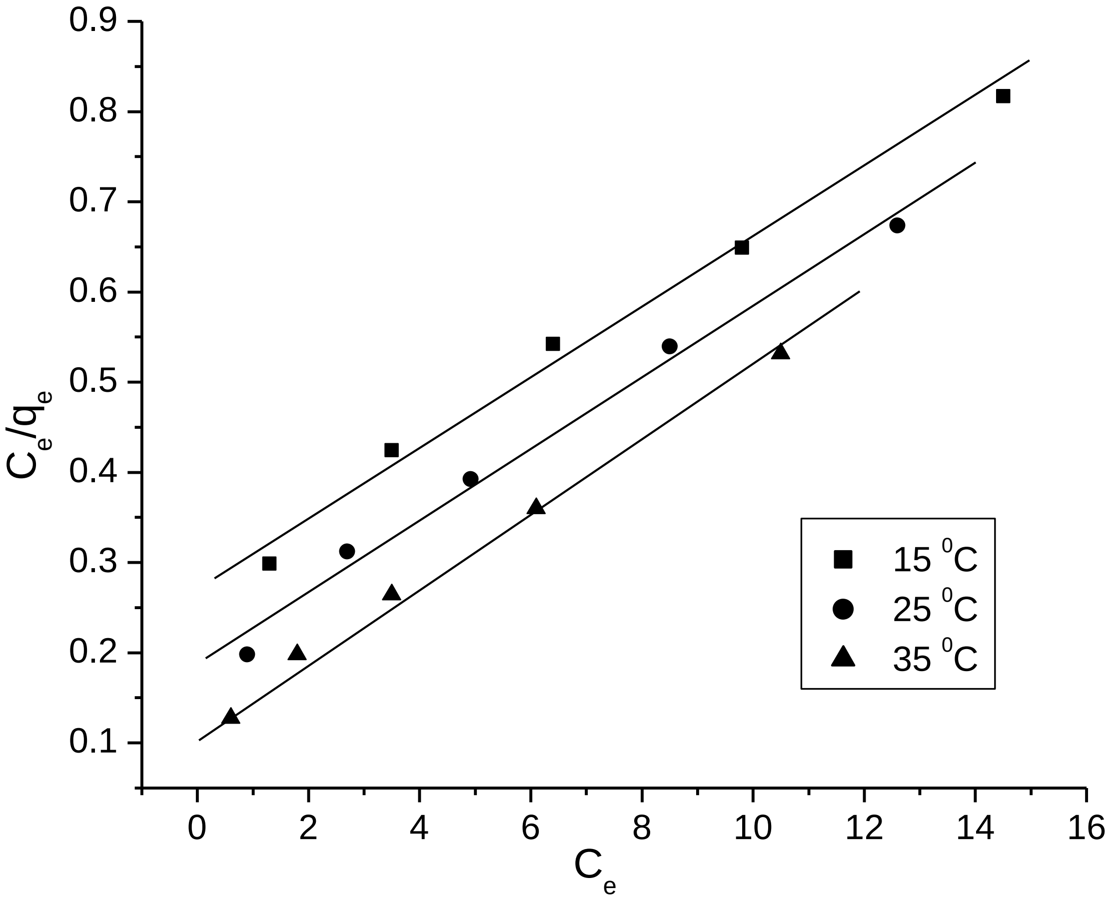


Fig. 20. Plot of C_e/q_e vs C_e for Langmuir isotherm

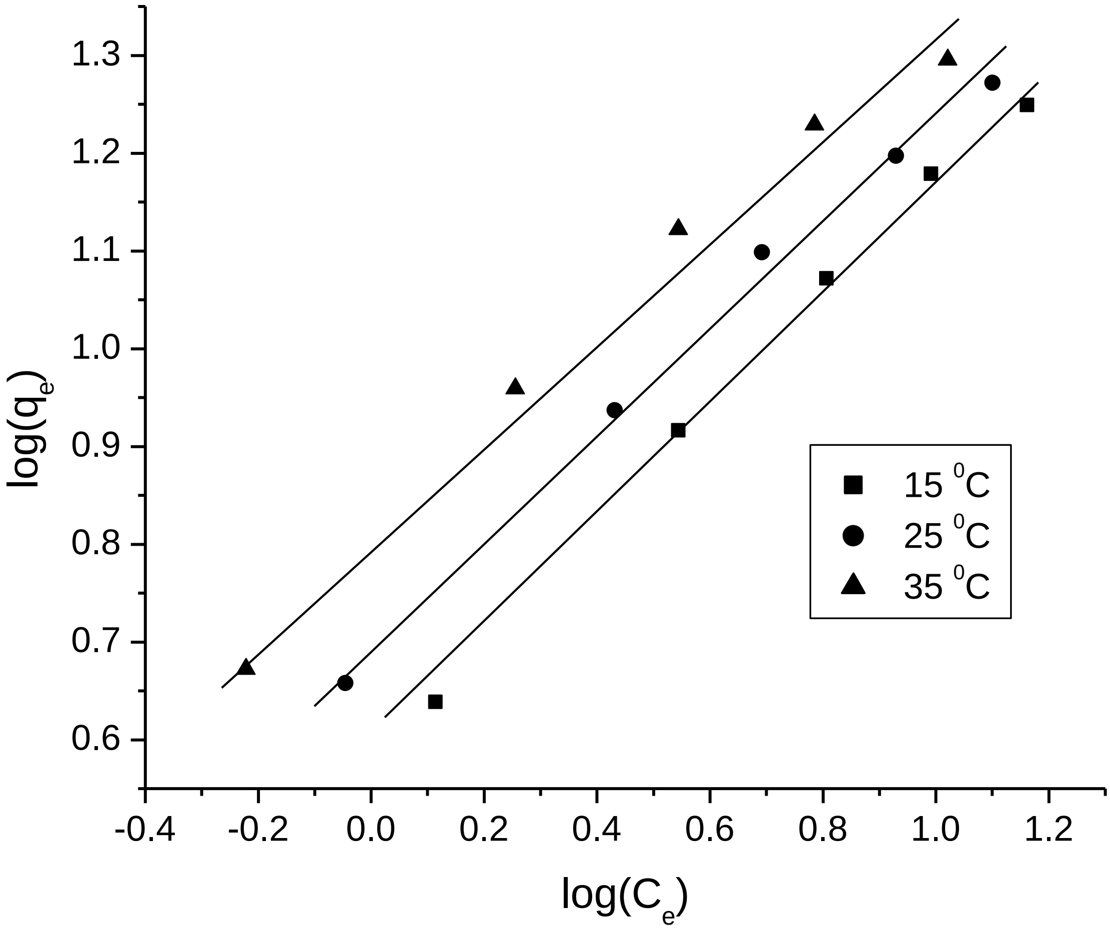


Fig. 21. Plot of log q_e vs log C_e for Freundlich isotherm

Table. 2a. Second-order kinetic constants for the BG adsorption on the PAA-K hydrogel

Temperature (K)	**Pseudo-second-order kinetic constants**		
	K_2 (g / mg min) × 10^4	**q_e (mg/g)**	**R^2**
288	3.39	17.30	0.98
298	4.12	17.54	0.99
308	5.37	17.85	0.99

Table. 2b. Langmuir and Freundlich isotherm constants

Temperature (K)	**Langmuir constants**		
	Q_m (mg/g)	**α**	**R^2**
288	24.90	0.13	0.99
298	25.60	0.20	0.98
308	26.31	0.33	0.98
Temperature (K)	**Freundlich constants**		
	K_F (mg/g)	**n**	**R^2**
288	3.82	1.69	0.99
298	4.96	1.85	0.99
308	6.47	1.95	0.98

4.4.4 Evaluation of thermodynamic parameters

Temperature dependence of the adsorption process is associated with several thermodynamic parameters such as Gibbs free energy change ΔG^o, standard enthalpy change ΔH^o and standard entropy change ΔS^o. Thermodynamic considerations of a sorption process are necessary to determine whether the process is spontaneous or not. The value of ΔG^o can be determined from the following equation

$$\Delta G^o = - RT \ln K \qquad (15)$$

Where K is the thermodynamic equilibrium constant.

The effect of temperature on thermodynamic constant is determined by

$$d \ln K/dt = \Delta H^o/RT^2 \qquad (16)$$

Integrating and rearranging equation (11) we get

$$\ln K = -(\Delta H^o/RT) + \Delta S^o/R \qquad (17)$$

and Gibbs free energy is also given by

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (18)$$

The equilibrium constant K has been determined by plotting ln(q_e/C_e) versus q_e and extrapolating to zero as shown in **Figure 22**. The ΔH^o and ΔS^o values were calculated from the slope and intercept of linear plot of lnK versus 1/T (**Figure 23**). The calculated values of the thermodynamic parameters are reported in **Table 3**. The negative value of ΔG^o indicates that the dye adsorption process is feasible and positive value of ΔH^o shows that the adsorption process is endothermic in nature.

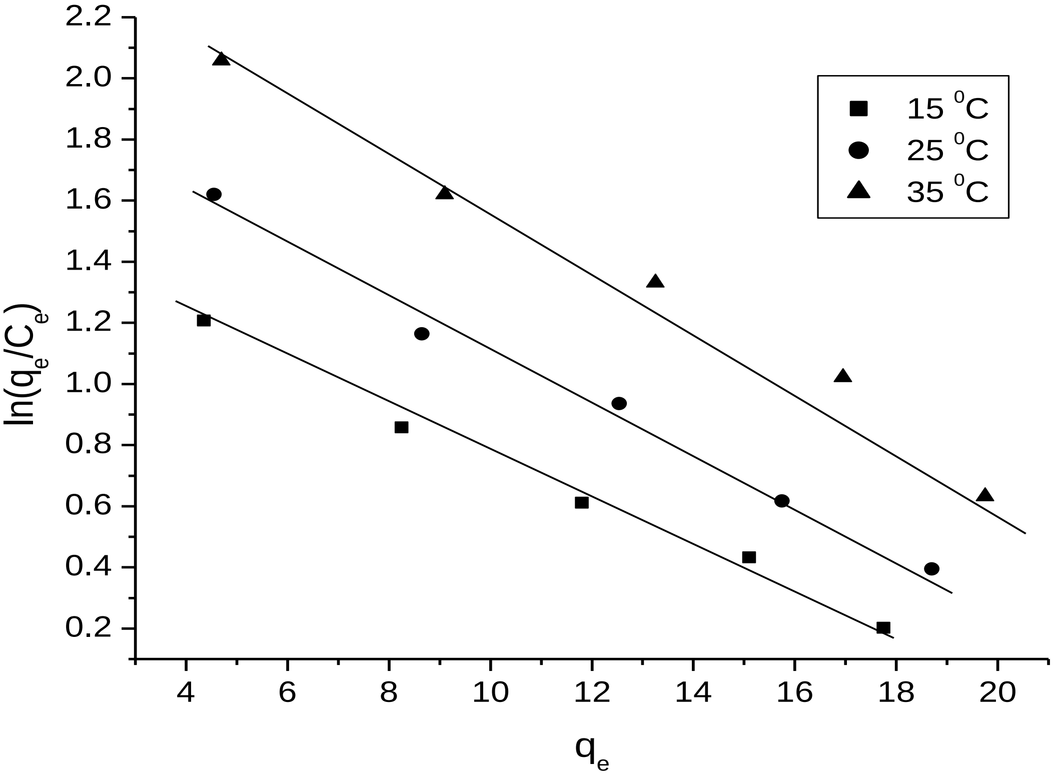


Fig. 22. Plot of ln (q_e/C_e) vs q_e for K values at different temperatures

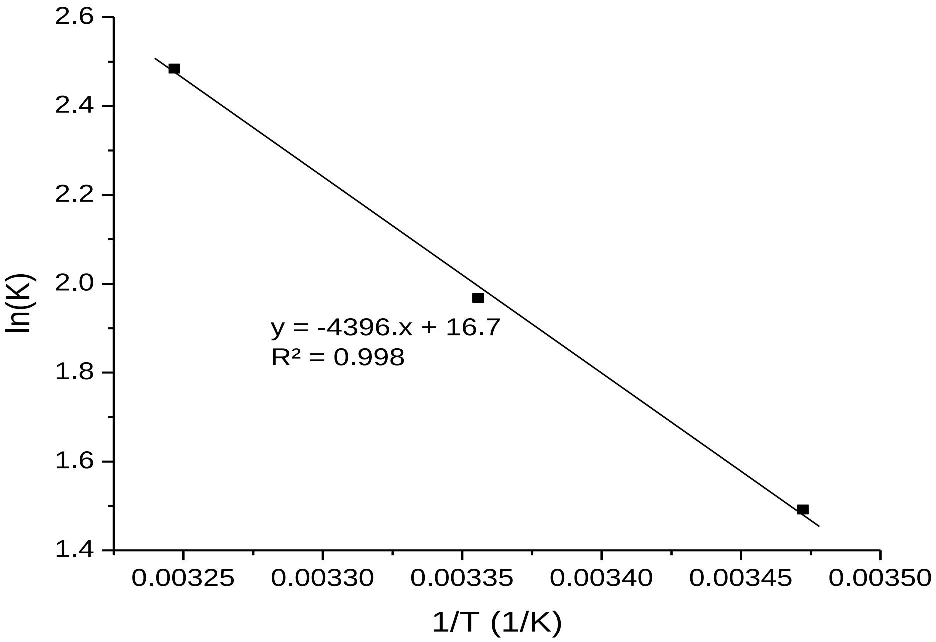


Fig. 23. Plot of ln K vs 1/T

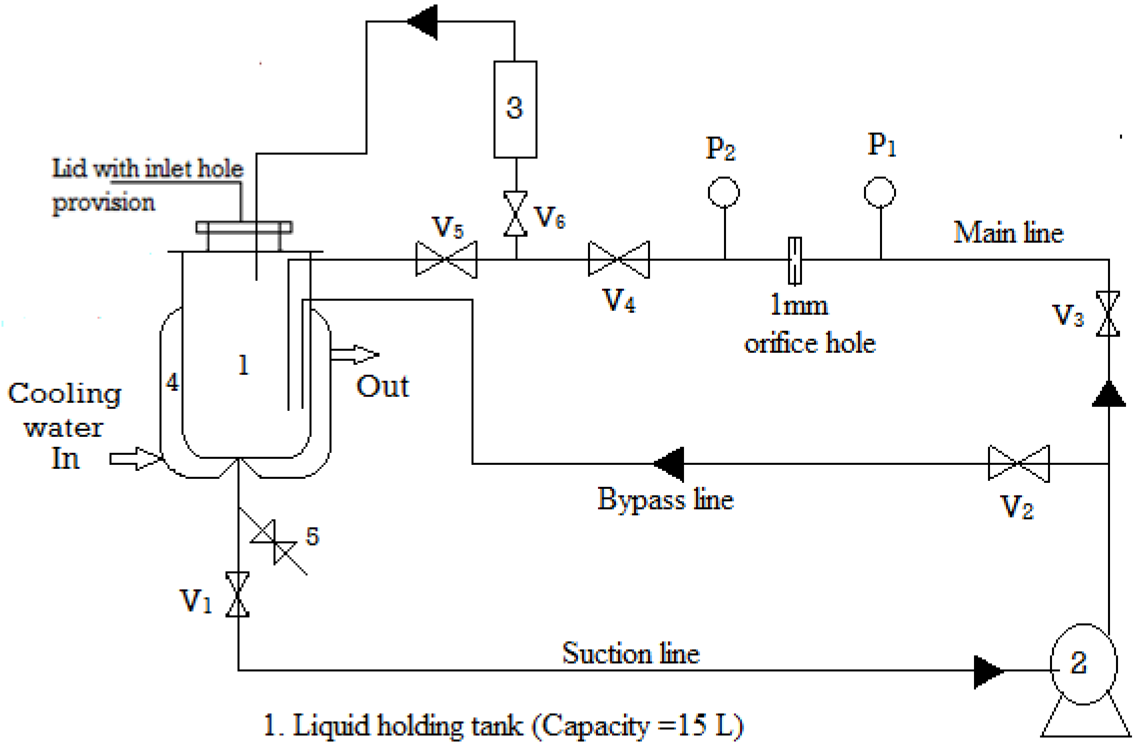
Table. 3. Thermodynamic parameters of adsorption of dye onto PAA-K hydrogel

Temperature (K)	**lnK**	**ΔG^o (J/mol)**	**ΔH^o (J/mol)**	**ΔS^o (J/mol.K)**
298	1.49	-3532.61	36548.34	139.17
308	1.96	-4924.31		
318	2.48	-6315.92		

4.5. Studies on dye wastewater treatment using combination of hydrodynamic cavitation and hydrogel

4.5.1 Design and Fabrication of Sophisticated Experimental setup (Hybrid system):

For the treatment of model dye wastewater, an in-house fabricated hydrodynamic cavitation reactor coupled with the packed bed adsorption unit has been used. Typical hybrid system used for the investigation of degradation and subsequent adsorption of crystal violet dye molecules was shown in **Figure 24.** In-house fabricated hybrid system mainly consists of a 10 L holding tank, plunger pump (Power = 1.5 HP), pressure gauges and valves (as shown in figure.1) at the required places to control the pressure and flow rates in the pipe lines. The outer side of the holding tank was provided with the jacket to supply the hot/cold fluid to maintain the required temperature inside the holding tank. The Suction line of the plunger pump was connected to the holding tank and discharge line was bifurcated in to two lines such as bypass line and process line (main line). The bypass line connected to the holding tank contains a manual control valve to main the desired inlet pressure at the cavitating device (orifice) in the main line. In addition to that, a variable frequency drive (VFD) has also been provided alternatively to adjust the speed of the plunger pump. Geometrical dimensions of the orifice based cavitating device were shown in **Figure 25**. The hybrid system (including pipe lines and holding tank) has been made up of stainless steel (SS-304) and SS-316 grade have been used for the construction of orifice in order reduce the erosion and corrosion of orifice. **Figure 26** shows the picture of the hybrid system.



1. Liquid holding tank (Capacity =15 L)
2. Plunger pump
3. Hydrogel packed bed
4. Cooling Jacket
5. Drain valve

$V_1, V_2, V_3, V_4, V_5, V_6$ = Manual control valves
P_1 and P_2 = Pressure gauges

Fig.24. In-house fabricated experimental setup (hybrid treatment system)

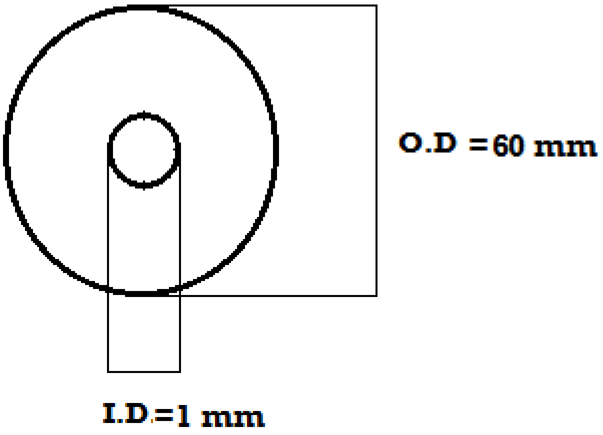


Fig.25. Geometrical dimensions of orifice cavitation device

Fig.26. Hydrodynamic cavitation+Hydrogel packed bed (hybrid system)

4.5.2 Specifications of the hybrid system:

- Plunger pump power rating: 1.5hp (with Variable frequency drive (VFD) for changing RPM of the pump).
- Piping Material: SS-316, diameter of all pipes 17 mm.
- Orifice device : inner dia. = 2 mm hole at the centre, outer dia. = 25 mm, Plate thickness 1mm. made up with iron plate
- Upstream pressure (P_1) : 0 – 20 bar
- downstream pressure (P_2) : 0 – 20 bar
- Tank capacity : 15 Liters (Dia.=25cm, Length=31cm)

- Material Of Construction (MOC) of Reactor with cooling jacket : SS-316
- 250 Watts UV-Visible lamp
- 10 Cm x 5 cm (LxB) Hydrogels packed bed

4.5.3 Specifications of the Total organic carbon analyzer:

- **Model :** TOC- Lcpn (Shimadzu Japan)
- Works on combustion technique with PC Control software.
- **Measurement Range:** 50 ppb-3000 PPM
- **Measurement Time :** 20 minutes
- **Measurements Items:** Total Carbon, Inorganic Carbon, TOC, Non-Purgable Organic Carbon.
- **Acid Addition:** Automatic
- **Calibration :** Multipoint
- **Dilution :** Automatic

4.5.4 Synthesis of pure poly (acrylic acid) hydrogel

The basis for the selection of PAA hydrogel for the removal of dyes from the aqueous solution is mainly due to its high hydrophilic nature of the polymer compared to other polymers such as Polyethylene glycol, Polyacrylic-acrylamide etc. It has capability to absorb 99 % of water and able to swell. Due to this extraordinary properties PAA hydrogel were selected for further dye removal studies.

The synthesis of in-situ emulsion nanocomposite hydrogel using cavitation technique was carried out as follows: Water (69 g) containing SDS (0.54 g) was added to the reaction mixture and the entire solution was thoroughly deoxygenated by bubbling with argon for 45 min at room temperature. Initially 36 g of AA was added and the solution was irradiated for 10 min in the ultrasound reactor to form uniform monomer droplets. The temperature of the reaction mixture was maintained at 60 °C using a water bath. The liquid mixture was then subjected to sonication. 0.3 g of ammonium persulphate (APS) initiator in 5 mL distilled water was added drop wise into the reaction mixture. The polymerization reaction was completed within 40 min. Within the initial 15 min of sonication, a viscous mass was formed indicating the formation of pure poly(acrylic acid) hydrogel. The resulting polymerized hydrogel was then dried in an oven for 48 h at 80 °C.

The experimental setup has been prepared to conduct the polyacrylic acid hydrogel synthesis using ultrasonic irradiation. The reason for choosing the ultrasonic assisted synthesis of polyacrylic acid hydrogel will take less time for synthesis and have more dye adsorption capacities rather than the conventional synthesis of polymer hydrogels. The experimental setup for PAA hydrogel synthesis has been shown in **Figure 9a**.

4.5.5 A case study on Malachite green dye removal by hydrodynamic cavitation (HC) and hydrogel based hybrid technique:

4.5.6 Experimental and analytical method:

Hydrodynamic cavitation based degradation of malachite green was carried out using fixed solution volume of 5 L and for a constant circulation time of 90 min. The initial concentration of malachite green was 500 ppm. The temperature of the solution during experiments was kept constant at 35^0C. The absorbance of malachite green was monitored using UV-Spectrophotometer (Shimadzu-1800) and then the concentration of dye was calculated by analyzing the absorbance of dye solution at the wavelength of 618 nm. The concentration of Malachite Green was then calculated using the calibration curve prepared for

Malachite Green. Experiments were conducted at constant inlet fluid pressure of 2 bar. The samples were withdrawn at regular intervals of 15 minutes and the total time fixed for decolorisation was 90 minutes.

4.5.7 Results obtained

The colour degradation of malachite green (MG) through hydrodynamic cavitation has been analyzed using UV-Visible Spectroscopy. For every 15 min of time intervals sample has been collected and UV analysis was done for finding out the concentration of MG remaining in the waste water. The observed UV spectra profile of MG degradation through hydrodynamic cavitation has been shown in **Figure 27**. The maximum wave length of MG absorbance in UV-spectroscopy is 618 nm.

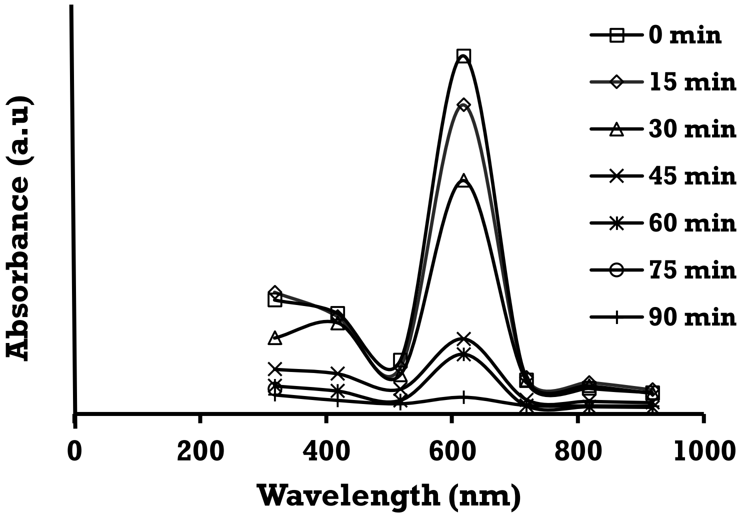


Fig.27. UV Spectra profile of MG absorbance at different time intervals

The effect of degradation of MG using single hydrodynamic cavitation (HC) and combination (hybrid) of HC and Hydrogel beads (such as Polyacrylic acid hydrogel) has been studied. The ultrasonically prepared polyacrylic acid hydrogel beads having a total weight of 25 gm and 500 ppm of MG solution is used for carrying out the experiment. These beads are initially immersed in the hydrodynamic cavitation reactor for absorbing the MG dye present in the water. A fixed total time of 90 min has been kept for degradation and adsorption of MG dye through HC and Hydrogel respectively. For every 15 min of time interval samples are collected and analysed for finding out the MG concentration present in the water. It has been observed that the degradation of MG is more in the combined HC and Hydrogel than the single hydrodynamic cavitation technique. The degradation profile of MG in terms of concentration Vs time for both single and hybrid process has been shown in **Figure 28**.

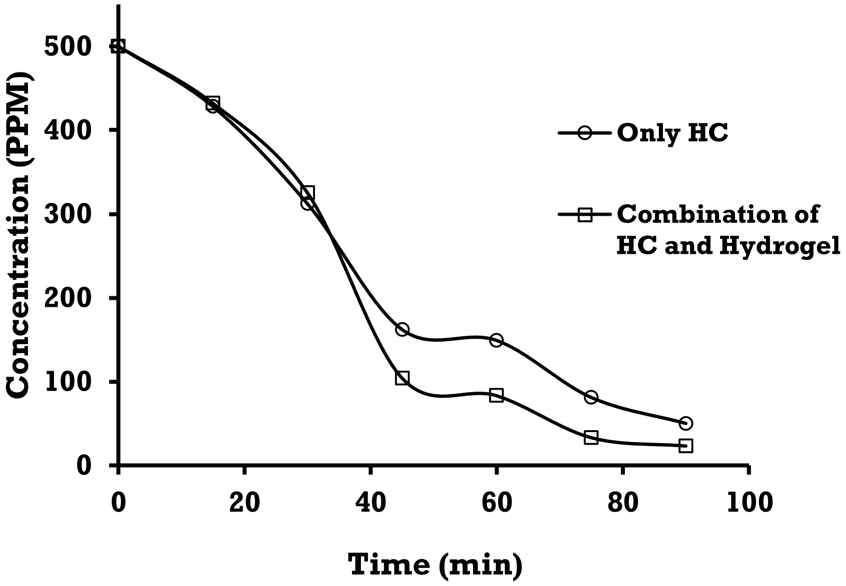


Fig.28. MG degradation with respect to time

the MG adsorbed hydrogel beads are shown in **Figure 29** During the adsorption of MG dye, hydrogel beads are able to swell due to uptake of water. It was also observed from experimental analysis that the initial weight of hydrogel beads are 25 g and final weight of swollen hydrogels was found to be 88.42 g.

Fig.29. MG adsorbed PAA hydrogel beads

4.6 Sonochemical synthesis of graphene Oxide (GO) from natural graphite powder:

We also attempted the step for preparation of graphene oxide (GO) nanoparticles and incorporated into the PAA hydrogel to make the PAA-GO nanocomposite hydrogel for its application in waste water treatment with the combination of hydrodynamic cavitation. The deatailed description of its synthesis and application in waste water treatment is given below.

4.6.1 Experimental

The GO was prepared from graphite powder by using modified Hammer's method in presence of ultrasonic irradiation using an ultrasonic horn (Dakshin ultrasonic probe sonicator, 50 Hz frequency, 230 V). In this method, Graphite powder (2 g) and sodium nitrate (2 g) were weighed and added to 60 mL of H_2SO_4 solution (98 wt %) at 0 ^{O}C by keeping it in the ice bath. Prepared mixture was ultrasonicated for 10 min. After that 6 g of $KMnO_4$ is gradually added to the above mixture under ultrasonication for 30 min. During the addition $KMnO_4$ small amount of gaseous fumes will release into the atmosphere and the reaction progressed to form a paste. After 30 min of ultrasonication the reaction should be stopped by the gradual addition of 150 mL DI (Deionized water) to the above reaction mixture and then ultrasonicated for 5 min. After which 50 mL of H_2O_2 (30 wt %) was added drop by drop to the above reaction mixture. The mixture was filtered and washed with 150 mL HCl solution (10 wt %) to remove metal ions and then washed with 100 mL DI water to remove the acid. Graphite oxide from the solution was separated by using normal filtration.

4.6.2 Conversion of graphite oxide to graphene oxide:

The resultant graphite oxide powder was further synthesized to make graphene oxide by the exfoliation of above graphite oxide powder in 300 mL of DI water under ultrasonication for 30 min. After completion of ultrasonication the solution was filtered and the powder was dried in an oven at 40-50^{0}C for 2 h.

4.6.3 Incorporation of graphene oxide nanoparticles into the PAA polymer hydrogel

The synthesis of in-situ emulsion nanocomposite hydrogel using cavitation technique was carried out as follows: Water (69 g) containing SDS (0.54 g) was added to 36 g of AA and the solution was irradiated for 10 min in the ultrasound reactor to form uniform monomer droplets. The temperature of the reaction mixture was maintained at 60 °C using a water bath. The liquid mixture was then subjected to sonication. 0.3 g of ammonium persulphate (APS) initiator in 5 mL distilled water was added drop-wise into the reaction mixture. The polymerization reaction was completed within 40 min. Within the initial 15 min of sonication, a viscous mass was formed indicating the formation of pure poly(acrylic acid) hydrogel. The resulting polymerized hydrogel was then dried in an oven for 48 h at 80 °C. PAA-GO hydrogel was prepared in a similar manner, except for the addition of 0.5 g of GO nanoparticles to acrylic acid during polymerization.

4.6.4 Characterization of Graphene Oxide (GO)

X-ray Diffraction analysis: Ultrasonically prepared GO sample were subjected to XRD analysis for finding out the structural properties of these compounds. The obtained XRD patterns for the synthesized GO are shown in **Figure 30**. Early published experimental XRD pattern of grapheme oxide demonstrated arising of a strong 001 reflection peak at $2\theta\sim10^0$ with a basal spacing of $d_{001} = 6.33A^0$. Vaclav Stengel, Snejana et al reported the basal spacing of $d_{001} = 6.718\ A^0$ for GO. The XRD pattern exhibit GO diffraction peaks at $2\theta\sim10^0$ and the calculated d-spacing of our own prepared GO sample is around $d_{001} = 6.53A^0$. The XRD results of our own synthesized GO are in good agreement with previously published XRD results.

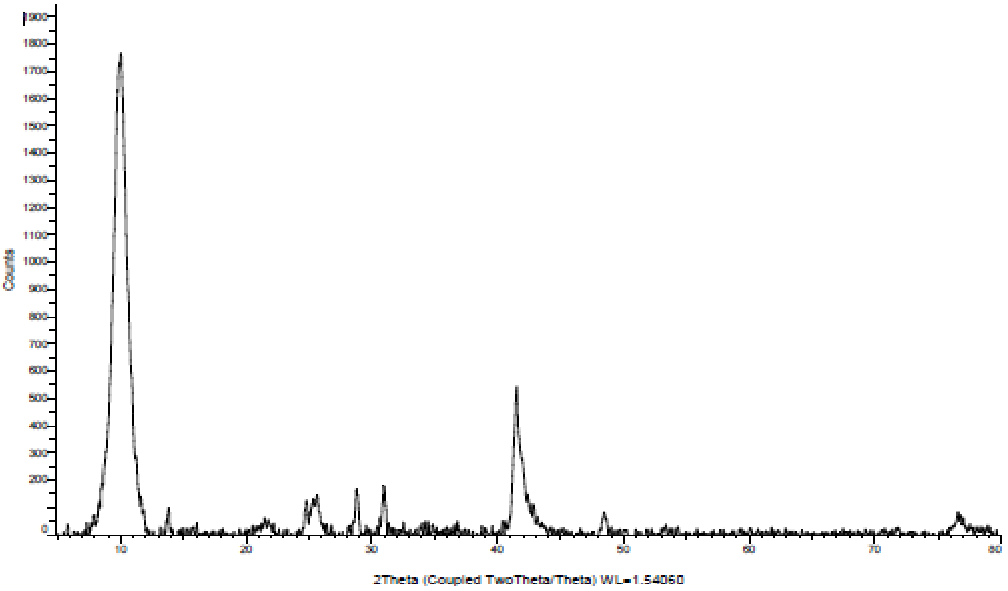


Fig.30. XRD pattern of Graphene Oxide

Field Emission Scanning Electron Microscopic (FESEM) analysis: The morphology of the GO has been studied by carried out FESEM analysis. FESEM image of GO for evaluation of their morphologies has been shown in **Figure 31**. It was found that many exfoliated layers of sheets are present in the image. The FESEM image of conventionally prepared GO shows the agglomerated crystalline phase. But in the case of ultrasonically prepared no agglomerated crystalline phase could be observed in their morphology. One can observe only segregation of fine crystals in their morphology due to the ultrasonication effect.

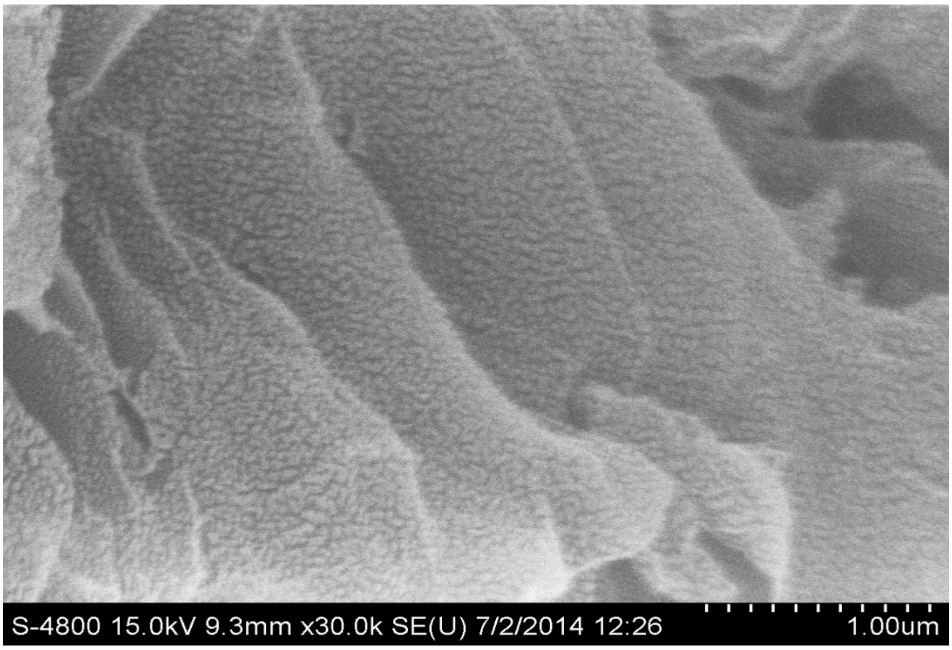


Fig.31. FESEM image of Graphene Oxide

Transmission electronic microscope (TEM): Transmission electronic microscope (TEM) images of ultrasonic synthesized GO and PAA-GO nanocomposite hydrogel samples are shown in **Figures 32 and 33**.

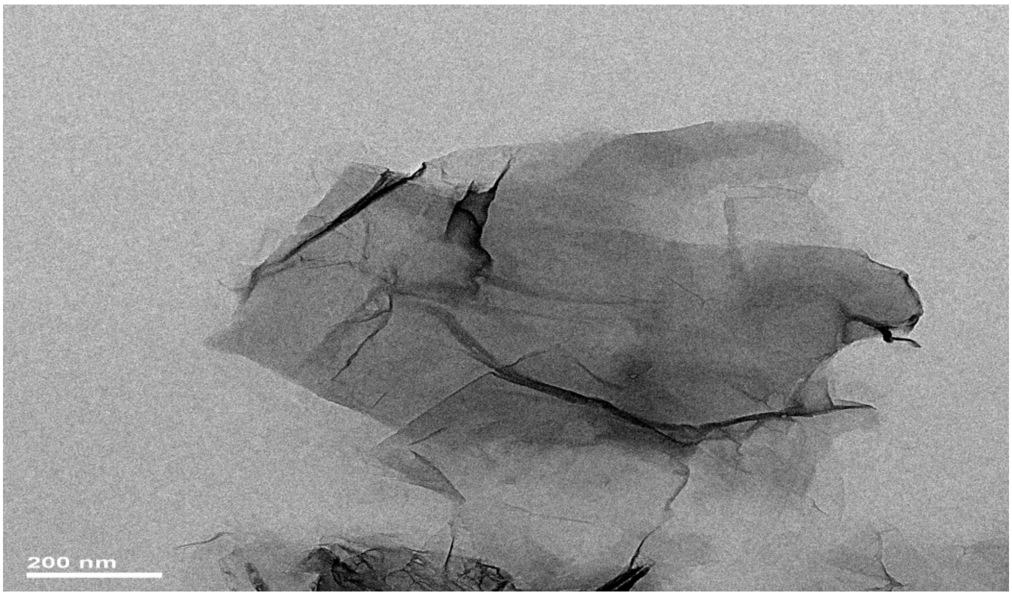


Fig.32. TEM image of Graphene Oxide

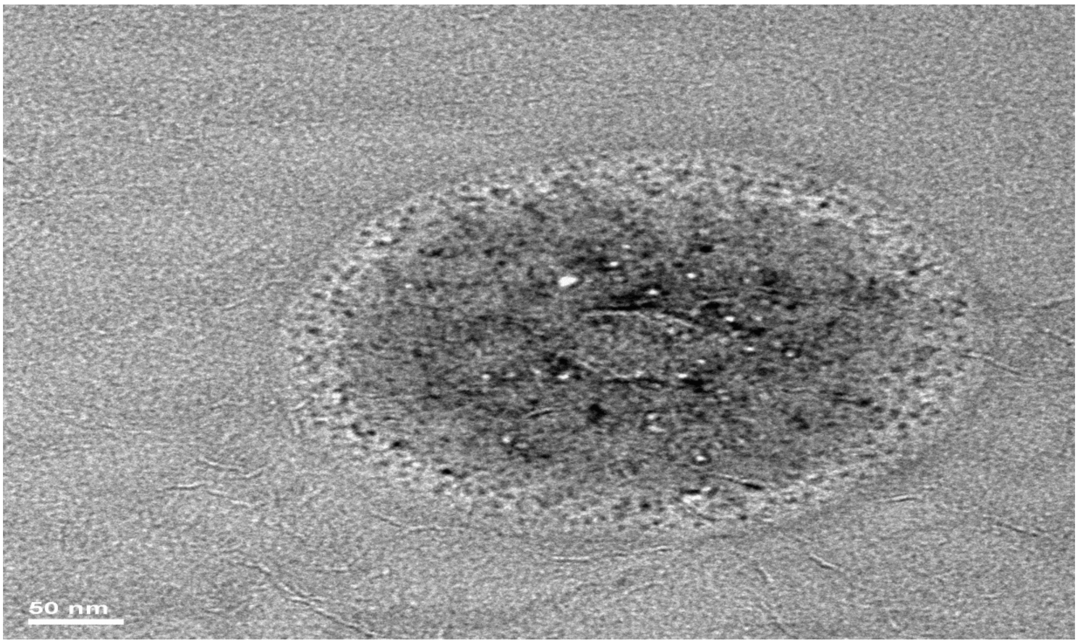


Fig.33. TEM image of PAA-GO nanocomposite hydrogel

4.6.5 PAA-GO nanocomposte hydrogel application in waste water treatment

The above ultrasonic synthesis of PAA-GO hydrogel has been used for the degradation of MG dye with the combination of hydrodynamic cavitation, but it has not given desired results. **Figure 34** shows the ultrasonically prepared PAA-GO nanocomposite hydrogel. It was observed that PAA-GO hydrogel has more strength than the pure PAA hydrogel due to the addition of GO nanoparticles into it.

Fig.34. Ultrasonically prepared PAA-GO nanocomposite hydrogel

4.7 A case study on Malachite green dye removal by Hydrodynamic cavitation combination with bentonite clay nano-composite poly acrylic acid (PAA) hydrogels:

We also attempted the step for preparation of modified bentonite clay nanoparticles and it was incorporated in to the PAA hydrogel matrix to make the PAA-Bentonite clay nanocomposite hydrogel for its application in waste water treatment with the combination of hydrodynamic cavitation. The deatailed description of its synthesis and application in waste water treatment is given below.

4.7.1 Experimental

4.7.2 Materials

Acrylic acid (AA) from Avra Synthesis Pvt, Ltd, Hyderabd, Ammonium Persulphate (APS) from Molychem, Mumbai, India, sodium dodecyl sulfate (SDS) from SD Fine Chemicals Ltd, Mumbai, Malachite green dye (CV) were of analytical grade and procured from Universal Chemicals, India, and Natural Bentonite clay was obtained from Thermo Fisher Scientific India Pvt, Ltd, Mumbai. Millipore deionized water was used for all experiments.

4.7.3 Sonochemical synthesis of modified bentonite nanoclay from Natural bentonite powder:

Initially, pristine bentonite clay was washed 3–4 times with demineralized water. Impurities such as silica and iron oxides were removed by a differential sedimentation technique. The mixture was stirred for 1 h and kept undisturbed overnight. After filtration, the solid was exposed to slow evaporation, till the desired dryness was achieved. Modification of bentonite was carried out by ion exchange reaction. The following procedure was used to carry out for ion exchange reaction so as to obtain modified bentonite nanoclay. 10 g bentonite clay (calculated on the basis of CEC of bentonite used) was mixed in 100 mL water containing 2 mL of hydrochloric acid and then solution was heated to 70 °C. HCl was added into clay solution as acidic environment facilitates the distribution of quaternary ammonium salts inside the gallery spacing of clay. CTAB solution (0.05 M) was dispersed into bentonite containing aqueous solution. The dispersion was stirred vigorously for 12 h at 70 °C. Unreacted amines were removed by Continuous washing of precipitate using hotwater. The final precipitate was thoroughly dried in an oven at 80 °C for 24 h to obtain the modified bentonite nanoclay.

4.7.4 Synthesis of in situ emulsion nanocomposite hydrogel using cavitation technique:

Bare and nanopartcles incorporated polyacrylic acid hydrogels have been prepared by in-situ emulsion ultrasound polymerization technique. **Figure 35** show the typical synthesis procedure of PAA-Bentonite clay nanocomposite hydrogel using ultrasound polymerization technique. In a typical synthesis procedure, Water (69 g) containing SDS (0.54 g) was added to the reaction mixture and the entire solution was thoroughly deoxygenated by bubbling with argon for 45 min at room temperature. Initially 36 g of AA was added and the solution was irradiated for 10 min in the ultrasound reactor to form uniform monomer droplets. The temperature of the reaction mixture was maintained at 60 °C using a water bath. The liquid mixture was then subjected to sonication. 0.3 g of ammonium persulphate (APS) initiator in 5 mL distilled water was added drop wise into the reaction mixture. The polymerization reaction was completed within 40 min. Within the initial 15 min of sonication, a viscous mass was formed indicating the formation of pure poly(acrylic acid) hydrogel. The resulting polymerized hydrogel was then dried in an oven for 48 h at 80 °C. PAA-Bentonite clay loaded hydrogel was prepared in a similar manner, except for the addition of 1 g of modified Bentonite nanoparticles to acrylic acid during polymerization. During the studies done by different researchers on hydrogels loaded with clays, different amounts of clays are added to the hydrogels ranging from 0.5 g clay to 2 g clay by taking basis of quantities of monomer, initiator and solvent. **Figure 36** shows the pictures of bare PAA and PAA-Bentonite clay nanocomposite hydrogels

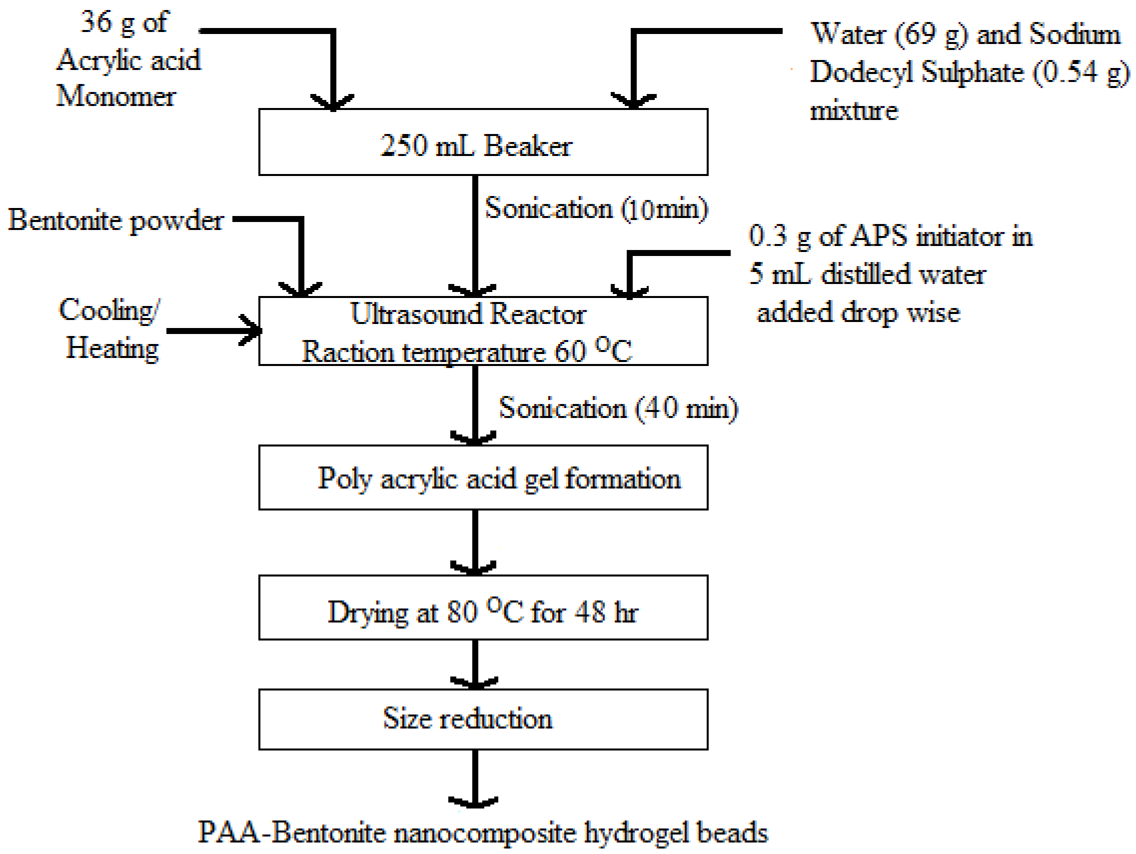


Fig.35. Typical synthesis procedure of PAA-Bentonite clay nanocomposite hydrogel using ultrasound polymerization technique

Image of Bare PAA hydrogels

Image of PAA-Bentonite nanocomposie hydrogels

Fig.36. Pictures of bare PAA and PAA-Bentonite clay nanocomposite hydrogels

4.7.5 Characterization of modified bentonite clay

Ultrasonically prepared modified bentonite clay sample were carried out for XRD analysis for finding out the structural properties of these compounds. The obtained XRD patterns for the synthesized modified bentonite clay are shown in **Figure 37**. The patterns show peaks at 2θ =7.12, 12 and 19.801. The peaks which are observed at 2θ values are in good agreement with the previously published XRD patterns for bentonite nanoclay.

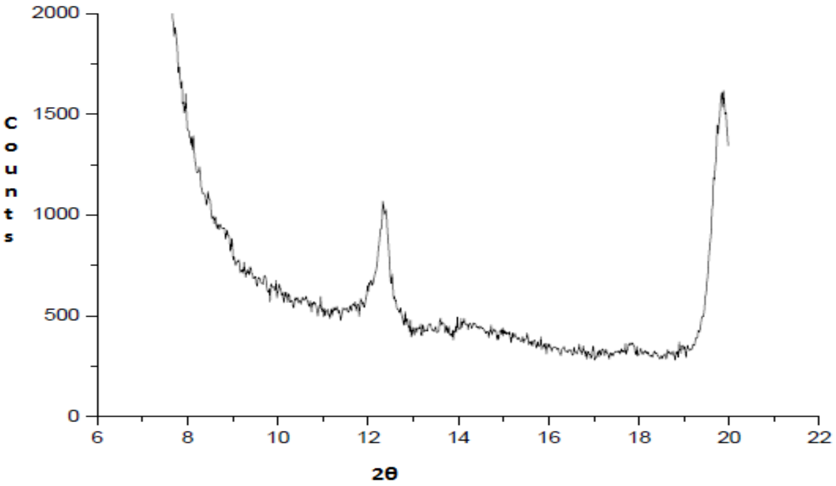


Fig. 37. XRD pattern of modified bentonite nanoclay

The average crystallite size of the modified bentonite clay was estimated using Scherrer equation. It was found that, the average crystallite of modified bentonite clay is around 50 nm

$$d = \frac{k\lambda}{\beta cos\theta} \qquad (19)$$

Where,

‘d’ is crystallite size in nanometer

‘k’ is shape factor constant, which is 0.89

‘β’ is the full width at half maximum (FWHM) in radian

‘λ’ is the wave length of the X-ray which is 1.540598 nm for Cu target Kα radiation and

‘θ’ is the Bragg diffraction angle.

Transmission electronic microscope (TEM) images of ultrasonic synthesized modified bentonite nanoparticles samples are shown in **Figure 38**.

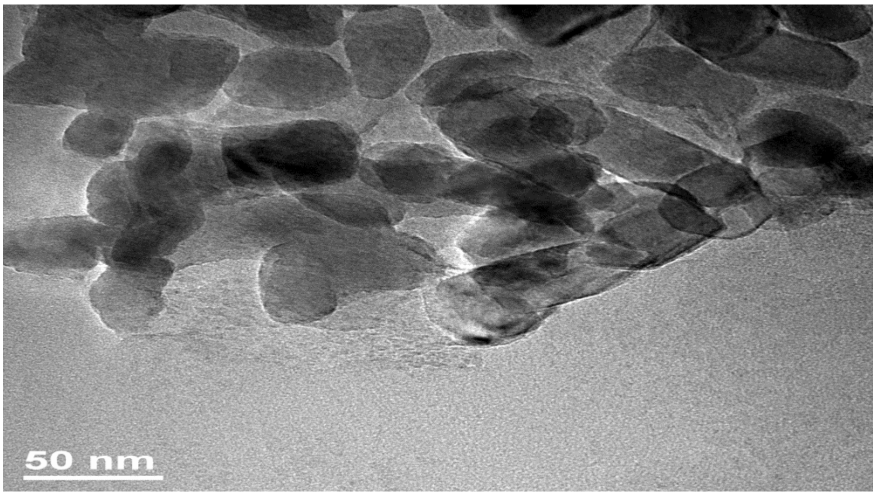


Fig.38. TEM image of modified bentonite nanoparticles

The above ultrasonic synthesis of PAA-Bentonite clay nanocomposite hydrogel has been used for the degradation of MG dye with the combination of hydrodynamic cavitation.

Initially 500 mg/L of malachite green has been taken and dissolved in 5 L of tap water for colour degradation studies. A total weight of 50 gm of hydrogels was used. Color degradation has been confirmed by carrying out ultraviolet spectrophotometry absorbance analysis for every 15 minutes.

From the obtained results it has been observed that, 90% of colour degradation has been attained in the HC alone. While 94.05, and 95.4% color degradation were obtained in the HC+PAA hydrogel and HC+Bentonite PAA hydrogels respectively. **Figure 39** shows the decolourization profile of MG dye in various systems such as Hydrodynamic cavitation (HC), combination of HC and PAA hydrogels and combination of HC and PAA-Bentonite nanocomposite hydrogel

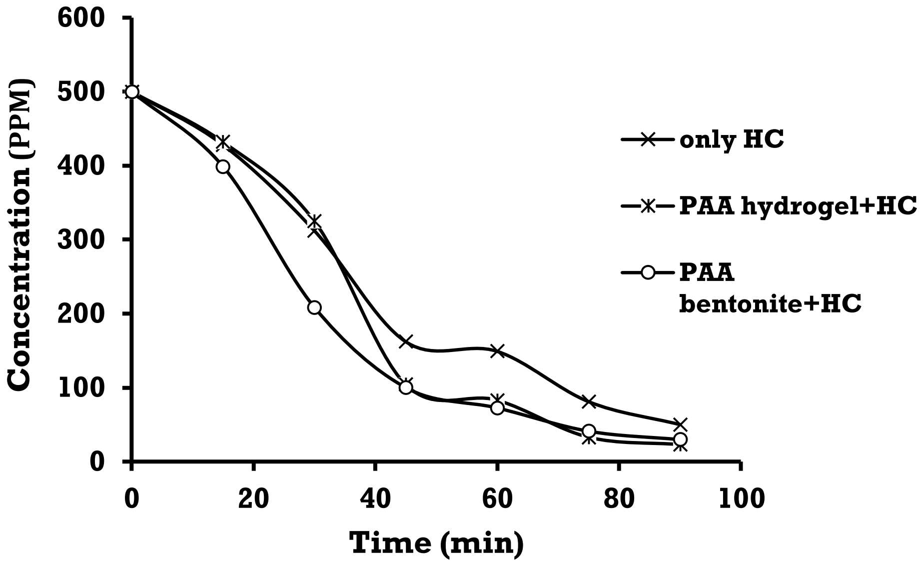


Fig.39. Concentration degradation profile of MG dye in various systems

4.8 Removal of crystal violet dye from aqueous media using HC combined with PAA-Bentonite clay nanocomposite hydrogel.

4.8.1 Materials and Methods

For the synthesis of polymer nanocomposite hydrogels and its further application in dye reclamation studies, following chemicals were purchased from the reputed chemical manufacturers and suppliers in India. Acrylic acid monomer (98 %) was obtained from Avra Synthesis Pvt. Ltd, Hyderabad, India. Sodium dodecyl sulfate (SDS), sodium hydroxide pellets (NaoH) and 98 %sulfuric acid (H_2SO_4) were procured from S. D. Fine Chemicals Ltd., Mumbai, India. Ammonium per sulfate was procured from Molychem Ltd. Mumbai, India. Crystal violet dye ($C_{25}N_3H_{30}Cl$) was obtained from Sisco Research Laboratories Pvt. Ltd. Mumbai, India. Natural bentonite powder was purchased from Thermo Fisher Scientific India Pvt Ltd, Mumbai. The chemicals used for this study were of analytical grade and has been used as received from the supplier.

4.8.2 Analytical procedure

To know the decolourization of crystal violet dye in aqueous solution, at fixed time intervals 15 ml of aliquots were drawn from the outlet of the process and tested using UV-Vis Scanning Spectrophotometer (Evolution 300 supplied by Thermo scientific, England). The absorbance values at respective wave lengths have been recorded using scanning method over a given wave length range, which covers the maximum absorbance wavelength (λ_{max}) of CV dye is 590 nm. Finally the concentration of CV dye has been determined from the standard calibration chart prepared for crystal violet dye. TOC analyzer (TOC l_{CPN} analyzer, Shimadzu, Japan) was used to investigate the percentage removal total organic carbon from aqueous solution.

4.8.3 Decolourization of CV through HC alone

The above ultrasonic synthesis of PAA-Bentonite clay nanocomposite hydrogel has been used for the degradation of MG dye with the combination of hydrodynamic cavitation. Figure.4 shows the ultrasonically prepared PAA- Bentonite clay nanocomposite hydrogel. It was observed that PAA- Bentonite clay nanocomposite hydrogel has more strength and high dye absorption capacity than the pure PAA hydrogel due to the addition of 0.5 gm of bentonite nanoclay into it. **Figure 40** shows the UV-Visible absorbance spectra of degradation of CV dye in hybrid system at regular time intervals.

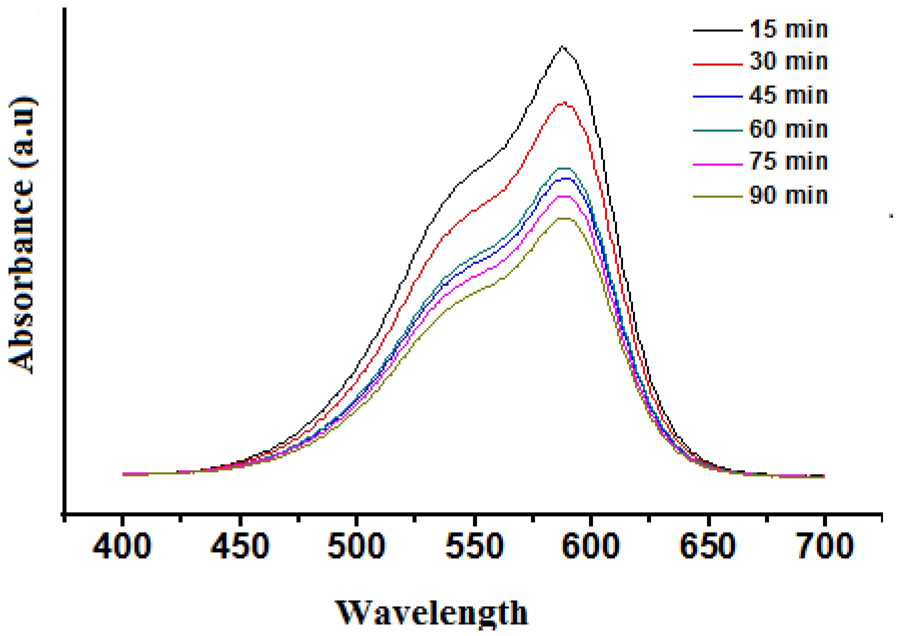


Fig. 40. UV-Visible absorbance spectra of degradation of CV dye in hybrid system at regular time intervals [CV dye 500 mg/L; HC inlet pressure 3 bar; pH=6.5; Hydrogel loading=30 gm/L]

4.8.4 Effect of inlet pressure

Effect of inlet pressure to the cavitation device (orifice) on the decolourization of crystal violet dye has been investigated. Initially 50 mg/L of dye stock solution has been prepared and pumped through the orifice using plunger pump. Variable frequency drive was used to control the number of piston strokes of the plunger pump per minute. Simultaneously, a control valve in the bypass line was adjusted to fix the inlet pressure to the cavitating device (orifice). The effect of inlet pressures such as 1.5, 3, 5, 7 bar on dye decolourization were studied. At every 15 min samples were collected and analysed for UV absorbance in order to know the concentration of CV dye remains in the water. **Figure 41** shows the concentration of crystal violet dye Vs time.

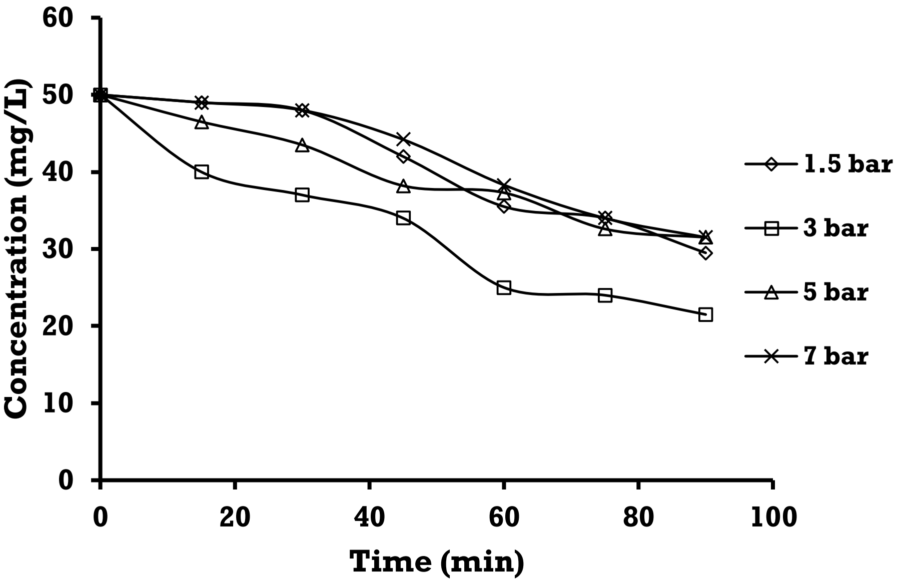


Fig. 41. Concentration of crystal violet dye Vs time

The hydrodynamic characteristic of the cavitating device (circular Venturi) has been studied by measuring the flow rate in main line. The calculated Cv for a circular venturi at an inlet pressure of 3 kg/cm^2 is 0.21 (Cv = 0.21) according to the following equation.

$$Cv = \frac{P_2 - P_v}{\frac{1}{2}\rho v_0^2} \tag{20}$$

Where

P_2 = Fully recovered downstream pressure in kg/cm^2

P_v = Vapor pressure of the dye solution in kg/cm^2

ρ = density of the dye solution in kg/m^3

v_0= Velocity of the dye solution at the throat of the cavitating constriction in m/s

4.8.5 Effect of clay content in hydrogel

Effect of clay content in nanocmposite hydrogel on the decolourization of crystal violet dye has been investigated along with hydrodynamic cavitation. In the typical experimental runs, 500 mg/L of dye stock solution and 20 g of bare PAA hydrogels, 0.5 and 1g of bentonite clay loaded PAA hydrogels have been used individually for the investigation of decolourization of CV dye at the optimized inlet pressure of 3 bar. Every experiment has been carried out by placing the hydrogels in the acrylic bed, which was connected to the HC system after orifice (cavitating device). At every 15 min, samples were collected and analysed for UV absorbance and TOC in order to know the percentage decolourization of CV dye and total organic carbon removal. **Figure 42** shows the effect of clay content in hydrogel on percentage decolourization of crystal violet dye and total organic carbon removal by combination of hydrodynamic cavitation and hydrogel. **Figure 43** shows the effect of clay content in hydrogel on percentage removal of TOC.

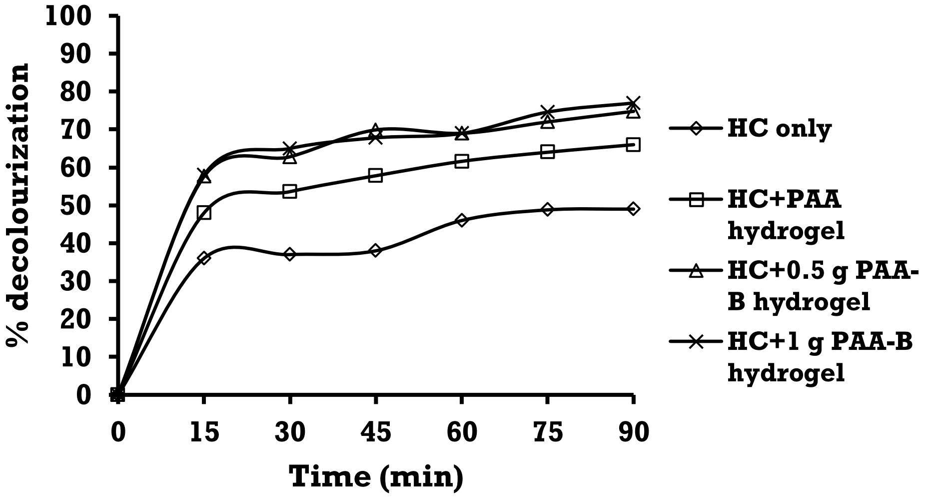


Fig. 42. Effect of clay content in hydrogel on % decolourization of crystal violet dye [CV dye 500 mg/l; HC inlet pressure 3 bar]

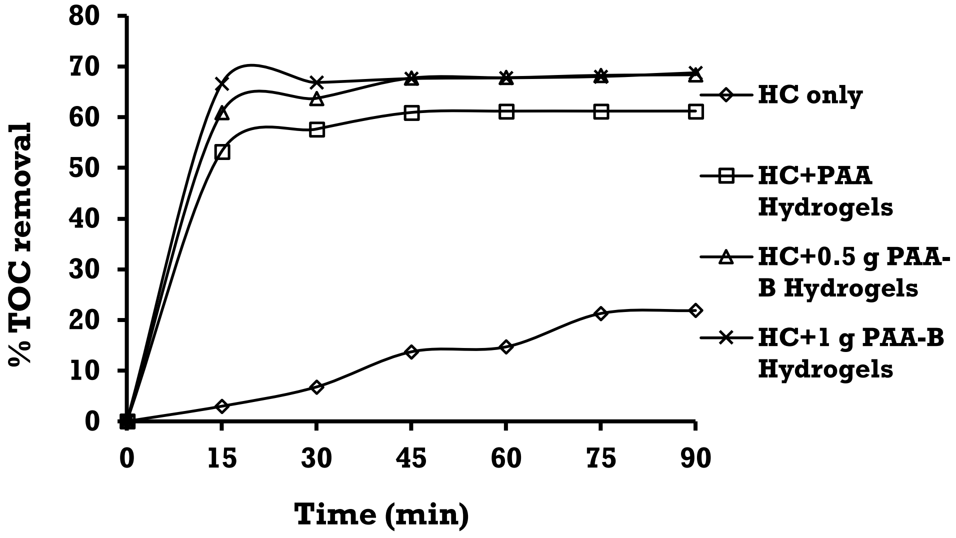


Fig. 43. Effect of clay content in hydrogel on percentage removal of TOC [CV dye 500 mg/l; HC inlet pressure 3 bar]

4.8.6 Effect of quantity of hydrogel loading

Effect of quantity of hydrogel loading on the decolourization of crystal violet dye has been investigated with the couple of hydrodynamic cavitation. In the typical experimental runs, 500 mg/L of dye stock solution and 20, 30, 40 g of 0.5 g bentonite clay loaded PAA nanocomposite hydrogels have been used individually for the investigation of decolourization of CV dye at the optimized inlet pressure of 3 bar. Every experiment has been carried out by placing the bydrogels in the acrylic bed, which was connected to the HC system after orifice (cavitating device). At every 15 min, samples were collected and analysed for UV absorbance and TOC in order to know the percentage decolourization of CV dye and total organic carbon removal. **Figure 44** shows the effect of quantity of hydrogel loading on % decolourization of crystal violet dye and total organic carbon removal by combination of hydrodynamic cavitation and hydrogel.

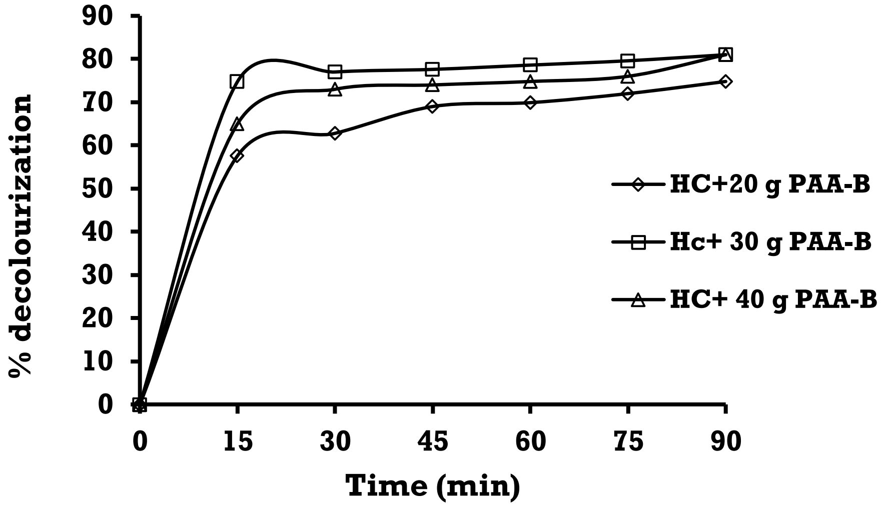


Fig. 44. Effect of quantity of hydrogel loading on % decolourization of crystal violet dye [CV dye 500 mg/l; HC inlet pressure 3 bar]

4.8.7 Effect of pH on dye removal in hybrid technique

Effect of the initial pH of the solution on the CV dye removal has been investigated. Initially, 2 L of 500 mg/L of dye stock solution have been prepared. Diluted sodium hydroxide and sulfuric acid was used for adjusting the pH of the dye solution. It was observed that the solution contains the pH of 2 has shown the better results in terms of decolourization and degradation of organic carbon. About 94 % of decolourization and 77.06 % of TOC removal was achieved. It was also observe that, with increasing pH of the solution from 2 to 10, the decolourization of CV dye was also has been gradually reduced. **Figure 45a** and **45b** shows the effect of pH on decolourization of crystal violet dye and percentage removal of crystal violet dye respectively.

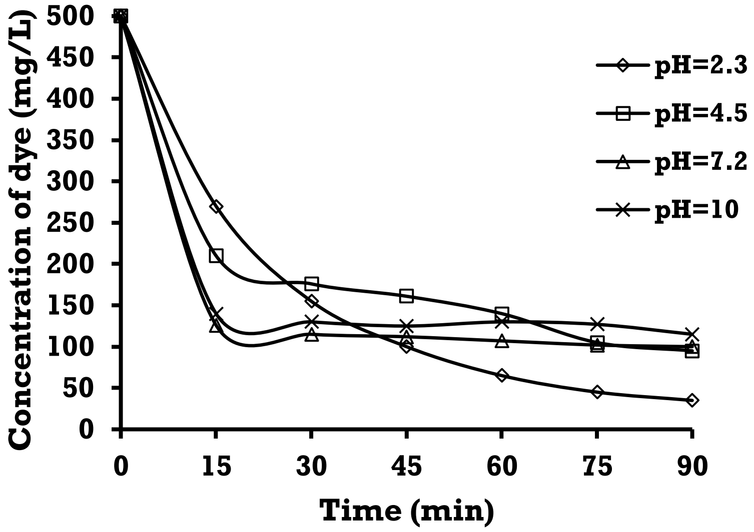


Fig. 45a. Effect of pH on decolourization of crystal violet dye [CV dye 500 mg/l; HC inlet pressure 3 bar, Inlet Flow rate of packed bed = 0.5 l/h]

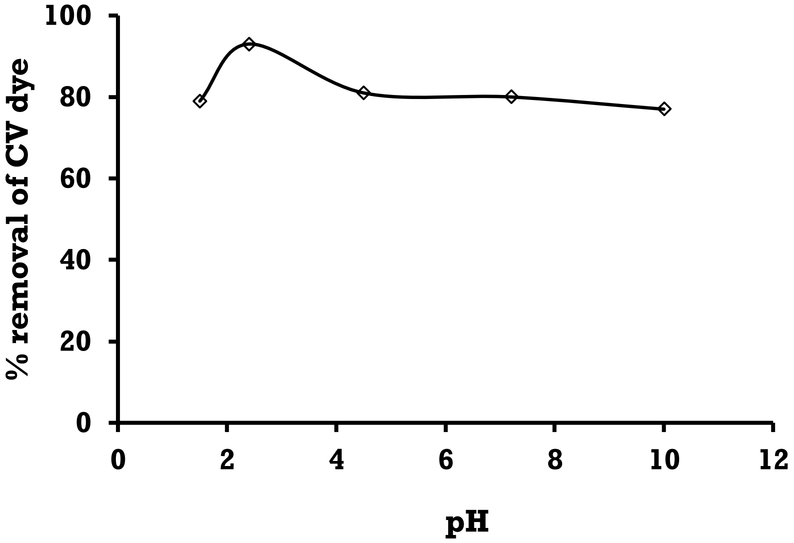
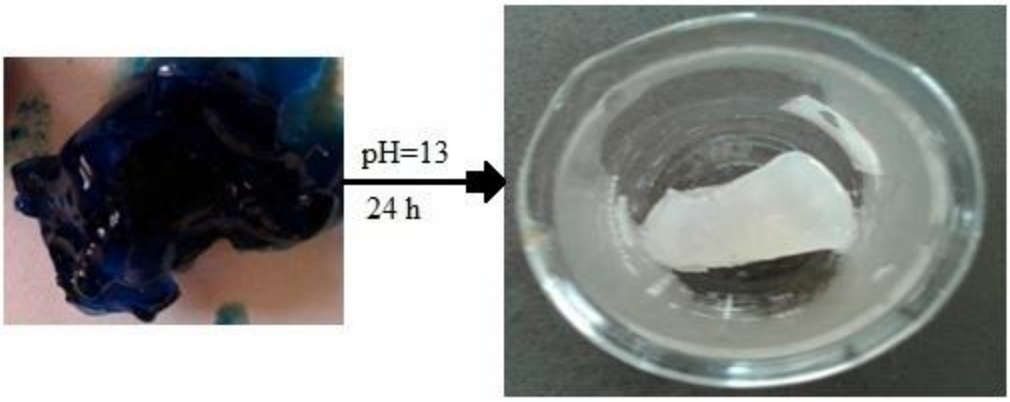


Fig. 45b. Effect of pH on percentage removal of crystal violet dye [CV dye 500 mg/l; HC inlet pressure 3 bar, Inlet Flow rate of packed bed = 0.5 l/h]

4.8.8 Regeneration of hydrogels for reuse:

A regeneration step has been attempted for reuse of polyacrylic acid hydrogel beads. The regeneration step has been carried out in the presence of basic solution (pH=13) for 24 h. Sample image of the regenerated PAA hydrogel bead has shown in the **Figure 46**.



CV dye adsorbed PAA hydrogel after 90 min

Regenerated PAA hydrogel

Fig. 46. Pictorial image of regenerated PAA hydrogel

4.8.9 Comparison of hydrogel packed bed adsorption and hydrodynamic cavitation

Synergetic effect of combined processes has been evaluated on the basis of percentage reduction of TOC of single and combined process. The synergetic index of the HC combined with hydrogel adsorption has been calculated to evaluate the efficiency of the combined process of HC and Hydrogel adsorption to compare it with individual process (HC and hydrogel adsorption alone). The synergetic index (f) of HC combined with hydrogel adsorption has been calculated by using the following equation shows synergetic effect of hybrid process.

$$\mathrm{f}_{(\mathrm{HC+adsorption})} = \frac{\mathrm{k}_{(\mathrm{HC+adsorption})}}{\mathrm{k}_{(\mathrm{HC})} + \mathrm{k}_{(\mathrm{adsorption})}} \qquad (21)$$

$$= \frac{0.026}{0.003+0.025}$$

$$= 0.928$$

4.9. Treatment of real textile industrial wastewater using hydrodynamic cavitation combined with hydrogel packed bed adsorption

Textile dye waste water has been collected from Badlapur textile industry, Mumbai, Maharashtra. Characteristics of collected wastewater were shown in below **Table 6**.

Table. 4: Characteristics of industrial wastewater

S.NO	**Characteristics**	**Value**
1	pH	9.3
2	Total Organic carbon (TOC)	211 mg/L
3	Total Dissolved Solids (TDS)	303 mg/L

4.9.1 Degradation through HC alone

Degradation of organic pollutants in wastewater has been studied in the presence of HC alone. The original sample with an initial TDS of 303 mg/L and TOC of 211 mg/L was diluted to the ratio of 1:1. Experiments were carried out at the dilution ratio of 1:1 and at the inlet pressure of 10 bar. Degradation of dye solution was achieved by passing of dye solution through the cavitating device for 90 min in a recirculation mode. At every 15 min samples were collected and analysed for TOC in order to know the mineralization rate of organic pollutants in wastewater. Degradation of organic carbon was achieved up to 15.33 % in 90 min of degradation study has been confirmed from the TOC analysis

4.9.2 Degradation through addition of H_2O_2 in HC

Addition of hydrogen peroxide (H_2O_2) produce the additional supplement of •OH radicals to the •OH radicals generated by the HC, leads to the double the quantity of •OH radicals which enhance the rate of degradation of organic pollutant is extremely higher compared to individual advanced oxidation process (HC). Hydrogen peroxide (H_2O_2) is known as a common oxidizing agent can be used for the treatment of waste water due to its adequate oxidation potential of 1.78 V. Experiments were conducted using the hybrid process of HC and H_2O_2 at 10 bar inlet pressure. 6 mg/L of H_2O_2 addition was carried out to study the mineralization rate of organic pollutants in the presence of hybrid process. From the TOC analysis, it was found that HC combined with H_2O_2 shows the 68.71 % of degradation of organic carbon in 90 min.

4.9.3 Absorption through Hydrogel alone

In order to know the performance of the 0.5 wt % of PAA-Bentonite clay nanocomposite hydrogel, batch absorption test has been carried out. In a typical experimental run, 2 L of diluted (ratio of 1:1) wastewater and 30 g of bare PAA hydrogels (0.5 bentonite clay loaded PAA hydrogels) have been used. At every 15 min, samples were collected and analysed for TOC analysis in order to know the percentage removal of organic carbon. Hydrogel adsorption shows the 50.43 % of removal of organic carbon in 90 min.

4.9.4 Degradation and subsequent absorption through HC and Hydrogel

In a typical experimental run, 2 L of diluted (ratio of 1:1) wastewater and 30 g of bare PAA hydrogels (0.5 bentonite clay loaded PAA hydrogels) have been used for the investigation of mineralization rate of TOC at the inlet pressure of 10 bar. Every experiment has been carried out by placing the hydrogels in the acrylic bed, which was connected to the HC system after orifice (cavitating device). At every 15 min, samples were collected and analysed for TOC analysis in order to know the percentage removal of organic carbon. HC combined with hydrogel adsorption shows the 80.36 % of removal of organic carbon in 90 min. **Figure 47** shows the performance of various systems on removal of TOC.

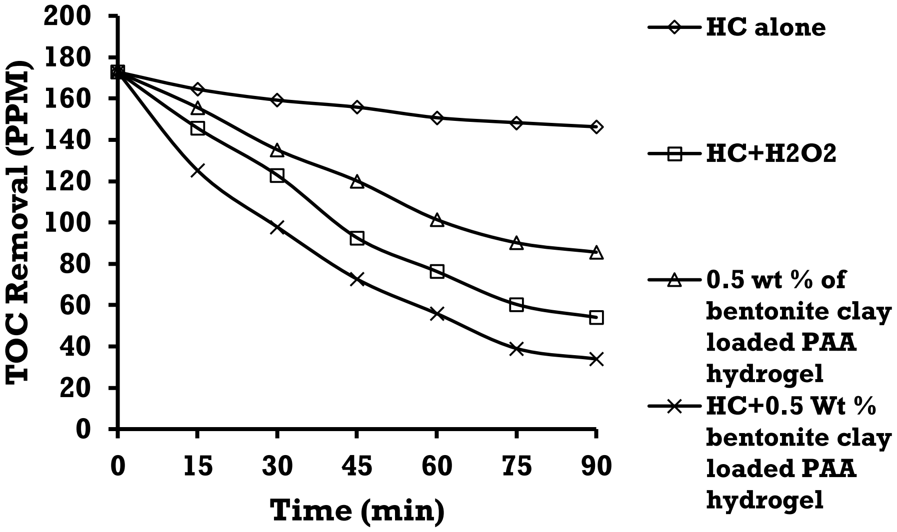


Fig. 47. Performance of various systems on removal of TOC

4.10 Power consumption and cost effectiveness of hybrid sytem

Electrical power consumption plays an important role in estimating the cost effectiveness of the hydrodynamic cavitation based processes, since electric energy consumption represents a significant fraction of the operating cost of such processes. Costing of the process has been evaluated on the basis of energy dissipated in the system, considering the approximate cost of electricity in India as Rs. 5.06/kWh.

4.10.1 Combination of hydrodynamic cavitation and Hydrogel (Hybrid system):

Electrical power supplied = 750W and treatment volume = 2 L.

Energy required = 750/2 W/L = 375 kW/m^3.

Power consumption = energy required X treatment time

= 375 X 1.5 =562.5 kWh/m^3

Cost of electrical energy (considering 1 kWh = Rs. 5.06/–)

= 562 X 5.06 = **2843.72 Rs./m^3**

4.10.2 Cost of the synthesis of polymer nanocomposite hydrogels:

Amount of hydrogels required for the treatment of 1 m^3 of dye wastewater = 15kg/m^3

(a). Cost of the chemicals for synthesis of 60 gm of dried nanocomposite hydrogels = Rs. 43.219/-

(b). Cost of Energy for synthesis of nanocomposite hydrogels:

Electrical power supplied = 150W and reaction volume = 106 ml = 0.106 L.

Energy required = 150/0.106 W/L = 1415.09 kW/m^3.

Power consumption = energy required X reaction time

= 1415.09 X 0.666 = 942.44 kWh/m^3

Cost of electrical energy (considering 1 kWh = Rs. 5.06/–)

= 942.44 X 5.06 = **4768.74 Rs./m^3**

(c). cost for synthesis of 15 kg of nanocomposite hydrogels = Rs. 10,804/-

Total cost for the synthesis of 15 kg of nanocomposite hydrogels (b+c) = Rs. **15,572.74/-**

5. Result / Findings

Poly(acrylic acid)-bentonite-FeCo (PAA-B-FeCo) hydrogel nanocomposite has shown the maximum dye removal above 75 % in the pH range of 9 to 11. At higher pH, the COOH functional groups of acrylic acid present in the hydrogel matrix dissociates to form COO$^-$ ions, which is responsible for higher adsorption of dye in basic pH. The adsorption of the CV dye increases with increase in temperature. A maximum of about 87 % removal was obtained at 35 ^{0} C, hence remaining experiments were carried out at 35 ^{0}C. Different amounts of hydrogel (0.5, 1, 1.5, 2 g) loaded in 30 mg/L concentration of 100 mL CV dye solution among them 2 g of hydrogel sample shows about 95 % of dye removal. Combined effect of ultrasound and hydrogel adsorption was evaluated and compared, with hydrogel alone, 87 % removal was achieved in 15 h and with combination of ultrasound 97 % removal was achieved in only 5 h.

Poly (acrylic acid)-Kaolin (PAA-K) hydrogel composite has been used for the removal of the brilliant green (BG) dye over the pH range of 4–9. it has been observed that the maximum adsorption takes place at pH value of 7. The extent of removal of dye increases with an increase in the pH till an optimum value of 7, beyond which it gradually decreases. The maximum extent of removal obtained at 35 ^{0}C was 56.24 % for the conventional method and 88.3 % for ultrasonic method. In different amounts of hydrogel (0.5, 1, 1.5, 2 g) and 100 mL of fixed concentration (30 mg/L) BG dye solution. The higher dye removal, close to 100%, was reached when 2 g of ultrasonically synthesized hydrogel was used. At the same time when the conventionally synthesized hydrogel was used, 2 g hydrogel was able to remove only 63 % dye.

Novel energy efficient technique HC+Hydrogel was successfully applied for the removal of crystal violet dye. It was observed that 49 % of decolourization and 18 % of mineralization rate was achieved with the HC only. Extent of decolourization and mineralization of CV of dye was achieved from 49 to 75 % and 18 to 67 % respectively when; the hydrogels were combined with HC. It was conformed that, coupling of hydrogels with HC made the process efficient way for the removal dyes from aqueous streams. At pH 2.4 the combined system has been removed 93 % of decolourization of Crystal violet dye. Synergetic effect of combined processes has been evaluated on the basis of reaction rate constant data of single and combined process. The synergetic index of the HC combined with hydrogel adsorption has been calculated to evaluate the efficiency of the combined process of HC and to hydrogel adsorption compare with individual process. The synergetic index (f) of HC combined with hydrogel adsorption to be 0.928. It has been found that the removal of Malachite Green dye is 96 % in the combined HC and Hydrogel than the single hydrodynamic cavitation technique.

6. Discussion and Analysis

PAA-B-FeCo hydrogel was synthesized by ultrasonic polymerization of AA and cross-linked by B-FeCo. The network formation of crosslinked polymer hydrogels shows a good swelling behavior due to the presence of B-FeCo. Adsorption process for dye removal was shown to be highly efficient for higher pH and temperature. The lower concentration and higher quantity of hydrogel is more favorable for maximum removal efficiency. The combined effect of hydrogel and ultrasound show a higher percent removal of the dye as compared to hydrogel alone. The FTIR spectrum confirms the presence of carboxyl group in all hydrogel samples. The equilibrium data for adsorption was followed using both Langmuir and Freundlich isotherms. The negative value of ΔG^o indicates the feasibility and spontaneity of the adsorption process. The positive value of ΔH^o suggests the endothermic nature of the adsorption.

The use of ultrasound during polymerization reaction has been shown to uniformly disperse the kaolin clay in the polymer matrix enhancing its adsorption properties considerably for the removal of Brilliant Green from aqueous solution as compared to hydrogel prepared by conventional method. The extent of Brilliant Green removal has been observed to increase with an increase in pH (till optimum value), temperature, adsorbent and adsorbate concentrations as well as the kaolin clay content in the hydrogel. It has been observed that the maximum BG removal by PAA-K hydrogel was achieved for the initial dye concentration of 30 mg/L at a temperature of 35 ^{0}C and pH 7. Adsorption kinetics investigation revealed that the pseudo-second-order model fits the experimental data well. Also the Freundlich and Langmuir adsorption isotherm models explain the experimental results satisfactorily.

It was observed that PAA- Bentonite clay nanocomposite hydrogel shows physically in more strength and high dye absorption capacity than the pure PAA hydrogel due to the addition of 0.5 gm of bentonite nanoclay in to it.

In the case of crystal violet dye removal using hydrodynamic cavitation and hydrogel, the decolorisation time is decreases when the pH of the solution in basic media. From experimental, it was observed that the decolorisation is favours in acidic media and decreases in basic media whereas in the case of malachite green dye removal, decolorisation is favours in basic media. The enhancement in the decolorisation/degradation rate at lower pH in case of crystal violet dye can be attributed to the fact that dye molecule is present in the molecular state at lower pH, and hence can easily locate itself at the gas–water interface of cavities due to hydrophobic nature and thus, is more readily subjected to the ·OH radical attack and also to the thermal decomposition. Whereas in the basic medium the dye molecules gets ionized and becomes hydrophilic in nature there by remaining in the bulk liquid.

The most important parameter in the case of hydrodynamic cavitation based degradation of pollutant is the inlet fluid pressure to the cavitating device. The inlet fluid pressure and the velocity at the throat are dependent on each other and it affects the cavitating condition inside the orifice, so optimization of inlet pressure is necessary in order to get maximum cavitational effects. It was found that decolorisation rate increases with an increase in inlet pressure reaching to the maximum at 3 bar inlet pressure and then decreases.

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PART - III

1. Recommendation including remedial measures relevant to the environmental problems studied under the project.

   The dye degradation studies under this project reveal the hydrogel assisted hydrodynamic cavitation technology able to remove near complete removal of organic pollutants presents in wastewater. After sufficient use of hydrogels can be decompose or dump in the land. The basic advantage involved in this project is regeneration of hydrogels can be done to reuse again in the treatment process. The liquid waste release from the regeneration process can be treating with the electrolysis process. These are the main remedial measures to reduce the environmental problems through effective utilization of this technology.

2. Utility of the findings of the Project for industry / other organizations (Pl. also specify the manner in which these could be utilized).

   The developed hybrid technology will be mainly useful for the treatment of textile dye wastewater. This technology can be used to degrade/remove the most of the organic pollutants and colour substances from the waste water. The two techniques involved in this hybrid technology such as hydrodynamic cavitation and hydrogel packed bed will be useful for the degradation and subsequent adsorption of organic pollutants present in the wastewater. For the utilization of this technology in the industrial scale, it requires bulk quantity of hydrogels to treat the large quantity of wastewater. After single use of hydroels for adsorption of organic pollutants, it can be regenerate to reuse about two or three times in the packed bed for re-adsorption. Regeneration of hydrogels is a simple process; it can be done by passing the basic solution through the packed bed or simply dipping the hydrogels in the basic solution over a period of 24 hr. The healed hydrogels further to be subjected for drying about 2 to 4 days in a hot air oven to obtain the hardened hydrogels.

3. Whether any patents have been filed or are likely to be filed on the basis of the project work.

   Patent has not yet been filed on the basis of this project work. We would like to file the patent on the basis of the project work

4. List of research papers/published/accepted on the work done under the project.

   (Two copies of the reprints/accepted/submitted paper also to be enclosed)

   [1]. Bhaskar Bethi, Shirish H. Sonawane, Bharat A. Bhanvase, Sarang Gumfekar, Nanomaterials based Advanced Oxidation Processes for Waste Water treatment: A review, Chemical Engineering Processing: Process Intensification, **Accepted**, **Impact Factor 2.156**.

   [2]. Bhaskar Bethi, S.H. Sonawane, G.S. Rohit, C.R. Holkar, D.V. Pinjari, B.A. Bhanvase, A.B. Pandit. Investigation of TiO_2 photocatalyst performance for decolorization in the presence of hydrodynamic cavitation as hybrid AOP, Ultrasonics Sonochemistry, 28, 2016, pp. 150-160. **Impact Factor 4.556**.

   [3]. S.R. Shirsath, A.P. Hage, M. Zhou, S.H. Sonawane, M. Ashok kumar. Ultrasound assisted preparation of nanoclay Bentonite nanoclay-FeCo nanocomposite hybrid

hydrogel: A potential responsive sorbent for removal of organic pollutant from water, Desalination, 281, 2011, Pages 429–4373. **Impact Factor 4.3**.

[4]. Sachin R. Shirsath, Anup P. Patil, Rohit Patil, Jitendra B. Naik, Parag R. Gogate. Shirish H. Sonawane. Removal of Brilliant Green from wastewater using conventional and ultrasonically prepared poly (acrylic acid) hydrogel loaded with kaolin clay: A comparative study. Ultrasonics Sonochemistry 20 (2013) 914–923. **Impact Factor 4.556**.

[5]. S.R. Shirsath, D.V. Pinjari , P.R. Gogate , S.H. Sonawane, A. B. Pandit. Ultrasound assisted synthesis of doped TiO_2 nano-particles: Characterization and comparison of effectiveness for photocatalytic oxidation of dyestuff effluent, Ultrasonics Sonochemistry, 20, 1, (2013), 277-286. **Impact Factor 4.556**.

5. Whether any research fellow associated with the project has been awarded Ph.D. etc. or any other higher degree and if so, name of the fellow and the title of the thesis may be given.

   One of the fellows associated with this project has been awarded the Ph.D degree based on the research work carried out through this project.

   Name of the fellow: Sachin Rangnath Shirsath

   Title of the thesis: Studies on effect of cavitation on different physical and chemical processes.

Annexure-IX

FORMAT FOR EXECUTIVE SUMMARY OF RESEARCH PROJECTS FUNDED BY THE MINISTRY OF ENVIORNMENT, FOREST & CLIMATE CHANGE

(Not more than 3 Pages)

1. **Title of the Project:**

   Synthesis of Polymer Nano Hydrogel and Development hybrid wastewater treatment system using Cavitation Technique and Hydrogel.

2. **Name of Members of Research Team and their designation**

   I. Dr. Shirish Sonawane,

   Principal Investigator,

   Associate Professor,

   Chemical Engineering Department

   II. Mr. Bhaskar Bethi,

   Junior Research Fellow

3. **Number and date of Sanction letter:** F. No. 10-1/2010-CT (WM), dated 28/12/2013

4. Duration of the Project: 2 years 7 months (Including extended period)

5. Total outlay of the Project: 34,29,300

6. Date of start of Project: 28-12-2013

7. Date of completion of Project: 31-07-2016

8. Brief introduction:

Hydrogels are three dimensionally dense cross linked polymer network structures composed of functional hydrophilic groups which have the ability to absorb significant amount of water and solute molecules. Hydrogels are also known as smart materials which show response and swelling when there is small change in external environment. The response of hydrogel is dependent on the presence of hydrophilic functional groups such as –OH, –COOH. These groups make the hydrogel hydrophilic and due to capillary action and difference in the osmotic pressure, water diffuses into the hydrogel. A number of adsorbents are used in dye adsorption, e.g. activated charcoal, clay materials such as bentonite, flyash, kaolin and montmorillonite. These adsorbents generate secondary waste and some of the materials are not efficient adsorbents because of their limitations in the cation exchange capacity, lower adsorption rate, etc. Hence, the enhancement of adsorption process has been achieved using cavitation, changing cation exchange capacity or hybrid nanocomposites. Nanocomposite hydrogels are loaded with the different types of clays like bentonite, Kaolin have been studied in this project for removal of various dyes such as crystal violet, Malachite green and brilliant green.

In this project, Ultrasonic irradiation is used to initiate the emulsion polymerization to form hydrogel through the generation of free radicals as well as the uniform distribution of clay across the hydrogel polymer matrix. Enhancement of adsorption process by combining it with ultrasonic cavitation has been studied at lab level. Hydrodynamic cavitation combined with packed bed hydrogel process has been developed with the aim of treatment of bulk quantity of wastewater.

9. Objectives

- Synthesis of polymer hydrogel and incorporation of nanoparticles into the polymer matrix.
- Comparative study of cavitation effect and gel adsorption onto model pollutants.
- Development of simplified process for removal of these textile dye compounds. Testing effectiveness of developed system for industrial waste water treatment.

10. Work done

Synthesis of poly(acrylic acid)-bentonite-FeCo (PAA-B-FeCo) hydrogel nanocomposite via ultrasound assisted in situ emulsion polymerization was carried out. The response of the nanocomposite hydrogel was evaluated using a cationic dye, crystal violet (CV) under different temperature, pH, and cavitation environment. Removal of brilliant green dye from water using a poly (acrylic acid) hydrogel composite (PAA-K hydrogel) prepared by incorporation of kaoline clay has been investigated. The composite has been synthesized using ultrasound assisted polymerization process as well as the conventional process. The optimum conditions for the removal of dye are pH: 7, temperature: 35 ^{0}C, initial dye concentration is 30 mg/L and hydrogel loading 1 g. Combined novel hybrid technique (hydrodynamic cavitation + hydrogels packed bed adsorption) has been studied for dye degradation and subsequent adsorption of dye molecules. A lab scale hybrid system consists of 5 L of capacity have been fabricated in in-house for carrying out the experiments. Polyacrylic acid (PAA)/nanocomposite hydrogels which includes PAA-Bentonite clay nanocomposite and PAA-Greaphe oxide nanocomposite hydrogels have been synthesized via ultrasound assisted emulsion polymerization technique. Synthesized hydrogels have been characterized by XRD and TEM analysis. Operational parameters such as effect of inlet pressure, effect of bentonite clay content in PAA hydrogel, effect of hydrogel quantity loading in packed bed, effect of pH on removal of dye pollutants have been investigated using hybrid technique. Initially the azo type of dyes such as malachite green and crystal violet dye removal have been studied using the lab scale hybrid system.

11. Results / findings

Poly(acrylic acid)-bentonite-FeCo (PAA-B-FeCo) hydrogel nanocomposite has shown the maximum CV dye removal above 75 % in the pH range of 9 to 11. A maximum of about 87 % removal was obtained at 35 ^{0}C. 2 g of hydrogel sample loading in the reactor shows about 95 % of dye removal. Adsorption by hydrogel alone, obtained 87 % removal of CV dye in 15 h and with combination of ultrasound 97 % removal was achieved in only 5 h.

In the case of poly (acrylic acid)-Kaolin (PAA-K) hydrogel composite for adsorption of brilliant green dye, the maximum adsorption takes place at pH value of 7. The maximum extent of removal obtained at 35 ^{0}C was 56.24 % for the conventional method and 88.3 % for ultrasonic method. The higher dye removal, close to 100%, was reached when 2 g of ultrasonically synthesized hydrogel was used. At the same time when the conventionally synthesized hydrogel was used, 2 g hydrogel was able to remove only 63 % dye.

In the case of HC+Hydrogel, 49 % decolourization of Cv dye and 18 % of mineralization rate was achieved with the HC only. Extent of decolourization and mineralization of CV of dye was achieved from 49 to 75 % and 18 to 67 % respectively when; the hydrogels were combined with HC. At pH 2.4 the combined system has been removed 93 % of decolourization of Crystal violet dye. It has been found that the removal of Malachite Green dye is 96 % in the combined HC and Hydrogel than the single hydrodynamic cavitation technique.