Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.21923

104 (2018) 111–120
February

Shrimp shell waste – a sustainable green solution in industrial effluent treatment

S. Vishali*, Picasso Sengupta, Rajdeep Mukherjee, Nihal Rao

Department of Chemical Engineering, SRM University, Chennai 603 203, Tamil Nadu, India, Tel. +91-94438 83562; email: meet.vishali@gmail.com (S. Vishali), Tel. +91-9710430335; email: picassosengupta@gmail.com (P. Sengupta), Tel. +91-9831685593; email: rjdp0494@gmail.com (R. Mukherjee), Tel. +91-9790961478; email: nihal1050@gmail.com (N. Rao)

Received 25 September 2017; Accepted 11 January 2018

ABSTRACT

In this study, the capacity of wasted natural material *Fenneropenaeus indicus* (Shrimp) shell, as a coagulant, was appraised in the treatment of simulated paint factory effluent (SPFE) by colour and turbidity. The study was conducted by varying different operational parameters. The proposed case to treat a litre of SPFE was 400 mL of eluate made from 4% (wt/vol) of shrimp shell powder (SSP) and 3 N NaCl, at its own initial pH (8.4–8.6). The outcome was 93.67% (colour) and 81.77% (turbidity). The optimized conditions were applied on real paint factory effluent. The evaluated sludge volume (SV_f) and sludge volume index were boosted and the hindered settling velocity (V_{HS}) was in declined trend with the upgrade in initial concentration of effluents, in the settling studies. The final volume of sludge was ranged between 190 and 260 mL/L and its dry weight was between 32.7 and 38.1 g/L, respectively. The presence of chitosan, an active component, responsible for coagulation was confirmed by Fourier transform infrared spectroscopy. The results were contrasted with chemical coagulant chitosan and it confessed that, being a biodegradable and universally abundant, the SSP has a capacity to become a sustainable green alternate for chemical coagulants in the paint factory effluent treatment.

Keywords: Paint factory effluent; Shrimp shell; Chitosan; Coagulant; Settling

1. Introduction

Pollution is the biggest problem which this world faces today and it has multiplied day by day. Today, environmental pollution is the common hazard all of us face and curbing is the only available solution. Industrialization and the waste it generates is one of the most harmful source of pollution. One such sector is paint industry. Paint industry effluent is one of the potential pollutants when it comes to environmental pollution and as such, like any other form of pollution, it should be dealt firmly. One of the most significant things about paints is the fact that most of the effluent (85%) from paint industry comes up from cleaning of the industrial equipment. Paint is an amalgamation of resins, binder, solvents and additives. A basic and significant method of classifying paints can be made on the basis of primary solvent used for disposal of waste in the industry. Based on these, paints can be categorized as solvent based, water based, organic solvent based and can also be dry (powder) [1].

The toxic ability of paint to cause massive harm can be attributed to the high content of chemical oxygen demand (COD), biochemical oxygen demand, suspended solids, colour, heavy metals, oils and greases. Paints which use water as a solvent while coating are generally referred to as water-based paints and a special advantage that they have compared with others is that they reduce volatile organic carbon discharge. Based on the source level reduction and product change policies of industrial pollution prevention, using water as the solvent, that greatly reduce the use of organic solvents for cleaning operations. The disposal of paint factory effluent without prior treatment causes great disturbances in aquatic life as well as human life including irritations and nausea. It can also lead to kidney problems

* Corresponding author.

and muscle weakness. Methods such as coagulation and flocculation, electrocoagulation, adsorption, Fenton-oxidation, electrochemical, biosorption and microfiltration have been attempted for the paint effluent treatment [2]. Among all these methods, coagulation is an appropriate technology for the treatment of effluents with high suspended solids, especially paint factory effluent [3].

Coagulants can be either derived from natural materials or synthesized using chemical components. The limitations identified in chemical coagulants viz., inefficient at low temperature, high cost, adverse effect on the human health, large sludge production, changes the pH of treated water, etc., forced to search for natural coagulants [4]. By scanning through the literature it was identified that several plant types, such as *M. oleifera*, *S. potatorum*, Cactus species, *P. vulgaris*, surjana seed, maize seed, tannin, gum arabic, *P. juliflora* and *I. dasysperma* seed gum, were performed as a coagulant in various effluent treatments [5–7].

They highlighted from their research that the natural coagulants are cost-effective, does not alter the pH of the treated water, highly biodegradable, produced low sludge volume and more specifically the treated water do not have any effect on human health or on the environment. To act as a natural coagulant, a material should convince the following specifications such as (i) high-molecular weight and (ii) able to neutralize the pollutants and most importantly it should be universally available as an agricultural and/or industrial residue [8].

Every year, some 6–8 million tonnes of waste crab, shrimp and lobster shells are produced globally, about 1.5 million tonnes in southeast Asia alone. In comparison with fish, only small part (around 40%) of a crustacean mass is eatable. Waste shells are often just dumped in landfill or sea in developing countries. In developed countries, disposal can be costly, up to US$150/tonne in Australia [9]. The potential value of such waste is being long time ignored [10]. Crustacean shells are 20%–40% protein, 20%–50% calcium carbonate and 15%–40% chitin. Dried shrimp shells are valued at a mere $100–$120 per tonne. The chitin/chitosan are the products obtained from the prawn shell waste that has the application in biomedical, food, personal care, water treatment, coatings/coverings and agriculture [11].

Chitosan, a linear cationic polymer of high-molecular weight (50,000-190,000 Da) obtained from the outer shells of crustaceans particularly crabs and shrimp, has recently been proposed for applications of heavy metal sorption, drinking water treatment and industrial effluent treatment [12,13]. It has already been used in various wastewater treatment plants. It has its applications on various zones such as agricultural and horticultural use, filtration, food industry, biomedical uses and supplementary for weight loss. Chitosan was used as a coagulant in the removal from natural water and milk processing plant wastewater [14,15]. The chitosan yield was found to be 57.69%, and it was analyzed for its physiochemical parameters, antibacterial and antifungal activity [16].

Solid waste management strategy includes that increasing waste reduction, developing new standards and technology and maximizing economic opportunities associated with waste management [17]. This strategy motivated us to not to waste sea-waste and utilize it as a coagulant for the paint factory wastewater treatment and to find the solution concurrently for both issues.

In this study, the capacity of the *Fenneropenaeus indicus* (Indian shrimp) shell powder (SSP) as a coagulant in the treatment of simulated paint factory effluent (SPFE) was evaluated in terms of colour and turbidity removal by varying the operational conditions. The obtained optimum conditions were tested on real paint factory effluent (RPFE). The results of shrimp shell waste were compared with chitosan.

2. Materials and methods

2.1. Effluent

2.1.1. Simulated paint factory effluent

All chemicals used in the experiment were of analytical grade (AR). They were bought from Merck, India. The simulated water-based SPFE was prepared by amalgamation of different proportions of commercially available white primer and an acrylic-based blue colourant (5% (v/v)) [18]. A syringe was used for measuring the paint volume. It was prepared as it was required. Five different samples with varying initial concentrations were prepared and labelled as sample numbers 1–5, respectively (Table 1).

2.1.2. Real paint factory effluent

The real water-based RPFE was collected from paint factory located in Chennai, South India. The physical–chemical properties of both the effluents were listed in Table 2. Standard methods were followed for determination of characterization [19].

2.2. Coagulants

2.2.1. Natural coagulant

Clean *Fenneropenaeus indicus* (Indian shrimp) shells were obtained from the local sea food market located in Chennai, South India. The shrimp shells were comprehensively washed with distilled water to remove the soft tissues within; sun dried for 24 h, powdered (SSP) with a kitchen mixer and sieved through a 0.5 mm sieve (Fig. 1).

2.2.2. Chemical coagulant

Chitosan is a linear cationic polymer of high-molecular weight commonly derived from chitin, obtained from the outer shells of shrimps was used as a conventional chemical coagulant. It was purchased as flakes and powdered, sieved to 0.5 mm size (Fig. 2).

Table 1
Concentration of SPFE

Sample number	Initial COD (mg/L)
1	1,200
2	1,350
3	1,850
4	2,200
5	2,700

Table 2
Physicochemical characteristics paint factory effluent

Concentration (except for pH, colour and turbidity, viscosity)		
Parameters	Simulated paint factory effluent (SPFE) sample no. 5	Real paint factory effluent (RPFE)
pH at 25°C	8.4–8.6	7.03
Colour	Blue	Dark black
Total dissolved solids, mg/L	214	1,234
Total suspended solids, mg/L	11,286	300
Oil and grease, mg/L	19	15
Sulphate as SO_4, mg/L	24	115
Chemical oxygen demand (COD), mg/L	2,700	1,760
Biochemical oxygen demand, mg/L (3 d incubated at 27°C)	1,254	880
Turbidity, NTU	5,210	198.5
Viscosity, kg/m s	0.0144	0.015

2.3. Preparation of coagulant extract

2.3.1. Shrimp shell

A known weight of SSP was mixed for 15 min at 200 rpm in 100 mL of solvent named as eluent. This is to extract the active component chitosan from SSP. The resultant solution was allowed to settle for 10 min. A measured volume of eluate, that is, the supernatant liquid, was applied as a coagulant in the treatment of paint factory effluent [20].

Fig. 1. Shrimp shell and shrimp shell powder (SSP).

2.3.2. Chitosan

A 1 g weight of chitosan powder was suspended in 100 mL of 0.5 M HCl solution. It was stirred using magnetic stirrer for 10 min and kept aside for about 1 h to dissolve. It was made up to 1 L using double distilled water to obtain a 100 mg/L solution. To avoid the change in the property of chitosan, the solutions were prepared freshly.

Fig. 2. Chitosan flakes and powder.

2.4. Experimental procedure

2.4.1. Coagulation

A regular six stirrer arrangement jar test apparatus (Deep Vision-India) with base floc illuminator and inbred speed (up to 300 rpm) and timer was used for the batch coagulation process. The length and breadth of stirrer paddles are 8 and 2 cm, respectively (Fig. 3).

Six beakers of 2,000 mL volume were used to hold the effluent in the batch coagulation process. SPFE (1,000 mL) was taken for each cycle with known volume of coagulant-eluate. It was then regulated to rapid mixing for 5 min at 200 rpm, followed by slow mixing for 20 min at 80 rpm and settling period of 60 min [2]. A sample of the supernatant liquid was taken at regular intervals during the settling period, and centrifuged at 10,000 rpm for 5 min. The clarified liquid was used for the measurement of residual colour and turbidity. The amount of sludge obtained was also noted.

The above process was recast to optimize the operating variables viz., eluent type (distilled water, NaCl and KCl), eluent concentration (1–5 N), coagulant dose (1%–5% (wt/vol)), coagulant-eluate volume (200–1,200 mL), initial pH (5–11)

Fig. 3. Jar test apparatus.

and initial concentration (1,200–2,700 mg/L) of the effluent. When studying the competence of chitosan as a coagulant, the coagulation process was repeated and the settling was rather quick this time by varying between 0 and 5 min. All the experiments were repeated at least thrice for concordance and the mean values were taken for plot.

The observed optimized conditions were applied on the treatment of RPFE.

2.4.2. Settling test

The settling studies were conducted to test the settleability of the flocs formed under optimized operating conditions. A litre of SPFE was taken in a volumetric cylinder (Fig. 4) and optimized volume of coagulant-eluate was added. A sequence of rapid mixing–slow mixing was performed then it was allowed to settle. The sludge bed height and the corresponding sludge bed volume were marked with respect to time [21].

2.5. Performance analysis

The coagulation process was evaluated in terms of removal of colour and turbidity. All the parameters mentioned in Table 2 were measured using standard procedures. Colour was measured using SL218 double UV visible spectrophotometer (Elico, India) at λ_{max} 612 nm for SPFE and at 252 nm for RPFE. Turbidity was measured using digital Nephelo-turbidity meter 132 (Elico, India) and expressed in nephelometric turbidity units (NTU). pH was adjusted using a digital pH meter MK VI (Elico, India).

3. Settling studies

Settling is a solid–liquid separation process based on the difference in the density. Settling is an important process in many of the wastewater treatment plants. It is the principal operation taking place in the primary settling tanks and the secondary settling tanks that are extensively used in the wastewater treatment plants. The purpose of settling is to remove coarse dispersed phase, coagulated and flocculated impurities, to settle the sludge and remove the suspended impurities. In order to study the settling mechanism of the particles, it is very important for us to understand the settleability of the particles.

Fig. 4. Photograph of the batch settling column.

The settling behaviour of the particles depends upon the concentration and the flocculation tendency of the particles. Based on the above stated factors the settling behaviour is classified into five regimes, that is, discrete particle settling, flocculent particle settling, hindered settling, comprehensive settling and zone settling. Beyond a threshold concentration of the sludge, hindered settling takes place, each particle get hindered by the other particle and this results in interparticle forces which are sufficiently strong to drag each other particle along the same velocity irrespective of velocity, size and density. It is also called zone settling because they settle collectively as a zone [21].

3.1. The batch settling curve and hindered settling velocity

The recommended shape and size for batch settling tests are cylindrical measuring flasks of 1–2 L volume. In the Imhoff cones, due to the reducing cross-sectional area the formation of concentration gradient is inevitable. The settling of the flocs is influenced by a number of factors such as the composition of the activated sludge, floc size distributions, surface properties, rheology, etc.

Batch settling curves can serve different purposes. It can be used quantitatively to determine the sludge settling tank (SST) capacity limit, for this the selection of an appropriate settling reservoir to avoid wall effects during the test is imperative. The height of the suspension-liquid interface at regular time intervals is recorded [22].

4. Results and discussion

4.1. Characterization studies

4.1.1. Coagulant

4.1.1.1. SSP The potential of SSP is mainly attributed by the presence of the chemical functional groups present in it. Fourier transform infrared spectroscopic (FTIR) analysis was conducted to detect the distinct functional groups present in the natural coagulant. Several peaks were observed at 667, 795, 1,073, 1,406, 1,644, 2,339 and 3,442 cm^{-1}, respectively. The steep peak at 3,442 cm^{-1} is due to the OH stretching vibration of water and amine. Alkene and amide group presence was also confirmed by the bending vibration at 1,644 cm^{-1}. The steep peak at 1,073 cm^{-1} indicated the –CO stretching vibration of ether groups. Thus, it reveals that SSP carries aliphatic grouping with ether linkages and amine groups. The wavelength of the main bands obtained for the standard chitosan and eluate of SSP (Fig. 5) is listed in Table 3. The peaks at similar wavelength affirmed the presence of chitosan, a key coagulant component, in SSP [2].

4.1.1.2. Chitosan Standard chitosan used as a chemical coagulant in the study was also analyzed in FTIR. Peaks were observed at 479, 667, 787, 1,077, 1,384, 1,633, 2,339 and

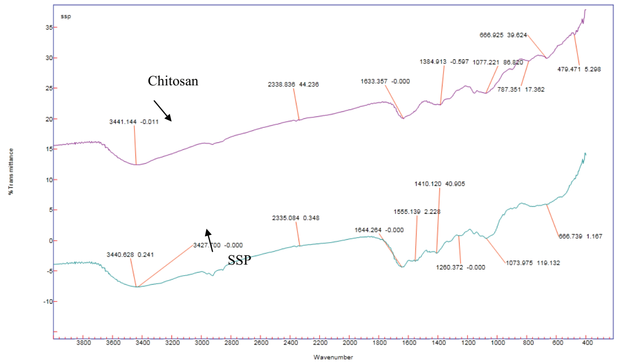


Fig. 5. FTIR spectrum of SSP and chitosan.

Table 3
Wavelength of the main bands obtained for the SSP and standard chitosan

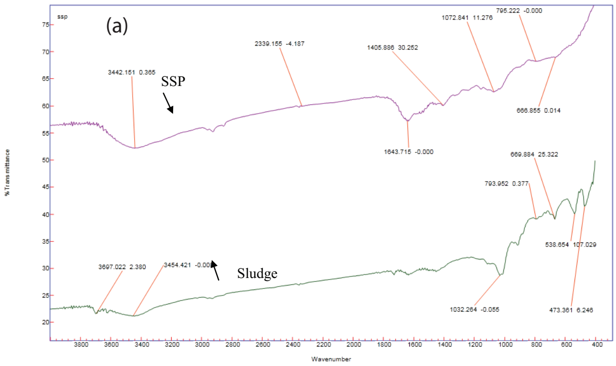
Vibration modes	SSP (cm^{-1})	Chitosan (cm^{-1})
OH out of plane bending	666.9	666.9
CO stretching	1,072.8	1,077.2
N–O stretching	1,405.9	1,384.9
C=C stretching	1,643.7	1,633.4
CH stretching	2,339.2	2,338.8
OH stretching	3,442.2	3,439

3,441 cm^{-1}, respectively. The spectra showed a broad absorption band at 3,000–3,500 cm^{-1} which can be attributed to the presence of OH stretching vibration and also amine stretching vibrations. The peak at 1,633, 1,384 and 1,077 cm^{-1} confirmed the presence of amide, nitro (N–O group) and C–O–C bond, respectively. Thus, the above results confirmed the presence of amine group in chitosan.

4.1.2. Sludge

4.1.2.1. SSP The spectra of the sludge formed, after the treatment of SPFE using optimized conditions of SSP showed a wide spectrum at 3,000–3,700 cm^{-1} which can be attributed to the presence of OH stretching vibration and also amine stretching vibrations. The peak at 3,697.02 indicates free stretch of O–H and the peak at 3,454.421 showed hydrogen bonded O–H stretch and amine stretch. The C–O bond presence is evident from the peak at 1,032 cm^{-1}. Strong alkyl halide (C–X) bonds were observed in the peaks between 500 and 800 cm^{-1}. In the case of SSP, peaks were observed at 667, 795, 1,073, 1,406, 1,644, 2,339 and 3,442 cm^{-1}, respectively. The steep peak at 3,442 cm^{-1} is due to the OH stretching vibration of water and amine. Alkene and amide group presence was also confirmed by the bending vibration at 1,644 cm^{-1}. The steep peak at 1,073 cm^{-1} was due to –CO stretching vibration of ether groups (Fig. 6(a)).

4.1.2.2. Chitosan In the case of sludge, produced after applying the chitosan, the peaks in the spectra above 3,400 cm^{-1} showed the presence of O–H and N–H bonds. Peak at 3,695.05 cm^{-1} indicates free strong O–H stretch and



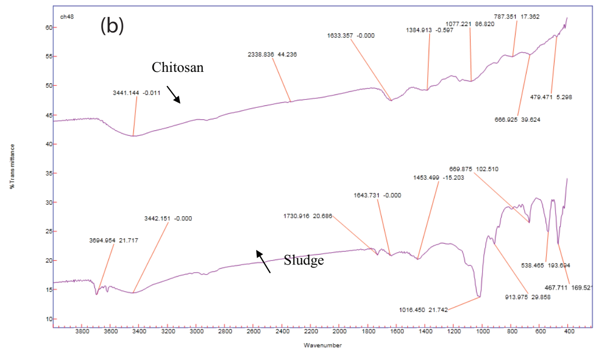


Fig. 6. (a) FTIR spectrum of SSP and sludge treated using SSP. (b) FTIR spectrum of chitosan and sludge treated using chitosan.

3,442.66 cm^{-1} indicated hydrogen bonded O–H stretch and N–H stretch. Another peak was seen at 1,730.89 cm^{-1} indicated acyclic vibration stretch. The presence of alkene and amide group was confirmed by the peak at 1,643.57 cm^{-1}. The peak at 1,453.6 cm^{-1} indicates variable –CH bending. The C–O bond presence was confirmed at 1,017.02 cm^{-1}. The presence of alkyl halide groups (C–X) was confirmed in the peaks obtained between 500 and 800 cm^{-1}. In case of chitosan, the peaks were seen at 479, 667, 787, 1,077, 1,384, 1,633, 2,339 and 3,441 cm^{-1}, respectively. The spectra showed a broad absorption band at 3,000–3,500 cm^{-1} which can be attributed to the presence of OH stretching vibration and also amine stretching vibrations. The 1,633 cm^{-1} peak is attributed to the presence of amide group and the peak at 1,384 cm^{-1} is attributed to the presence of nitro (N–O group). The C–O–C bond presence is evident from the peak at 1,077 cm^{-1} (Fig. 6(b)). The scanning electron microscopic (SEM) images of SSP and chitosan were given in Fig. 7.

4.2. Shrimp shell powder vs. simulated paint factory effluent

4.2.1. Impact of eluent type and concentration

For choosing the eluent type and concentration, 3% (w/v) of SSP was mixed with different eluent such as distilled water, 3 N of NaCl and KCl. The prepared coagulant was added in a litre of SPFE. It was detected that the lowest removal efficiency with a value of 73.66% colour removal and 13.06% turbidity removal for distilled water. The reason is the presence of high chitosan in the shrimp shell is insoluble in water. The NaCl solution exhibited its highest removal efficiency as 97% (Fig. 8).

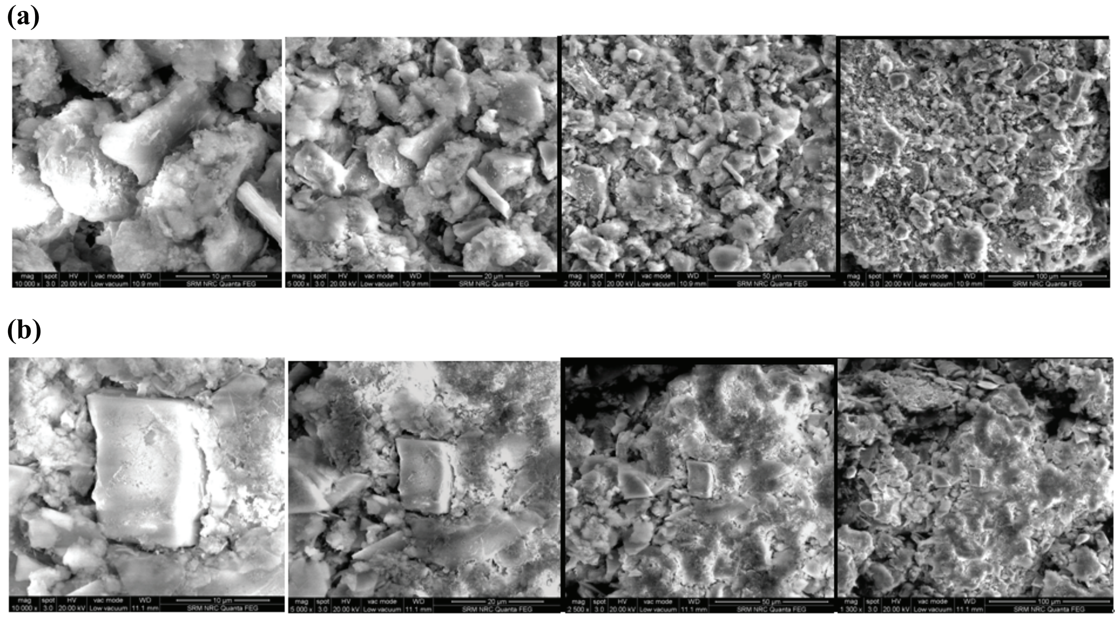


Fig. 7. SEM images of (a) SSP and (b) chitosan.

Further treatment was extended with 1–5 N of NaCl solution as an eluent. The trend showed the maximum colour and turbidity removal efficiency in the increasing order from 1 to 3 N and it was decreasing after that. The viewed maximum removal efficiencies are 96.57% for colour and 96.92% of turbidity at 3 N NaCl (Fig. 9).

The believed reason for this result is that 3 N NaCl might extract the maximum possible amount of chitosan from a known amount of SSP. It was also seen that since the NaCl has a higher degree of dissociation, it tends to extract more chitosan and beyond 3 N it natures the active compounds. Allied outcome was highlighted in the extraction of chitosan from crab shells in the treatment of paint industry effluent [23].

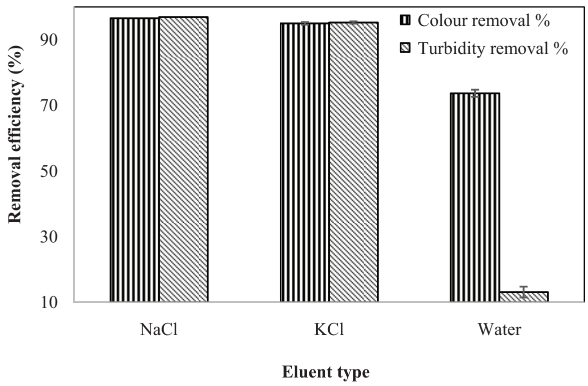


Fig. 8. Impact of eluent type on removal efficiency. SPFE volume: 1 L; initial pH of SPFE (actual): 8.4–8.6; initial concentration of SPFE: 1,200 mg/L; coagulant: extragens = 30 g of SSP: 3 N NaCl, 3 N KCl, distilled water; coagulant-eluate volume: 1 L.

4.2.2. Impact of shrimp shell powder dose

To treat a litre of SPFE, the used SSP dose was ranged from 1% to 5% (w/v) g (Fig. 10). The optimized value was viewed at 4% (w/v) g of SSP and the values were found out to be 87.28% for colour and 94.89% for turbidity. The removal efficiencies were increased with SSP dose till 4% (w/v) then it started declined due to the surface charge reversal of the excessive coagulant. Then, the colloidal destabilization occurred which does not favour the coagulation reaction. This result is in agreement with previous studies [12].

4.2.3. Impact of coagulant SSP-eluate volume

Various volumes (200–1,200 mL) of coagulant-eluate were applied on a litre of SPFE. 400 mL of coagulant-eluate proceeded well in colour removal (91.15%) as well as in turbidity removal (92.51%). The removal efficiency shows a gradual decrease when the coagulant volume was increased from 60 to 120 mL (Fig. 11). The reason is that since chitosan is an amide derivative and the pH of the SPFE was found out to be 8.4–8.6, the amount of OH– ions in paint wastewater

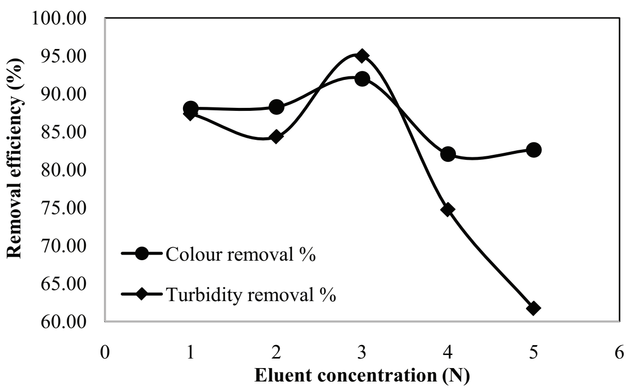


Fig. 9. Impact of eluent concentration on removal efficiency. SPFE volume: 1 L; initial pH of SPFE (actual): 8.4–8.6; initial concentration of SPFE: 1,200 mg/L; coagulant: extragens = 30 g of SSP: NaCl (1–5 N); coagulant-eluate volume: 1 L.

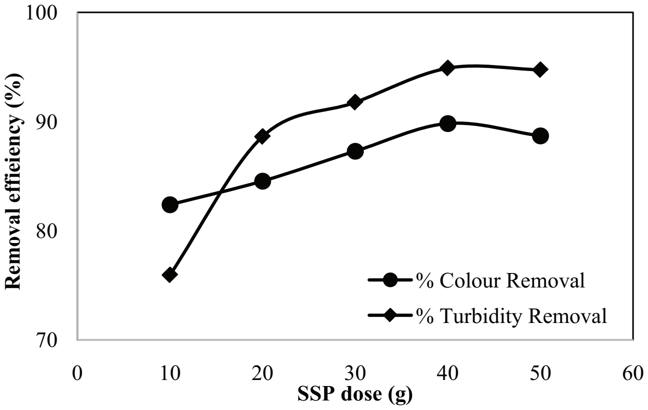


Fig. 10. Impact of coagulant SSP dose on removal efficiency. SPFE volume: 1 L; initial pH of SPFE (actual): 8.4–8.6; initial concentration of SPFE: 1,200 mg/L; coagulant: extragens = 10–50 g of SSP: 3 N NaCl; coagulant-eluate volume: 1 L.

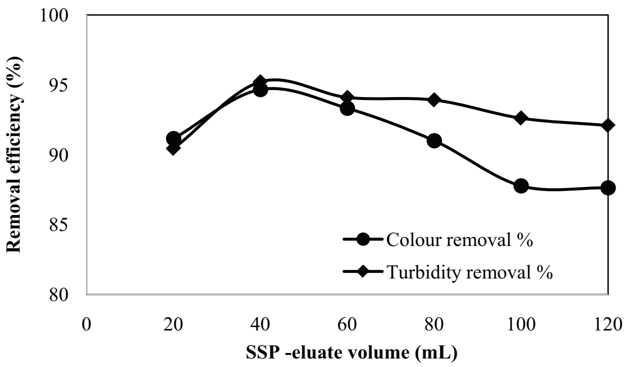


Fig. 11. Impact of coagulant SSP-eluate volume on removal efficiency. SPFE volume: 1 L; initial pH of SPFE (actual): 8.4–8.6; initial concentration of SPFE: 1,200 mg/L; coagulant: extragens = 40 g of SSP: 3 N NaCl; coagulant-eluate volume: 200–1,200 mL.

is believed to be high. As the dosage volume is increased and since the paint concentration volume is constant, this shows the presence of high amount of amide group will not be neutralized by the fewer amounts of OH– ions present in the paint wastewater. Thus, coagulation would not take place [24].

4.2.4. Impact of initial pH of SPFE

The actual initial pH of the SPFE was found out to be 8.4–8.6. The initial pH of the paint wastewater is an important factor in the treatment. By adding the varying quantity of HCl and NaOH solutions, the initial pH of the SPFE was maintained in the acidic/basic region. The treatment was being experimented in the region between pH 5 and 11 (pH 4 could not be done due to the formation of precipitate). The initial pH between 8 and 9 shows the maximum colour removal efficiency of 87.05% and turbidity removal efficiency up to 96.43% (Fig. 12).

It is most preferable and economical to treat the effluent at its own initial pH. Coincidental trend was marked in the treatment of olive mill effluent [25].

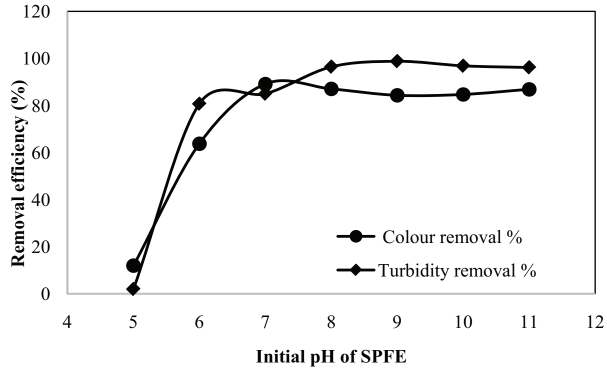


Fig. 12. Impact of initial pH of SPFE on removal efficiency. SPFE volume: 1 L; initial pH of SPFE: 5–11; initial concentration of SPFE: 1,200 mg/L; coagulant: extragens = 40 g of SSP: 3 N NaCl; coagulant-eluate volume: 400 mL.

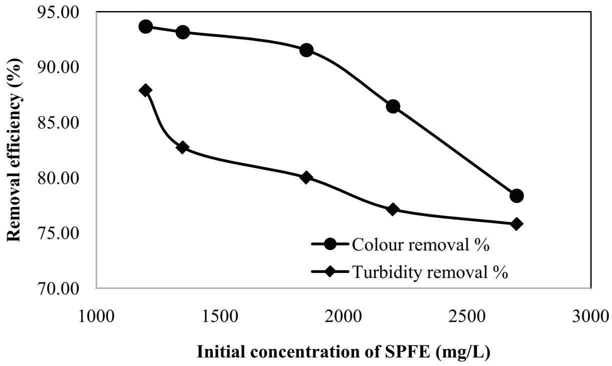


Fig. 13. Impact of initial concentration of SPFE on removal efficiency. SPFE volume: 1 L; initial pH of SPFE (actual): 8.2–8.6; initial concentration of SPFE: 1,200–2,700 mg/L; coagulant: extragens = 40 g of SSP: 3 N NaCl; coagulant-eluate volume: 400 mL.

4.2.5. Impact of initial concentration of SPFE

Five different initial concentrations of SPFE were prepared (1,200, 1,350, 1,850, 2,200 and 2,700 mg/L) and were numbered as sample no. 1–5, respectively. The different initial concentration of SPFE was treated with the optimized value of the coagulant solution. Fig. 13 exhibited higher colour and turbidity removal for initial paint concentration of 1,200 mg/L at 93.67% and 95.65%, respectively. This is due to the fact that the lower initial concentration, the toxic pollutants enabled the coagulant to easily coagulate. Lower the initial concentration more will be the ability of the coagulant to remove the pollutants efficiently. The output was contrasting with the results extracted in the treatment of paint effluent using *S. potatorum* as a natural coagulant [18].

4.3. Application on real paint factory effluent

The optimized operating variables derived after the treatment of SPFE was applied over a litre of RPFE (Fig. 14). The maximum removal efficiencies were 80.12% for colour and 70.25% for turbidity. The optimized operating conditions and the obtained maximum removal efficiencies were tabulated (Tables 4 and 5).

4.4. Impact of chitosan dose, volume, initial pH and initial concentration of SPFE on colour and turbidity removal

Chitosan stock solution was prepared with initial concentration ranged between 100 and 500 mg/L. The best results were achieved for 600 mL of 500 mg/L initial concentration of chitosan stock solution. The results were 99.96% colour removal and 99.98% turbidity removal (Figs. 15(a) and (b)). As the volume gradually increased, removal efficiency in terms of colour and turbidity also showed a raise with the maximum being at 600 mL after which the trend showed a gradual decline. The probable reason for this behaviour could be the fact that at higher volumes overdosing and charge reversal must have taken effect.

The colour removal efficiency was found to be 99.95% and the turbidity removal was 98.40% at initial pH 9. The actual initial pH of SPFE also ranged as 8.4–8.6. The effluent could be treated with its own initial pH (Fig. 16).

The best results were observed for lower initial concentration sample such as 99.57% and 99.97% for colour and turbidity removal, respectively. The most probable reason for this behaviour could be that increase in the initial concentration of pollutants decreased the removal efficiency for the fixed dose of chitosan (Fig. 17) [15].

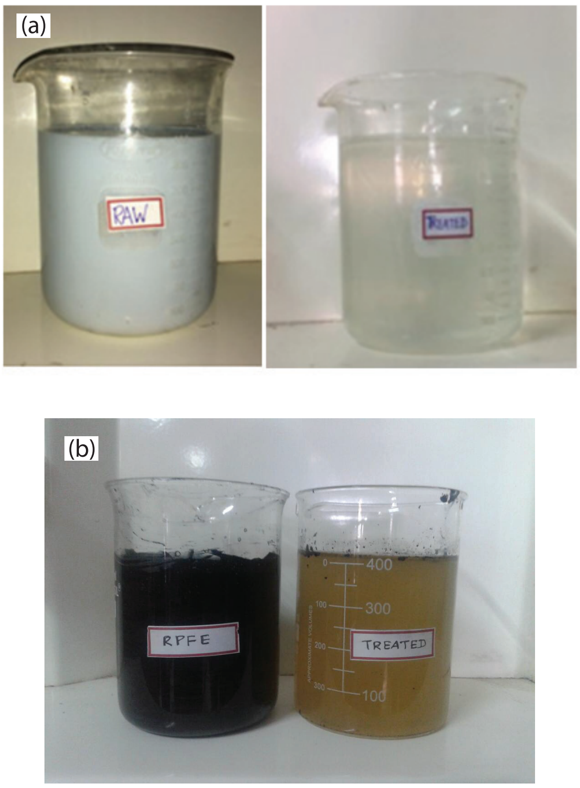


Fig. 14. Photographs of (a) SPFE and (b) RPFE before and after treatment using SSP.

4.5. Sludge settleability parameters

The batch test was performed in a column of 65 mm in diameter and 430 mm deep, and by gently stirring (1 rpm) the sample during settling. The volume of the sludge produced after a fixed settling span is the basis for the measurement of the

Table 5
Comparison of the treatment efficiency of the natural coagulant under optimum conditions

Coagulants	SPFE		RPFE	
	Colour removal %	Turbidity removal %	Colour removal %	Turbidity removal %
SSP	93.67	81.77	80.12	70.25
Chitosan	99.99	94.89	–	–

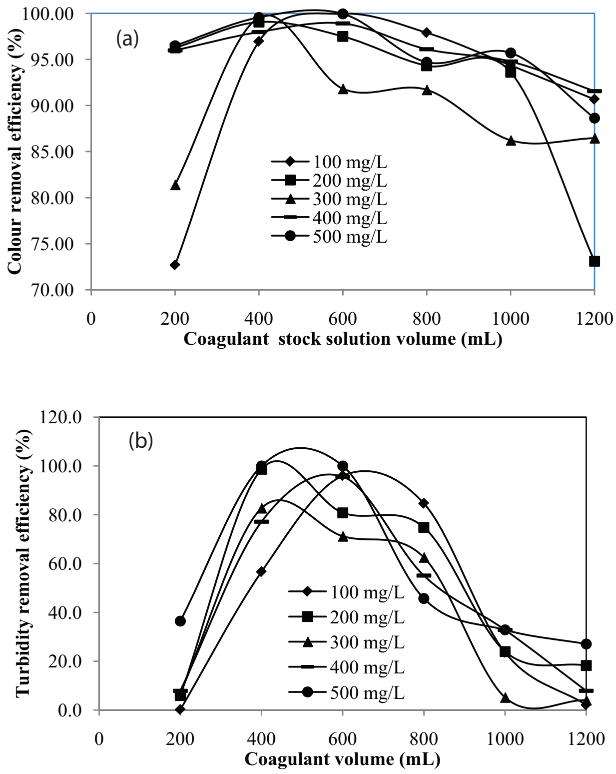


Fig. 15. (a) Impact of chitosan volume on colour removal efficiency. (b) Impact of chitosan volume on turbidity removal efficiency. SPFE volume: 1 L; initial pH of SPFE (actual): 8.4–8.6; initial concentration of SPFE: 1,200 mg/L.

Table 4
Optimized values of operational parameters to treat a litre of SPFE

Coagulant	Eluent and concentration	Dose and eluate volume	Initial pH (actual)	Initial concentration (mg/L)
SSP	3 N NaCl	40 g, 400 mL	8.4–8.6	1,200
Chitosan	0.1 N HCl	5 g, 600 mL	8.4–8.6	1,200

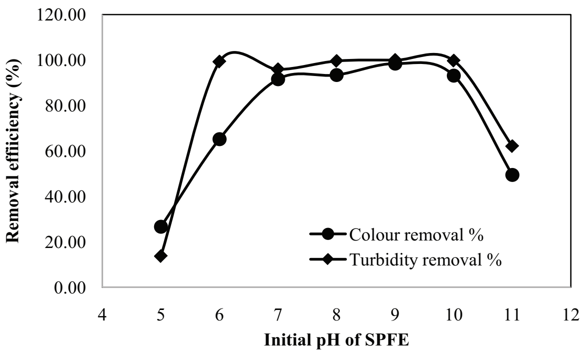


Fig. 16. Impact of initial pH of SPFE on removal efficiency. SPFE volume: 1 L; chitosan concentration: 500 mg/L; chitosan stock solution volume: 600 mL; initial concentration of SPFE: 1,200 mg/L.

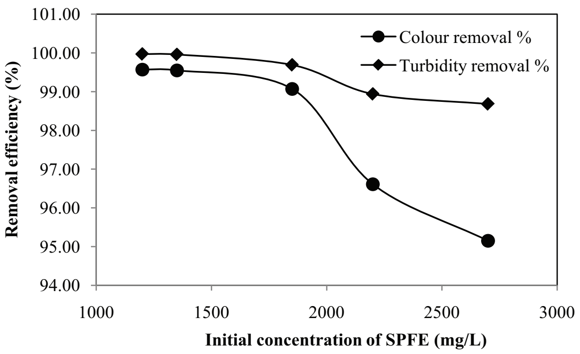


Fig. 17. Impact of initial concentration of SPFE on removal efficiency. SPFE volume: 1 L; chitosan concentration: 500 mg/L; chitosan stock solution volume: 600 mL; initial pH of SPFE (actual): 8.4–8.6.

sludge settleability parameters of the coagulant used. Among these, the sludge volume index (SVI) is the most known. It has been found to be influenced by the dimensions of the settling cylinder. These problems can be significantly reduced by conducting the test under certain prescribed conditions.

4.5.1. The sludge volume index

The SVI is defined as the volume (mL) occupied by 1 g of sludge after 30 min settling in a 1 L unstirred cylinder. It is ratio between the volume of sludge formed at 30 min of settling and the total suspended solids. The sludge volume of the sample after 30 min (SV_{30}) and final sludge volume (SV_f) was observed for various initial concentrations, it showed the inclined trend (Fig. 18). Typical SVI values can be found between 50 (very good settleability) and 400 mL/g (poor settleability). The SVI results of the SSP were ranged as 62.3–88.6 mL/g (Fig. 19), which indicated sludge with good settling properties. The dry weight of the sludge was ranged from 32.78 to 38.08 g.

$$\mathrm{SVI} = \frac{\mathrm{SV}_{30}\left(\frac{\mathrm{mL}}{\mathrm{L}}\right)}{X_{\mathrm{TSS}}\left(\frac{\mathrm{g}}{\mathrm{L}}\right)}, \frac{\mathrm{mL}}{\mathrm{g}} \tag{1}$$

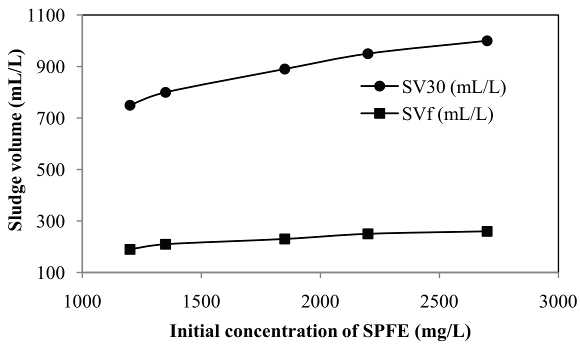


Fig. 18. Sludge volume as a function of the initial concentration.

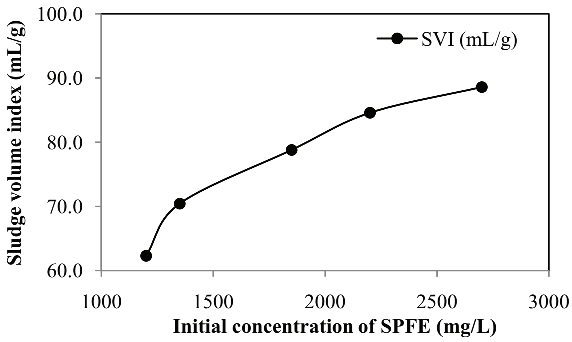


Fig. 19. Sludge volume index as a function of the initial concentration.

4.5.2. Batch settling curve and the hindered settling velocity

From the batch settling results, the plot was made between the sludge bed heights over time for five different initial concentrations of SPFE (Fig. 20). The particles are settled, due to the equilibrium between the gravitational forces. If the column is kept unstirred, then the velocity at which the interface moves downward is called the hindered settling velocity V_{HS} at the inlet SPFE concentration. By calculating the slopes of the linear part of the batch curves for different initial concentrations, the hindered settling velocity can be determined as a function of the solids concentration. It governs the determination of the limiting flux and thus the SSTs surface area. At higher concentrations, the settling particles will be increasingly hindered by surrounding particles, which slows down the V_{HS}.

Mathematically, the relation between the sludge concentration and the zone settling velocity can be described by an exponential decaying function, Vesilind equation.

$$V_{\mathrm{HS}} = V_o . \mathrm{e}^{(-r_V).(\mathrm{TSS})} \tag{2}$$

where V_{HS} is the hindered settling velocity of the sludge, cm/min; V_o is the maximum settling velocity, cm/min; TSS is the suspended solids concentration, g/L and r_V is a model parameter.

The observed hindered settling velocity from the batch settling curves was compared with V_{HS} calculated from Vesilind model (Fig. 21). The maximum settling velocity (V_o) and model parameter (r_V) are found to be 2.17×10^{-5} cm/min and 0.3350, respectively [21].

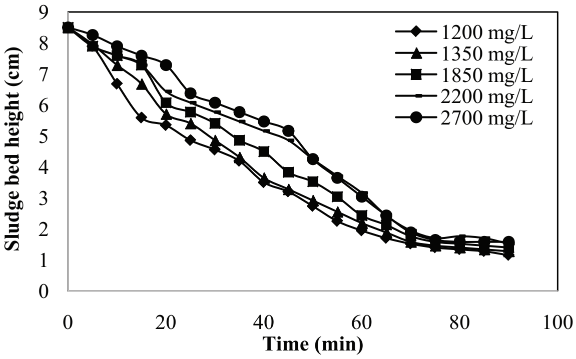


Fig. 20. Batch settling curves at different initial concentrations.

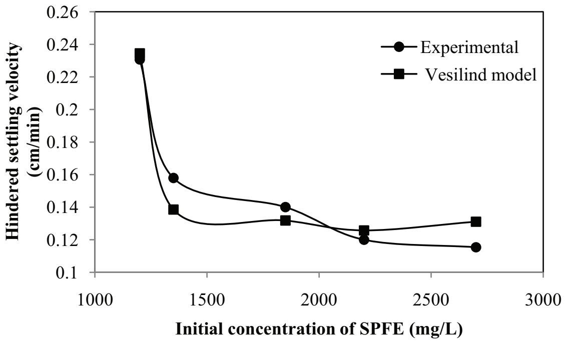


Fig. 21. Settling velocity as a function of the solids concentration.

5. Conclusions

The results of the present study revealed the following conclusions.

The presence of chitosan in the, sea food processing waste, *Fenneropenaeus indicus* (shrimp) shell built it as an efficient coagulant in the treatment of SPFE. It was recommended to use 400 mL of SSP-eluate prepared using 40 g of coagulant and 3 N NaCl, to treat a litre of SPFE at its actual pH (8.2–8.6). The optimized conditions exhibited its better removal while applied on RPFE as well. The results were compared with the outcome of commercial chitosan.

The SVI results were ranged as, 62.3–88.6 mL/g, indicated the very good settle ability of the SSP. The hindered settling velocity of the formed sludge was in the declining trend with the increase in the initial COD of the effluent. The maximum velocity (V_o) was found as 2.17×10^{-5} cm/min. By and large, being a universally luxuriant solid waste, and conforming to the results, shrimp shells could be a fitting coagulant for the paint factory effluent treatment. Sea food waste management and effluent treatment could be extended equally.

References

[1] B.K. Korbahti, N. Aktas, A. Tanyolac, Optimization of electrochemical treatment of industrial paint wastewater with response surface methodology, J. Hazard. Mater., 148 (2007) 83–90.

[2] S. Vishali, P. Rashmi, R. Karthikeyan, Evaluation of wasted biomaterial, crab shells (*Portunus sanguinolentus*), as a coagulant, in paint effluent treatment, Desal. Wat. Treat., 57 (2016) 13157–13165.

[3] A.E. Mohsen, H. Hassanin, M.M. Kamel, Appropriate technology for industrial wastewater treatment of paint industry, Am. Eurasian Agric. Environ., 8 (2010) 597–601.

[4] Y.Y. Chun, Emerging usage of plant based coagulants for water and wastewater treatment, Process Biochem., 45 (2010) 1437–1444.

[5] A. Diaz, N. Rincon, A. Escorihuela, N. Fernandez, E. Chacin, C.F. Forster, A preliminary evaluation of turbidity removal by natural coagulants indigenous to Venezuela, Process Biochem., 35 (1999) 391–395.

[6] A.K. Verma, R. Dash, P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters, J. Environ. Manage., 93 (2012) 154–168.

[7] M.V. Jadhava, Y.S. Mahajan, Assessment of feasibility of natural coagulants in turbidity removal and modelling of coagulation process, Desal. Wat. Treat., 52 (2014) 5812–5821.

[8] S. Dahiya, R.M. Tripathi, A.G. Hegde, Biosorption of lead and copper from aqueous solutions by pre-treated crab and arca shell biomass, Bioresour. Technol., 8 (2008) 179–187.

[9] http://www.nature.com/news/sustainability-don-t-waste-seafood-waste-1.18149

[10] http://www.muscatdaily.com/Archive/Features/Green-Living-Recycling-shrimp-waste-4vo7

[11] http://infohouse.p2ric.org/ref/19/18053.htm

[12] L. Rizzo, A.D. Gennaro, M. Gallo, V. Belgiorno, Coagulation/chlorination of surface water: a comparison between chitosan and metal salts, Sep. Sci. Technol., 62 (2008) 79–85.

[13] S. Vishali, R. Karthikeyan, S. Prabhakar, Utilization of seafood processing waste, as an adsorbent, in the treatment of paint industry effluent using a fixed-bed column, Desal. Wat. Treat., 66 (2017) 149–157.

[14] H. Zemmouri, M. Drouiche, A. Sayeh, H. Lounici, N. Mameri, Coagulation flocculation test of Keddara's water dam using chitosan and sulphate aluminium, Procedia Eng., 33 (2012) 254–260.

[15] F.H. Chi, W.P. Cheng, Use of chitosan as coagulant to treat wastewater from milk processing plant, J. Polym. Environ., 14 (2006) 411–417.

[16] P. Sneha, J. Aiswarya, S. Changam Sheela, M.C. Sanjay, Extraction and purification of chitosan from chitin isolated from sea prawn (*Fenneropenaeus indicus*), Asian J. Pharm. Clin. Res., 7 (2014) 201–204.

[17] P. Bishop, Pollution Prevention: Fundamentals and Practice, McGraw Hill International, McGraw Hill Book Co., Singapore, 2000.

[18] S. Vishali, R. Karthikeyan, A comparative study of *Strychnos potatorum* and chemical coagulants in the treatment of paint and industrial effluents: an alternate solution, Sep. Sci. Technol., 49 (2014) 2510–2517.

[19] APHA, Standard Methods for the Examination of Waste and Wastewater, 16th ed., American Public Health Associations, New York, NY, 1995.

[20] S. Vishali, R. Karthikeyan, *Cactus opuntia* (*ficus-indica*): an eco-friendly alternative coagulant in the treatment of paint effluent, Desal. Wat. Treat., 56 (2015) 1489–1497.

[21] C.M.V.L. Mark, H.N. Per, M.L.V. Carlos, B. Damir, Experimental Methods in Wastewater Treatment, IWA Publishing, Landon, UK, 2016.

[22] J.M. Thamer, S. Eman, Effect of settling time, velocity gradient, and camp number on turbidity removal for oilfield produced water, Egypt. J. Pet., (2018) (in press).

[23] M.B. Sciban, M.G. Antov, M.T. Klasnja, Extraction and partial purification of coagulation active components from common bean seed, Acta Period. Technol. (ACPTEFF), 37 (2006) 1–192.

[24] S. Vishali, A. Ayushi, Performance evaluation of *Cyamopsis tetragonolobus* (guar gum), as a natural coagulant, in the treatment of paint industry effluent, Desal. Wat. Treat., 62 (2017) 443–448.

[25] B. Meyssami, A.B. Kasaeian, Use of coagulants in treatment of olive oil wastewater model solutions by induced air flotation, Bioresour. Technol., 96 (2005) 303–307.