Conceptualizing Cavigulation Methodology by Integrating Cavitation and Coagulation and Application to Dye Wastewater Treatment

Krati Sharma[1,4] , Chethana M[1]., Vinay M. Bhandari[1*], Laxmi Gayatri Sorokhaibam[2], Vivek V. Ranade[1,5] and Deepak J. Killedar[3]

1. Chemical Engineering and Process Development Division
CSIR-National Chemical Laboratory, Pune, India
2. Visvesvaraya National institute of technology, Nagpur, India
3. Civil Engineering and Applied Mechanics Department
Shri G.S. Institute of Technology and Science, Indore, India

*Email: vm.bhandari@ncl.res.in

Abstract

The present work provides a proof of concept for a new hybrid process, cavigulation, by combining cavitation and coagulation and its application to dye wastewater treatment. Both acoustic and hydrodynamic cavitations were evaluated. Removal of a commonly used dyes such as Congo red was investigated by cavigulation in the concentration range of 50 to 500 ppm. A broad spectrum of coagulants including two inorganic coagulants; poly aluminium chloride, iron (III) chloride, and natural biocoagulants derived from *Moringa oleifera*, *Cicer arietinum* and *Acanthocereus tetragonus* were employed to substantiate the concept of cavigulation. A vortex diode device employing vortex flow for cavitation, was used for the hydrodynamic cavitation (HC) -based cavigulation. Cavigulation in the form of acoustic cavitation + coagulation, showed significant improvement over individual processes; acoustic cavitation alone was largely ineffective for dye removal. Increase over conventional coagulation to the extent of 24% and 48% was observed for the two inorganic coagulants-Iron (III) chloride and PAC SAB 18, while for *Moringa oleifera, Acanthocereus tetragonus*, and *Cicer arietinum* the increase was 27%, 33%, and 29% respectively. The pH has a large impact on the cavigulation process, similar to coagulation and the coagulant dose could be reduced by more than half by adjusting pH to 3. Auramine O dye removal was effective using hydrodynamic cavitation compared to coagulation. The developed cavigulation process, especially using biocoagulants, could be an effective alternative to the conventional chemical coagulation in the form of a green process in dye wastewater treatment.

1.   Introduction

The industry sectors such as textile industry, dye industry, or industries using dyes for different applications produce large volumes of wastewater that need to be treated appropriately to remove both biodegradable and non-biodegradable dyes prior to the discharge. The effluent is colored with complex characteristics of high chemical oxygen demand, dissolved and suspended impurities, heavy metals, etc[1]. The nature of dyes varies greatly in terms of properties such as molecular weight, complex structures; but most importantly, in terms of biodegradability. In recent years, use of refractory dyes, that are non-biodegradable, has increased significantly[2] posing serious limitations to not only discharge of waters but also to the conventional biological treatment processes[3]. The refractory pollutants can have undesirable effects even at very low concentrations, can pose health hazards apart from impacting the photosynthetic activity of flora and also the other aquatic life adversely[4].

Many conventional techniques for dye wastewater treatment that are not only well researched, but are also in commercial practice include both physical and chemical processes such as coagulation/flocculation, membrane filtration, adsorption, chemical oxidation, ion exchange, apart from biological processes[5,6] The biological treatment processes are largely ineffective for removing colour from the wastewaters[7]. In recent years, due to a large number of refractory dyes that are difficult to degrade, many of these conventional methods have severe limitations in effectively treating the wastewater or incur higher costs apart from generating secondary waste[8].

To overcome the limitations of conventional techniques, many advanced processes need to be applied at higher costs e.g. electro-coagulation, advanced oxidation processes of the type electro-oxidation, newer materials of the type of chemically modified adsorbents or nanocomposites, etc. Process integration of the type of ultrasound-assisted adsorption has also been reported to enhance dye removal[9]. In view of the pollution control norms which are getting stricter with time, there is a major challenge in not just treating these wastewaters effectively, but also techno-economically to achieve degradation of complex and recalcitrant pollutants. The present work is an attempt to devise and develop one hybrid process by effectively combining the conventional coagulation process with newer cavitation process.

In recent years, the use of acoustic and hydrodynamic cavitation for the treatment of industrial wastewaters has been shown to be effective and some newer forms of cavitating devices have been reported [5,10,11]. The cavitation process has a major advantage in terms of ease of operation, scalability, low cost of operation, and most importantly, no secondary waste generation since the organic pollutants largely get mineralized into water and carbon dioxide [12–15]. The cavitation process, an advanced oxidation process, involves generation, growth and collapse of the cavities through physical means. The collapse of the cavity or bubble is termed as implosion, opposite to explosion, and generates extreme conditions of temperature (~5000- 10000K) and pressure (~1000- 5000 atm) at the localized point of implosion. As a consequence, water splits and generates hydroxyl radicals which subsequently oxidize the organic pollutants. From industrial wastewater treatment point of view, only acoustic and hydrodynamic cavitation are most promising[16]. In the case of acoustic cavitation, cavities get generated by inducing ultrasound waves in the liquid medium (> 16 kHz), while in hydrodynamic cavitation, it is achieved by devising conditions of sudden pressure drop using constriction (cavitating devices) in the flowing fluid. Although significant work has been reported in the area of sonochemical reactors and its application in wastewater treatment, its implementation for actual industrial practice is still negligible due to the reasons of high cost of treatment and operational difficulties, especially in power dissipation. The impact of cavitation processes can be dramatically increased by combining it with other oxidation process employing catalysts or additives[17].

The conventional effluent treatment invariably employs coagulation processes for reducing part load of pollutants from the effluents Coagulation, in itself, is rarely a complete process and therefore requires subsequent treatment methods such as adsorption, oxidation to meet the desired pollution control norms. There are a number of coagulants commercially available in both inorganic and organic class ranging from low cost alum, ferric chloride to more expensive polymeric coagulants and organic coagulants. The effectiveness of the coagulation process can be significantly improved by the appropriate physical or chemical combination of one or more different coagulants to increase the floc size, improved settling, reduced sludge generation and to reduce the cost. Further improvements in this process can also be obtained by using natural bio-coagulants or their formulations[18].

Biocoagulants are emerging as a safe and economic option over chemical coagulants. *Moringa oleifera* is a naturally occurring tree found in India, South Saharan Africa and South-America. [19]. *Acanthocereus tetragonus* (also called barbed wire cactus, sword pear, dildo cactus, night blooming cereus, triangle cactus) belongs to Cactaceae family. *Cicer arietinum* commonly known as chickpea belongs to Fabaceae family and subfamily Faboideae. All three of them are reported as coagulants in water/wastewater treatment [18].

Though, extensive investigations on cavitation and coagulation have been reported for removal of different pollutants, hybrid technology using in-situ coupling of cavitation with coagulation is not reported so far. The present study is an attempt to provide proof of concept for a new cavigulation process in this regard that investigates combination of acoustic and hydrodynamic cavitation with coagulation for dye removal. Removal of one commonly used model dye, Congo red- an acidic dye, was investigated in detail. Use of inorganic coagulants, PAC SAB 18 and iron (III) chloride was compared to evaluate the effect of the new process. Three different natural biocoagulants namely, *Acanthocereus tetragonus*, *Moringa oleifera* and *Cicer arietinum* were also evaluated in this regard. Further, dye removal was compared with hydrodynamic cavitation by using the concept of cavigulation, for a cavitating device employing vortex flow- vortex diode. The present study is the first of its kind exploring and developing a suitable combination of cavitation and coagulation in the form of cavigulation; acoustic cavitation+coagulation and hydrodynamic cavitation+coagulation.

2.   Materials and Methods

2.1   Materials

Congo red is an anionic di-azo dye with molecular formula $C_{32}H_{22}N_6Na_2O_6S_2$. This is benzidine based dye with two azo groups and has an aromatic structure. Auramine O is a cationic dye containing amino and imino groups with molecular formula $C_{17}H_{22}ClN_3$. It is also combined with hydrochloric acid. This is a basic dye classified under Diarylmethane class. Orange G is an anionic azo dye with molecular formula $C_{16}H_{10}N_2Na_2O_7S_2$. Congo red (CR), auramine O (AO), and orange G (OG) dyes were purchased from Loba Chemie. The physiochemical properties of the dyes are given in **Table 1.** Chemical coagulants PAC SAB 18, polyDADMAC, Iron (III) chloride hexahydrate, and Iron (III) Chloride were procured from Sigma Aldrich. All the chemicals and reagents used in this study were of analytical

grade. All the solutions were prepared using distilled water. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH. The plant pads of biocoagulant, *Acanthocereus tetragonus* were collected from campus of National Chemical Laboratory (NCL), Pune, India. *Moringa oleifera* and *Cicer arietinum* biocoagulants were purchased from local market of Pune, India.

2.2   Preparation of bio-coagulants

Moringa oleifera seeds were de-shelled, and dried at ambient temperatures (40 ± 5^0 C) for one day before milling. The whole kernels were milled into a fine powder using a food blender. *Moringa oleifera* seed solution was made by dissolving 5 g of powder with 100 ml of distilled water and solution was stirred for 30 min to extract the active coagulant part and the extracted solution was used for the treatment of the synthetic dye wastewater. The detailed method has been reported in our previous work.[18]

Acanthocereus tetragonus pads were collected and washed thoroughly with tap water, and manually chopped into small pieces after removing the spines. The external skin as well as the inner off-white portion of the cactus pieces were ground with a food processor and extracted with water in equal weight by volume ratio. It was then filtered to remove the fibrous part. Fresh extracts were prepared for each batch run.

Cicer arietinum seeds were collected, and ground to make it into powdered form. The powder was used as coagulant and stored under refrigeration.

2.3   Experimental

The dye solutions of concentrations 50 mg/L, 100 mg/L, and 500 mg/L were prepared by using distilled water. The coagulation experiments were performed using jar test apparatus (Stuart SW6, UK) consisting six paddles and six beakers. The effect of concentration, coagulant dose was studied by using a rapid mixing at 200 rpm for 2 min followed by slow mixing at 40 rpm for 20Min.. A settling time of 30 minute was provided after which the supernatant was collected and filtered before each analysis. The acoustic cavitation and cavigulation (acoustic cavitation+coagulation) experiments were performed using UCB-100 Sonicator at 40 kHz and 250 W power for 15 minute. Hydrodynamic cavitation and

cavigulation (hydrodynamic cavitation+coagulation) were performed with hydrodynamic cavitation pilot plant designed at CSIR-NCL, Pune. The details of pilot plant and experimental are well discussed in our earlier work [11,20–22]. The setup consists of holding tank of 50 litre capacity and a multistage centrifugal pump of rating 2.2 kW. The pressure drop was adjusted using the control valve connected to the bypass line. Flow rate transmitter, pressure transmitter, and thermocouple are provided for the measurement of the flow rate, pressure, and temperature of the solution respectively. The temperature of the solution was kept constant using the coolant which is circulated in coils in the holding tank. The samples for the analysis were collected at predetermined time intervals.

Cavigulation experiments were performed adopting three different schemes as given below, while running the respective cavitation process:

Acoustic cavitation (Sonication)+ Coagulation

Scheme 1: Addition of coagulant with 2 min rapid mixing in jar test apparatus followed by 15 min of Cavigulation.

Scheme 2: Addition of coagulant (no mixing provided separately) followed by 15 min of Cavigulation.

Scheme 3: First 10 min only cavitation followed by addition of coagulant (no mixing provided after addition) and next 5 min Cavigulation.

Hydrodynamic Cavitation using vortex diode + Coagulation

Scheme 1: Addition of coagulant with 15 min mixing in Cavitation setup through bypass at low flow rate, followed by 2 h of Cavigulation.

Scheme 2: Addition of coagulant (no mixing provided separately) followed by 2 h of Cavigulation.

Scheme 3: First 1 h Hydrodynamic Cavitation followed by addition of coagulant (15 min mixing provided after addition through bypass at low flow rate), followed by 1 h Cavigulation.

2.4   Dye removal studies

The sample solution was filtered after each cavigulation and coagulation experiment using Whatman. 41 filter paper. The dye concentration was calculated on the basis of the absorbance values obtained using spectrophotometer (spectroquant pharo-100) at λ_{max} value of 498 nm, 475nm and 433 nm for CR, OG and AO dyes respectively. The percentage dye removal was evaluated taking difference in initial and final dye concentration using the formula:

$$\text{Percentage dye removal } = \frac{Co - Ce}{Co} \text{ X } 100$$

Where, Co is initial dye concentration (mg/L) and Ce is Final dye concentration (mg/L)

3.   Results and discussion

3.1   Coagulation

3.1.1   Effect of coagulant dose

Coagulant dosage is one of the most important parameters affecting the efficiency of coagulation. A coagulant dose lesser than the required may lead to insufficient floc formation while over-dosing of coagulants leads to the re-stabilization of the colloidal particles. This also determines the techno-economic viability of the process. The dye removal efficiency of various coagulants viz. inorganic coagulants; PAC (Polyaluminium chloride) SAB 18, iron (III) chloride hexahydrate and organic coagulant; polyDADMAC and effect of varying their coagulant doses for 50, 100 and 500 ppm of auramine O, Orange G, and Congo red dye is shown in **Figs. 1 to 3.**

It can be seen from **Fig. 1** that, the dye removal was in the range 23 to 30% for 30 ppm of coagulant dose of PAC SAB 18, iron (III) chloride hexahydrate and polyDADMAC respectively for 50 ppm of initial dye concentration of auramine O dye, which started decreasing with further increase of coagulant dose. There was a decrease or no significant increase in removal for all the three coagulants for increased doses. This behavior may be attributed to the re-stabilization or re-dispersion of charge particles of dye. This observation is in agreement with the results reported by Zonoozi et al.[23]. For 500 ppm of dye, not more

than 20% of dye removal could be achieved with any of the three coagulants, even at coagulant doses as high as 1000 ppm.. Similar dye removal efficiency of various coagulants used in the study has been observed for all three concentrations of auramine O dye.

Fig. 2 provides data for the Orange G dye removal. A gradual increase in dye removal with an increase in coagulant dose was observed using all the three coagulants for all the dye concentrations except in the case of polyDADMAC for 50 ppm initial dye concentration, where removal efficiency slightly decreased from 42.8% to 34.8% after 75 ppm of coagulant dose. For lower concentrations of dye, higher removal efficiency using iron (III) chloride hexahydrate was observed in comparison to PAC SAB 18 while for 500 ppm initial concentration only 11.43% dye removal was observed even at a high dose of ICH (1000 ppm) whereas up to 51.53% dye removal was achieved using PAC SAB 18 (1000 ppm) coagulant. The higher removal efficiency of polyDADMAC at lower doses may be due to the fact that these high molecular weight organic coagulants generally follow charge neutralization along with bridging mechanism with polymers, resulting in dense and easily settleable flocs even at lower doses [24].

The results of Congo red dye are presented in **Fig. 3.** With an increase in coagulant dose, a sudden increase in dye removal using PAC SAB 18 coagulant was observed, whereas a gradual increase in removal efficiency was observed in the case of ICH. The sudden increase in dye removal in the case of PAC SAB 18 may be due to over saturation of formation of amorphous hydroxide precipitate which promote the enmeshment of colloidal particles in a sweep floc enhancing the overall removal even at lower doses as it is reported that sweep flocculation mechanism is one of the predominant mechanism with metal coagulants[24]. The dye removal was found to be more than 95% at 20 ppm, 30 ppm and 200 ppm dose of PAC SAB 18 and 45 ppm, 60 ppm and 200 ppm dose of ICH for 50, 100 and 500 ppm of initial dye concentration respectively.

In spite of being an organic polymer, the requirement of comparatively higher doses of polyDADMAC than the other two coagulants to achieve the maximum removal was surprising. According to Razali et al.[25]addition of polyDADMAC destabilize the particles resulting in change in zeta potential value, and create microflocs. Up to 96% of dye removal was observed at 80 and 150 ppm of coagulant dose for 50 and 100 ppm of initial dye

concentration respectively. Even at polyDADMAC dose of as high as 500 ppm, only 55.46% dye removal was observed for 500 ppm of initial dye concentration.

3.1.2. Selection of coagulant

The results of **Figs. 1 to 3**, indicate that performance of coagulants depends on the nature of dyes, coagulant dose and also the initial dye concentration. Almost similar removal efficiency was achieved using all three coagulants for removal of auramine O dye irrespective of initial dye concentration and coagulant doses. Whereas polyDADMAC was observed to be most suitable for the removal of orange G dye at all the initial dye concentrations, PAC SAB 18 displayed high removal efficiency at higher dye concentration. In the case of Congo red dye, PAC SAB 18 and ICH were found to be highly efficient even at lower coagulant dose, on the other hand higher coagulant doses of polyDADMAC were required to achieve maximum removal, which was very less at higher initial dye concentration of Congo red dye (500 ppm) even at higher coagulant doses. Comparatively lower coagulant doses were sufficient for high removal of Congo red dye than required in the case of other two dyes for all the dye concentrations.

3.1.3. Effect of nature of dye

The removal of auramine O dye was lowest among the three dyes. Orange G was also found to be difficult to remove, though polyDADMAC showed up to 55% dye removal for the orange G dye. Congo red was observed to be an easily removable dye for which very high removal with all three coagulants was observed.

 The dye removal behaviour is expected to depend on molecular weight, structure of dye, solubility, and the nature of dyes. It is also a well-recognized fact that dyes having longer molecular chains or larger molecular weights are more favorable for removal by coagulation[26,27]. Many dyes with low molecular weight and cationic dyes may not get effectively removed using coagulation [26]. Among the dyes taken for the study, auramine O is the only cationic dye having the lowest molecular weight i.e. 303.83 g/mol and orange G is highly soluble among three, having a solubility of 80 mg/ml in water. The characteristics of auramine O and orange G dyes contribute to low removal of these dyes using coagulation. Among the three dyes, Congo red has high molecular weight of 696.66 g/mol and has a di-

azo long chain structure which indicates its easy removal. Kim et al. [28] also related the low removal of dye as a function of the solubility of dye.

3.2. Cavitation

3.2.1. Effect of initial dye concentration

Cavitation was studied (Acoustic and Hydrodynamic) for the removal of Congo red, auramine O, and orange G dyes. The effect of initial dye concentration (50, to 500 ppm) on the removal efficiency was investigated for all three dyes. For the HC, operating time was 2 h and the experiments were conducted at 0.5 and 2 bar pressure drop conditions. **Fig. 4** shows the extent of degradation of auramine O and Congo red dye. The dye removal in auramine O dye increased with an increase in initial dye concentration from 50 to 100 ppm for both the pressure drop conditions, while the degradation decreased with a further increase in initial dye concentration (100 to 500 ppm). In Congo red, the maximum dye removal was achieved at 50 ppm. The decrease in dye removal at higher dye concentration values may be due to a lack of availability of $OH^{\bullet}$ radicals responsible for oxidation of pollutant[29]. Saharan et al.[30] found an increase in the degradation of orange G dye (30-150 μM) with an increase in initial dye concentration using circular venturi, slit venturi, and orifice plate while Pradhan and Gogate[31] have observed lower degradation of pollutant at higher concentrations.

3.2.2. Effect of pressure drop

The pressure drop was varied from 0.5 to 2 bar. The effect of pressure drop is shown in **Fig. 4.** High pressure drop condition was favourable for the removal of both Congo red and auramine O dyes at all the initial dye concentrations. A dye removal of up to 45%, 73%, and 12% in the case of auramine O and 23%, 11%, and 10% in the case of Congo red was observed at 2 bar pressure drop for 50, 100 and 500 ppm of initial dye concentration respectively in 2 h. Saharan et al.[14] reported the effect of inlet pressure (3-7 bar) for the decolourization of acid red 88 dye and it was found that the rate of degradation increases up to 5 bar inlet pressure and then decreased. Gogate and Pandit[32] also discussed the importance of the optimum inlet pressure conditions at which maximum cavitational intensity can be achieved emphasizing the importance of the quantum of total collapse pressure generated as a result of the collapse of single cavity and the total number of cavities being generated in the

solution. However, degradation of orange G dye was very low, less than 5% irrespective of the initial dye concentration and pressure drop conditions.

Saharan et al.[30] reported degradation of orange G dye using orifice, slit venturi and circular venturi as cavitating devices and found that hydrophilicity or hydrophobicity of dye molecule is important in degradation. It relates to the state of pollutant molecule in the solution i.e. molecular or ionic state. If the pollutant is in molecular state, it can easily enter the region of gas water interface of cavities due to hydrophobic nature and thus more readily subjected to $OH^{\bullet}$ radical attack and also to the thermal decomposition[33]. Thus the overall decomposition is attributed to the pyrolysis and free radical attack occurred at both cavity and water interface and bulk liquid medium. While hydrophilicity relate to the ionic orientation of dye molecule to remain in the bulk solution and hence, less prone by $OH^{\bullet}$ radical attack. It was also reported that orange G molecules are in ionic (hydrophilic) form in basic pH range and very low decomposition was observed for orange G at pH range of 7.3-9 which is similar to. ~8.5 pH of this study. It has been also reported that only 10% of the $OH^{\bullet}$ radicals generated can enter the bulk medium[14]. Among the dyes, orange G has high solubility in water and also found to be most difficult to degrade whereas auramine O dye was observed to be easily degradable.

3.3. Cavigulation

Three different schemes in cavigulation have been developed to study the process. The schemes are formed in such a way that the individual effect of each coagulation and cavitation is explored and also the combined effect of the two processes, in a specified manner. It is to be noted that the rates of degradation of pollutants by cavitation and rates of removal of pollutants by coagulation could be widely different and the schemes are expected to highlight information in this regard that is not available in the literature. The combination in both the forms of cavitation (Hydrodynamic and acoustic) with coagulation was studied.

Scheme 1:

This scheme aims to evaluate the removal of pollutants by coagulation separately followed by the combined effect of coagulation and cavitation. The time for coagulation is provided separately in this scheme as mixing was done initially after which the solution is subjected to cavigulation. The comparison of the results of this scheme of cavigulation, with results of coagulation and cavitation separately, will help in understanding the enhancement if any due

to cavitation as no separate time for only cavitation has been provided in this scheme. The importance of providing extra coagulant mixing time is also highlighted.

Scheme 2:

The scheme-2 evaluates simultaneous processing effect of coagulation and cavitation. This scheme will help in understanding the competition of rates of coagulation and cavitation, as no extra time for cavitation or coagulation is provided and both processes are performed simultaneously, immediately after the addition of coagulant. The results would reveal dominance of the rate of any one process over the other.

Scheme 3:

Scheme-3 evaluates the removal of pollutants first through cavitation and then combined effect with coagulation. In this scheme, cavitation is done initially after which coagulant is added. The results obtained with this scheme will help in understanding the importance of providing separate time for only cavitation to investigate breakdown of pollutant species/ altering nature and composition of effluent stream in the process when performed separately. In general,

a) Cavitation or coagulation may take part in the overall process either completely or partially.

b) Any one of the processes may be assisting the other or

c) There may be dominance or interference of any one of the processes completely over the other which will result in affecting the overall efficiency of cavigulation.

3.3.1. Acoustic cavitation+coagulation

This study was carried out by taking Congo red (50 and 100 ppm) as the model pollutant. The efficiency of cavigulation process with two chemical coagulants; PAC SAB 18 and Iron (III) chloride and three biocoagulants; *Moringa oleifera*, *Acanthocereus tetragonus,* and *Cicer arietinum* was investigated.

For comparison, the individual processes were performed separately. The extent of dye removal (Congo red 50 and 100 ppm) using only acoustic cavitation for natural pH, pH 3 and pH 5 was negligible.

Effect of Schemes adopted

It was observed that the schemes adopted in cavigulation played a significant role in the understanding of the process. The major experimental findings are summarized in **Table 2.** From **Figs. 5** and **6** the comparative results for coagulation and cavigulation can be observed at natural pH for PAC SAB 18 and iron (III) chloride as chemical coagulants for the removal of 50 and 100 ppm of initial concentration of Congo red dye. High removal of 74% and 85% with scheme 2 and scheme 3 (15 ppm coagulant dose) of cavigulation respectively over 37% of coagulation using PAC SAB 18 was observed for 50 ppm of Congo red dye. Similarly, improvement in dye removal efficiency with scheme 3 of cavigulation using PAC SAB 18 (20 ppm dose) was attained over coagulation for 100 ppm of Congo red dye . Also in the case of iron (III) chloride (20 ppm dose), a higher dye removal of 46% was achieved with scheme 3 of cavigulation in comparison to only 22% with coagulation for 100 ppm of dye.

Figs. 7 to **9** show the comparative results using biocoagulants with natural pH condition of the dye solution. An improvement in dye removal using cavigulation over coagulation was in the range of almost 25% with schemes 2 and 3 (330 ppm coagulant dose) in the case of *Moringa oleifera*, 30% with scheme 3 (300 ppm coagulant dose) and almost 20% with scheme 1 and scheme 3 (860 ppm coagulant dose) in the case of *Acanthocereus tetragonus*, 29% with scheme 3 (400 ppm coagulant dose) in the case of *Cicer arietinum* for 50 ppm initial dye concentration. Also, for 100 ppm initial dye concentration, with schemes 1, 2 and 3 of cavigulation (300 ppm coagulant dose), very high removal over coagulation was observed using *Acanthocereus tetragonus*.

The formation of very large and dense flocs in scheme 2 and scheme 3 were observed in comparison to coagulation and scheme 1, which also reveal better efficiency with these two schemes. It should also be noted that, at all the points where scheme 1 was showing better removal efficiency, scheme 2 and scheme 3 were more efficient than scheme 1. Scheme 3 was observed to be more efficient than scheme 2 in all the cases. As no dye removal was observed with only cavitation, it can be concluded that, it may have assisted the overall cavigulation process to improve its efficiency.

In scheme 2 and scheme 3, cavitation may have assisted the overall process by changing the form of organic pollutant totally or partially as a result of which further addition of coagulant may enhance efficiency in these schemes of cavigulation. In scheme 3, a considerable time for cavitation (initial 10 min) to act upon the dye has been provided which likely improves efficiency of scheme 3 over scheme 2. Providing separate mixing of coagulant initially may not help as no time for cavitation was allowed to assist the process separately in scheme 1.

Effect of pH

A pH range of 3 to 5 and *Moringa oleifera* as a bio-coagulant/ PAC SAB 18 as a chemical coagulant were selected for the pH study. The results are depicted in **Figs. 10** to **11**. For the same coagulant dose, a higher extent of removal was obtained in acidic condition of pH 3, while almost the same removal has been observed at natural pH and pH 5 (except higher removal in the case of 20 ppm dose of PAC SAB 18 for removal of 100 ppm of Congo red dye at pH 5) using both the coagulants in cavigulation (three schemes) and coagulation. A decrease of pH leads to dye protonation thereby reduction of charge density and induce self-aggregation of dye molecules and as a result, less coagulant is required for destabilization[32]. Some studies, however reported that, pH does not affect the removal efficiency of biocoagulants[34] though, Patel and Vashi [35], reported increase in the removal of Congo red at a lower pH value with *Moringa oleifera* as a coagulant due to the change in the surface charge of the coagulant along with the stabilization of the suspension.

 In the case of PAC SAB 18 (10 ppm dose), 41%, 58% and 43% dye removal with schemes 1, 2 and 3 were observed compared to only 20% dye removal with coagulation at pH 5 for 50 ppm initial concentration of Congo red dye. At pH 5, an improvement of ~17% in removal efficiency with cavigulation (scheme 2) over coagulation was obtained using *Moringa oleifera* (800 ppm coagulant dose) for 100 ppm initial concentration of Congo red dye. In the case of highly acidic pH conditions i.e. pH 3, the removal efficiency of cavigulation (scheme 2 and scheme 3) using PAC SAB 18, was very less in comparison to coagulation at 2.5 and 5 ppm coagulant dose for removal of 50 and 100 ppm of initial dye concentration respectively. Also in acidic conditions (pH 3) only 41% dye removal was observed using cavigulation (scheme 2) which was up to 60% using coagulation for a 50 ppm initial concentration of Congo red dye. It is possible that in cavigulation, the high-frequency sound waves may

destroy partly the flocs formed. The instability of the flocs in acidic conditions has been reported in earlier studies [26].

Effect of selection of coagulant

The efficiency of cavigulation was observed to be dependent on the nature of coagulant. A lowering in efficiency with cavigulation in comparison to coagulation has been identified only in case- *Moringa oleifera* and iron (III) chloride as coagulants. **Fig. 12** shows the change in pH of the dye solution with increase in dose of all the coagulants used in the study which shows acidic nature of *Moringa oleifera* and iron (III) chloride**.** At low pH conditions, flocs are more fragile and may get dissolved in the solution due to high frequency sound waves, hence affecting the overall efficiency in cavigulation. In general, PAC SAB 18 as chemical coagulant and *Acanthocereus tetragonus* as biocoagulant were found to be most efficient coagulants in cavigulation.

3.3.2 Hydrodynamic cavitation+coagulation

The experiments were performed selecting auramine O and Congo red dyes with initial dye concentration of 100 ppm and 500 ppm respectively. PAC SAB 18 was selected as coagulant (coagulant doses of 25 ppm in the case of auramine O dye and 100 ppm in the case of Congo red dye). A pressure drop of 2 bar in cavitation and cavigulation was used. **Fig. 13** shows the comparative results of hydrodynamic cavitation, coagulation and cavigulation (hydrodynamic cavitation+coagulation) adopting three schemes for both the dyes. It has been observed that, in the case of auramine O dye, the removal using cavigulation was considerably higher than only coagulation but lesser than cavitation. In comparison to 73% of dye removal observed in cavitation, only ~ 50% dye removal was observed with all the schemes. In the case of Congo red dye, removal observed was 19% with scheme 1, and 26% with scheme 2 and 3 of cavigulation compared to 23% with coagulation, which was higher than that in cavitation alone. As discussed in the case of acoustic cavitation+coagulation, formation of flocs in cavigulation has been observed and found to play a significant role in improving efficiency in cavigulation, but in this case no such flocs were observed. Flocs formation at the intermediate stage of the process may occur, but may not withstand conditions of stress due to the motion of the fluid at high flow rate leading to the breakage of these flocs or floc formation may not

take place in the HC process leading to lower efficiency of cavigulation in form of HC+coagulation. More investigations are however required in this regard.

4. Conclusions

The present study clearly highlights the benefits of developing new hybrid technologies for dye wastewater treatment as cavigulation in form of acoustic cavitation+coagulation was observed to be very efficient for dye removal for Congo red dye wastewater when compared to the efficiency of coagulation and acoustic cavitation individually.

1. A separate time for cavitation assists the whole cavigulation process to improve its efficiency in the case of acoustic cavitation+coagulation for the removal of Congo red dye (Scheme-3).
2. Highly acidic condition in cavigulation at some points was not favorable and acidic coagulants were also effective at high doses.
3. Low coagulant doses were required in acidic conditions for attaining the same removal efficiency of Congo red dye in coagulation and cavigulation (AC+coagulation).
4. PAC SAB 18 amongst the chemical coagulants and *Acanthocereus tetragonus* amongst biocoagulants were found to be the most efficient
5. Study of cavigulation in form of coagulation+HC for removal of auramine O and congo red dyes accentuate the need for modifications for better removal efficiency.
6. Auramine O dye was found to be the most easily degradable using hydrodynamic cavitation compared to coagulation, while Congo red was easy to remove using coagulation but not with HC; Orange G was found to be most difficult to remove using either of the processes.

Overall it has been found that the molecular weight, structure and solubility of dye, nature of coagulants are the important parameters. It can be concluded a combination of two or more treatment processes is required to meet the desired level of removal.

Figures:
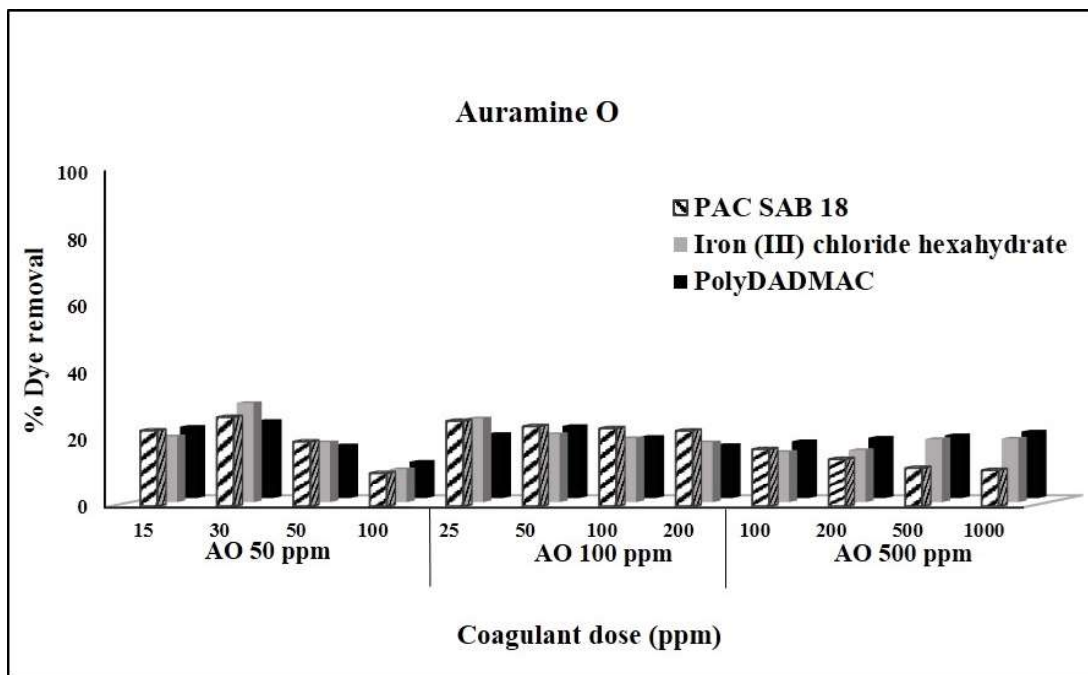
Fig. 1. Effect of coagulant doses on dye removal for auramine O dye
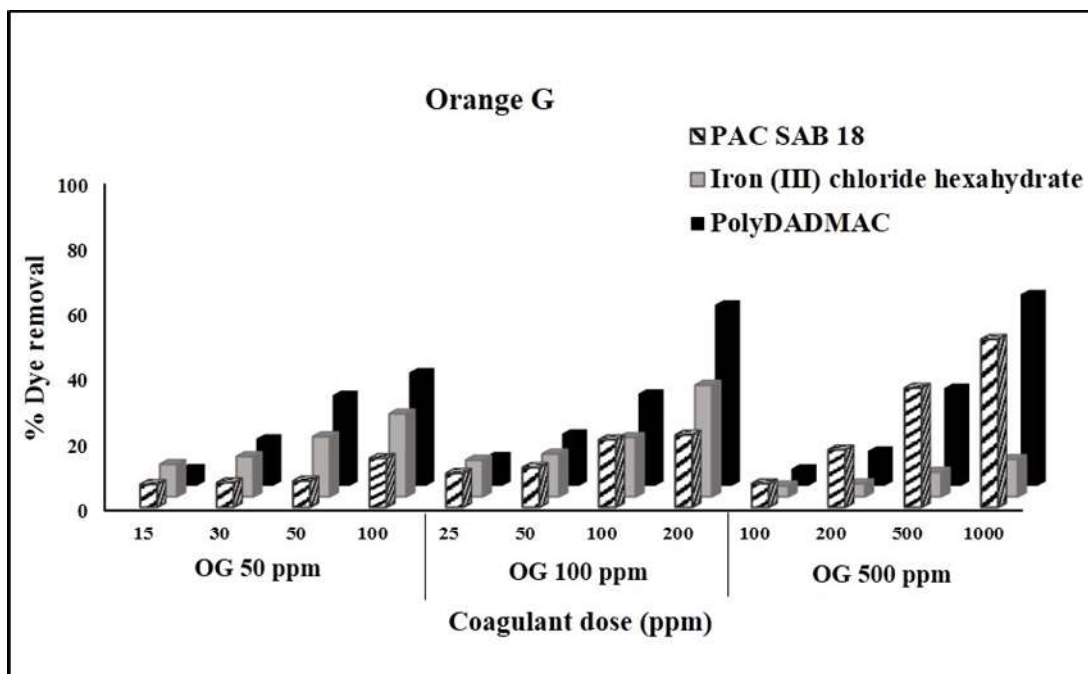
Fig.2. Effect of coagulant doses on dye removal for orange G dye
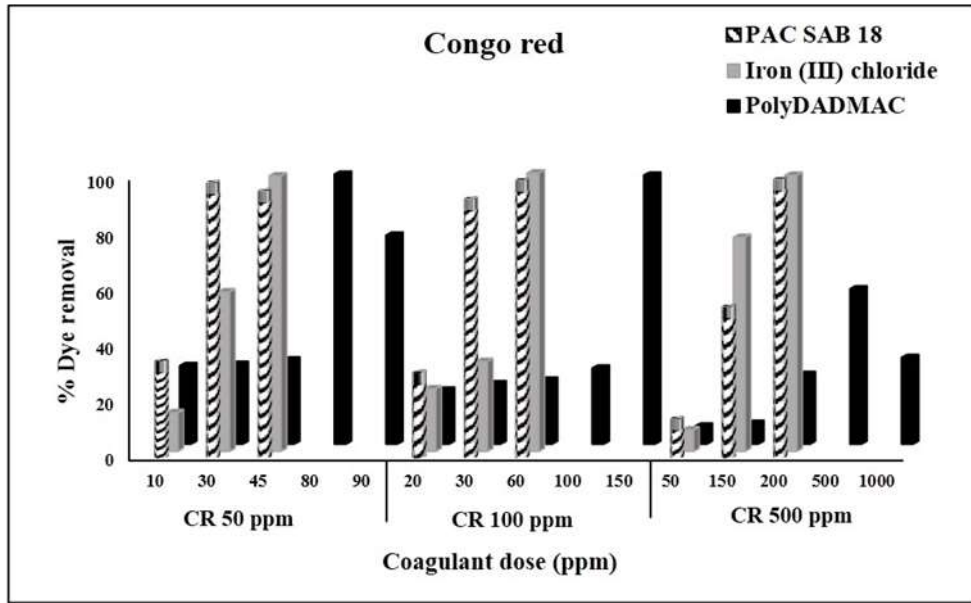
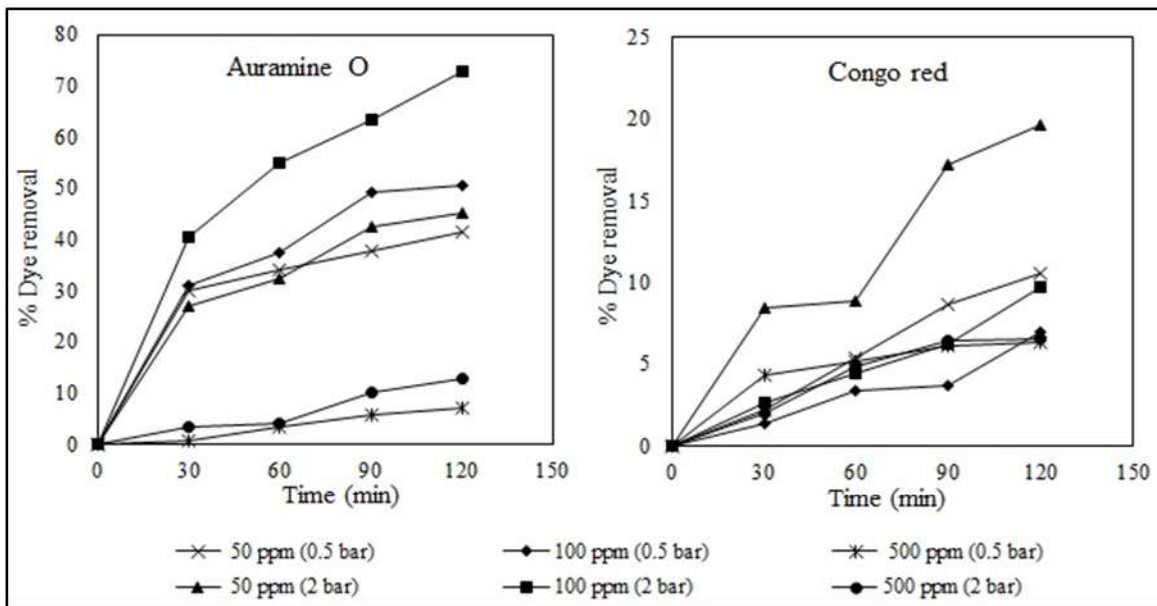**Fig. 3. Effect of coagulant doses on dye removal for Congo red dye**

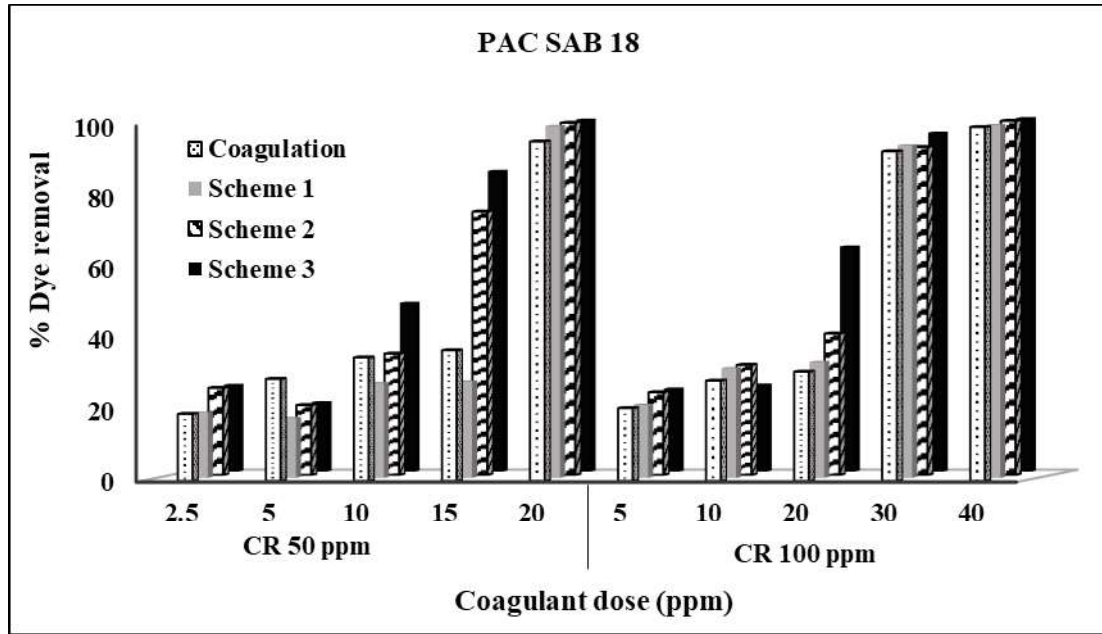**Fig. 4. Effect of initial dye concentration and pressure drop**

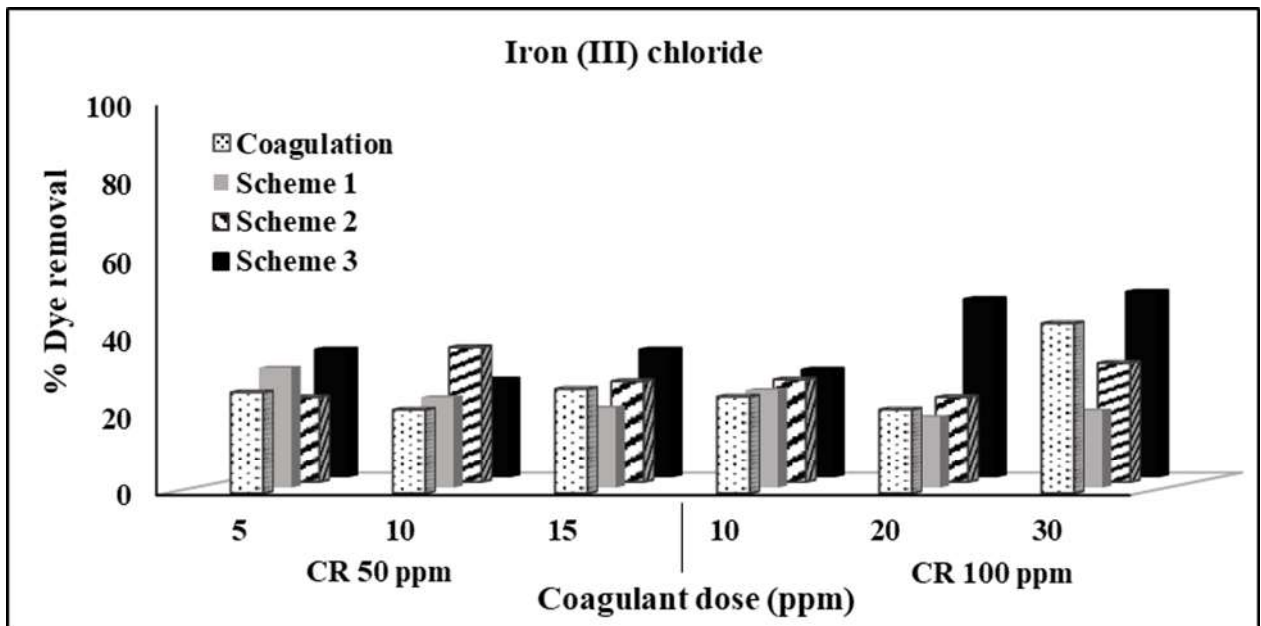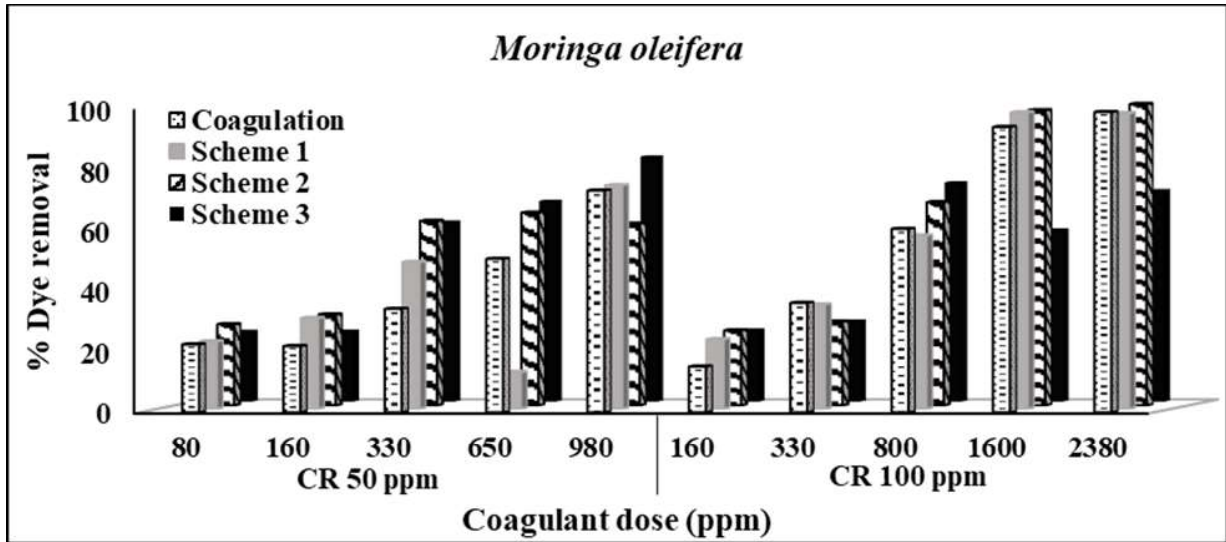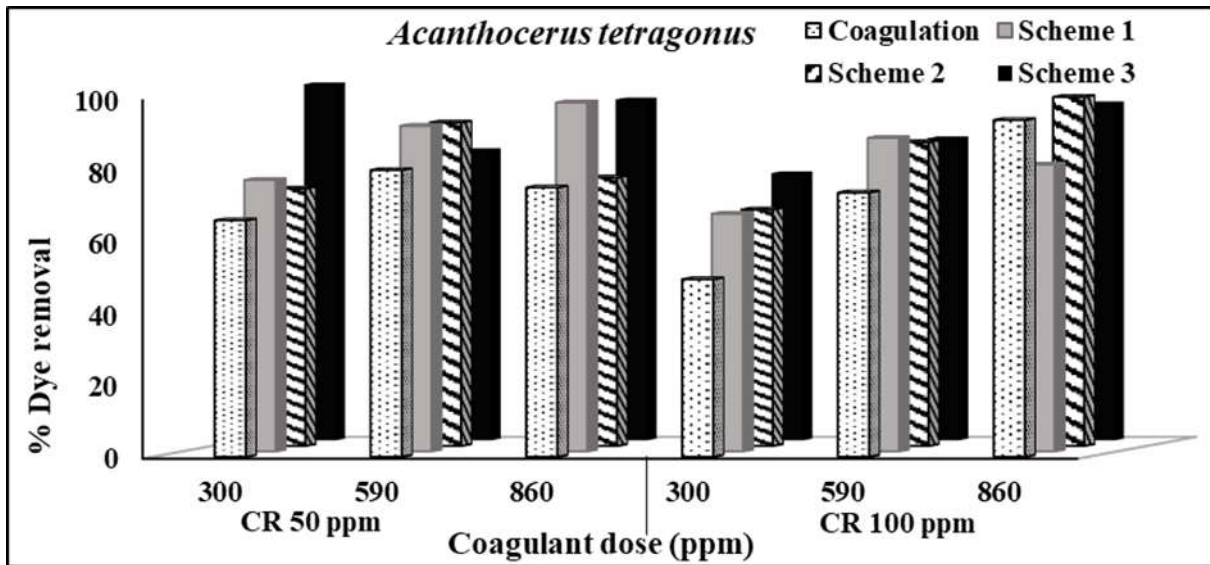**Fig. 5. Comparative results of cavigulation (three schemes) and coagulation using PAC SAB 18 as coagulant**

Fig. 6. Comparative results of cavigulation (three schemes) and coagulation using Iron (III) chloride as coagulant

Fig. 7. Comparative results of cavigulation (three schemes) and coagulation using
***Moringa oleifera* as coagulant**

Fig. 8. Comparative results of cavigulation (three schemes) and coagulation using
***Acanthocereus tetragonus* as coagulant**
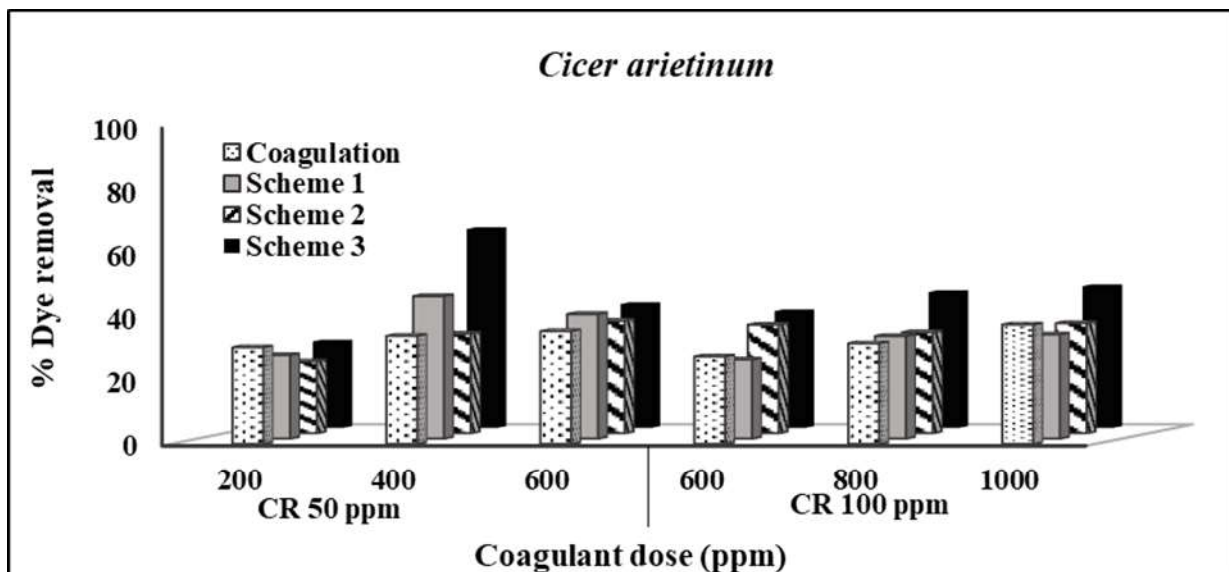
Fig. 9. Comparative results of cavigulation (three schemes) and coagulation using *Cicer arietinum* as coagulant

[a]Adjusted pH, [b]Natural pH
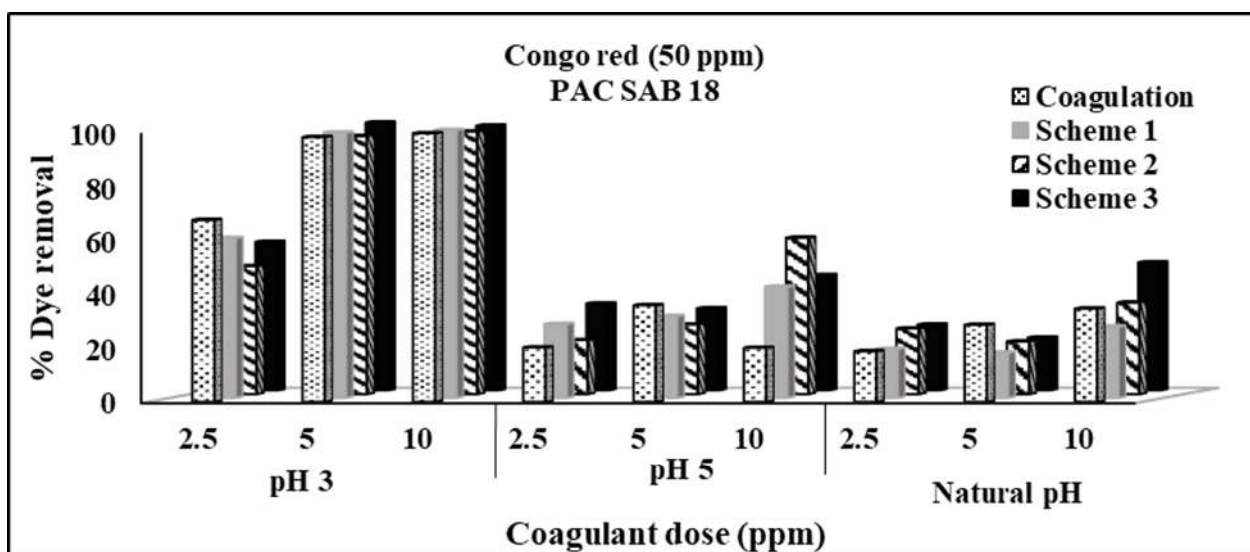
Fig. 10A. Effect of varying pH on efficiency of coagulation and cavigulation (three schemes) using PAC SAB 18 as coagulant
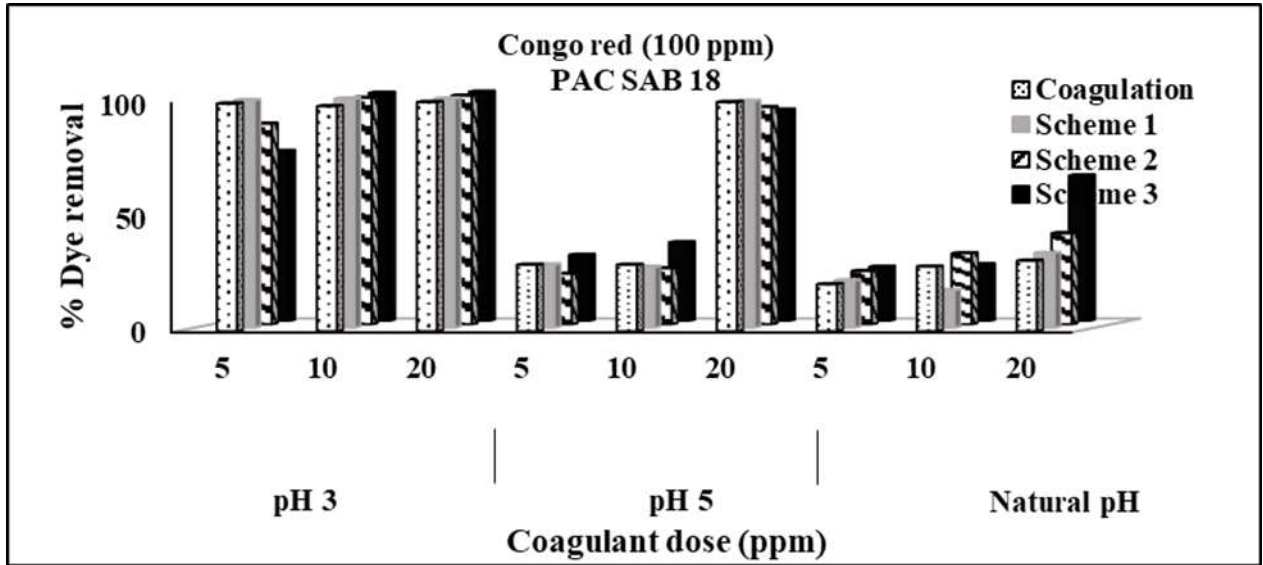
Fig. 10B. Effect of varying pH on efficiency of coagulation and cavigulation (three schemes) using PAC SAB 18 as coagulant
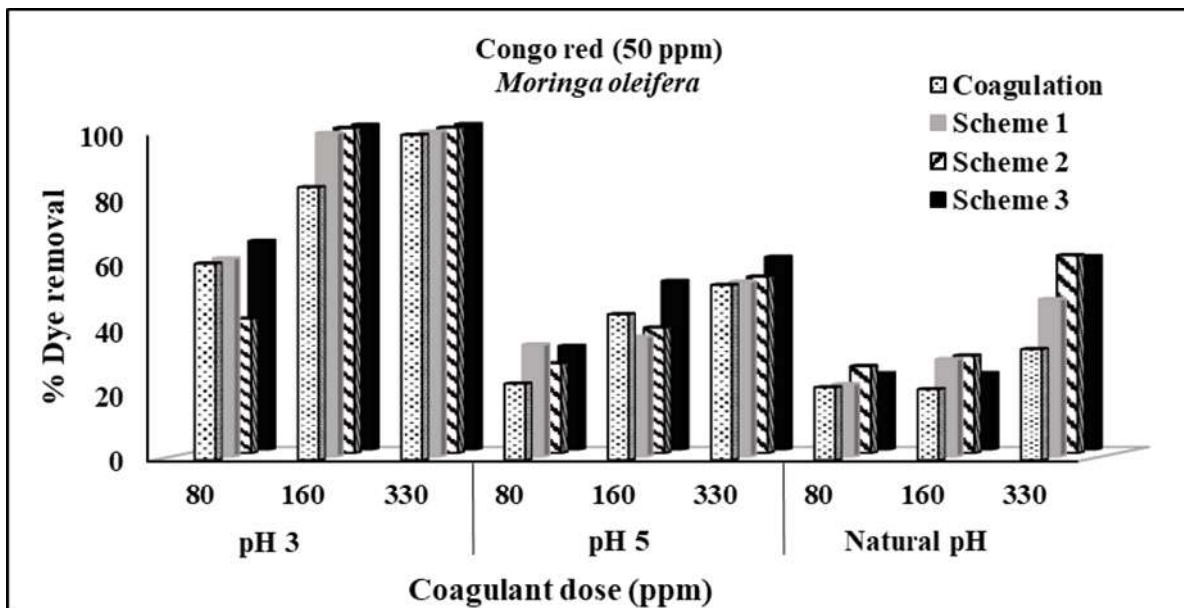

Fig. 11A. Effect of varying pH on efficiency of coagulation and cavigulation (three schemes) using Moringa oleiferaas coagulant
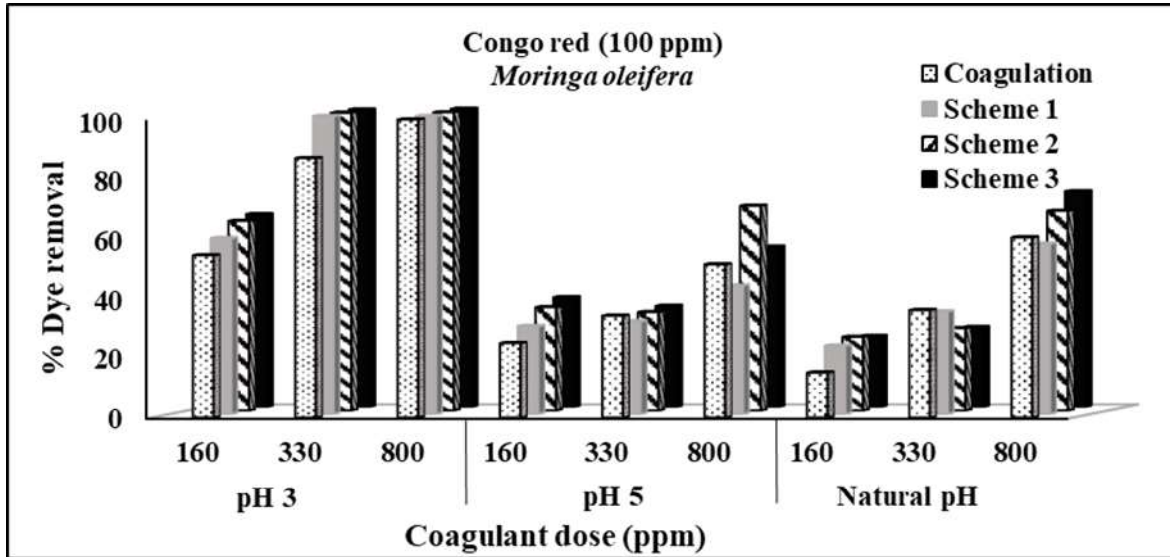
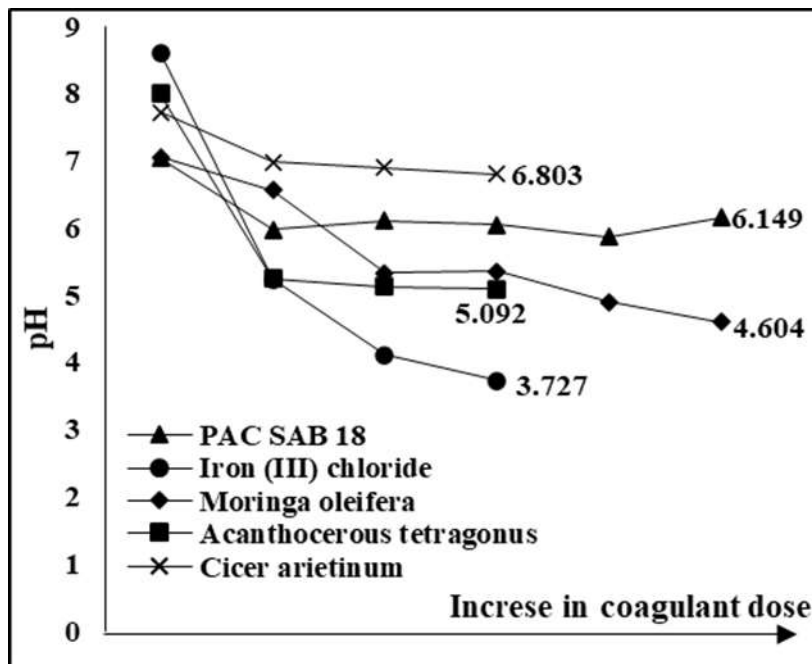**Fig. 11B. Effect of varying pH on efficiency of coagulation and cavigulation (three schemes) using *Moringa oleifera* as coagulant**

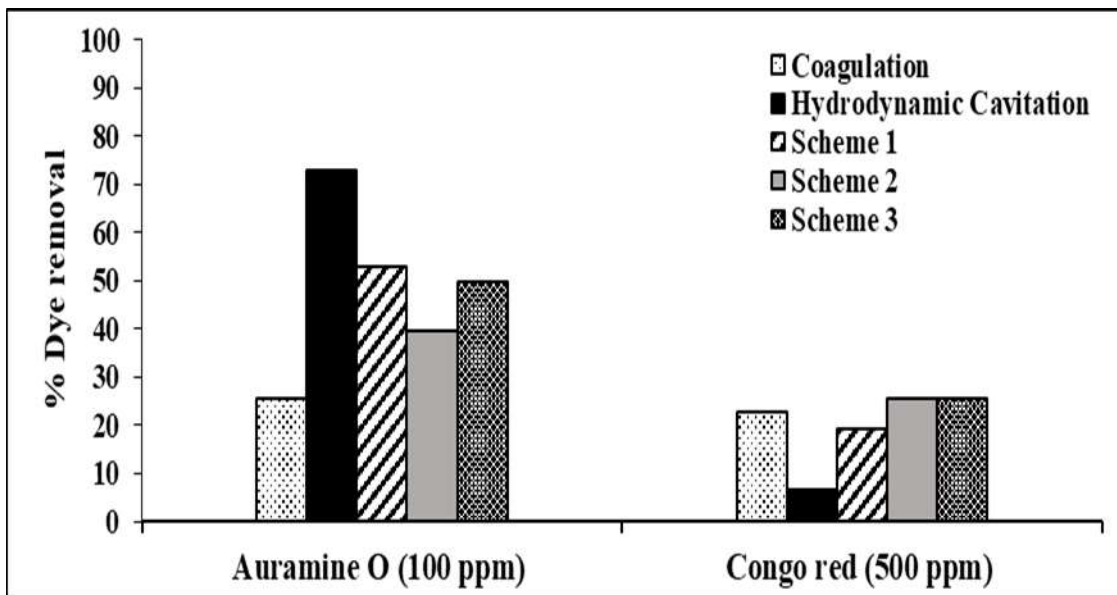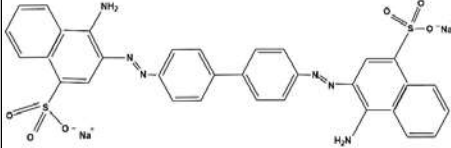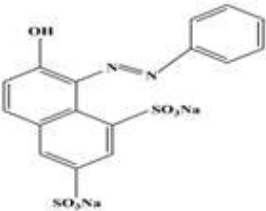**Fig. 12. Effect of increase in coagulant dose on pH**
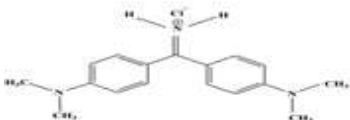
Fig. 13. Comparative results of cavigulation (three schemes), cavitation and coagulation using PAC SAB 18 as coagulant

Tables:

Table 1. Physicochemical properties of dyes

S. No.	Name of dye	Molecular Structure	Molecular Weight (g/mol)	Solubility in water (mg/ml)	Appearance
1.	Congo red		696.65	10	Solid powder
2.	Orange G		452.37	80	Solid powder
3.	Auramine O		303.83	10	Solid powder

Table 2. Comparative study of cavigulation (acoustic cavitation+coagulation), coagulation and acoustic cavitation

S. no.	Dye conc. (ppm)	pH	Coagulant	Coagulant dose (ppm)	Scheme	Percent dye removal		
						Cavigul-ation	Coagulation	Cavitation
1	50	6.5[b]	PAC SAB 18	15	2	74	37	0
2	50	6.4[b]	PAC SAB 18	15	3	85	37	0
3	100	5[b]	PAC SAB 18	20	3	63	31	0
4	50	5[a]	PAC SAB 18	10	1	41	20	0
5	50	5[a]	PAC SAB 18	10	2	58	20	0
6	50	5[a]	PAC SAB 18	10	3	43	20	0
7	50	3[a]	PAC SAB 18	2.5	2	48	68	5
8	100	3[a]	PAC SAB 18	5	3	73	99	9
9	100	3.8[b]	Iron (III) chloride	20	3	46	22	0
10	100	3.8[b]	Iron (III) chloride	30	1	20	44	0
11	50	7[b]	*Moringa oleifera*	330	2	61	34	0
12	50	6.9[b]	*Moringa oleifera*	330	3	59	34	0
13	50	5.7[b]	*Moringa oleifera*	650	1	12	51	0
14	100	4.9[b]	*Moringa oleifera*	1600	3	57	94	0
15	100	4.8[b]	*Moringa oleifera*	2300	3	70	99	0
16	50	3[a]	*Moringa oleifera*	80	2	41	60	5
17	100	5[a]	*Moringa oleifera*	800	2	68	51	7
18	50	5[b]	*A. tetragonus*	300	3	99	66	0
19	50	5[b]	*A. tetragonus*	860	1	97	75	0
19	50	5[b]	*A. tetragonus*	860	3	95	75	0
20	100	5.2[b]	*A. tetragonus*	300	1	66	50	0
21	100	5.2[b]	*A. tetragonus*	300	2	66	50	0
22	100	5.2[b]	*A.tetragonus*	300	3	75	50	0
23	50	5.9[b]	*Cicer arietinum*	400	3	63	34	0

Note: [a]Adjusted pH, [b]Natural pH

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[4] Present address: Department of Civil Engineering, Vasavi College of Engineering, Hyderabad
[5] Present address: Bernal Chair of Process Engineering, University of Limerick, Limerick, Ireland