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Evaluation of wasted biomaterial, crab shells (*Portunus sanguinolentus*), as a coagulant, in paint effluent treatment

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ABSTRACT

The ability of the wasted biomaterial crab shells, *Portunus sanguinolentus*, as a coagulant, in the treatment of simulated water-based paint industry effluent was evaluated. The treatment process was conducted in conventional jar test. The FTIR spectrum values endorse the existence of chitosan in *P. sanguinolentus*. The leverage of variables such as time (min), eluent type (deionized water, NaCl, and $BaCl_2$), eluent concentration (1–5 N), coagulant dose (1–6 g), coagulant volume (20–100 mL), initial pH (5–10), and initial concentration (3,100, 4,224, 5,650, 6,258, and 7,693 mg/L named as sample number 1–5, respectively) were investigated in terms of color, chemical oxygen demand, and turbidity. The optimized value of the above-mentioned variables were examined and the values are 20 min of slow mixing, 15 min of settling course, 3 N NaCl as an eluent, and 100 mL of 3 g crab shells eluate to treat 1 L of effluent under basic pH. The maximum removal efficiency was identified for higher initial concentration effluent, sample 5. The results were compared with conventional coagulant alum and ferric chloride from previous studies. The wasted biomaterial crab shells could act as propitious surrogate for conventional coagulants.

Keywords: Portunus sanguinolentus; Crab shell; Paint effluent; Coagulation; Eluate

1. Introduction

Environmental pollution is not a new term; it multiplies with industrialization. Paint is the mixture of binder, pigment, solvent, and resins. Based on the solvent type, it can be classified as water-based, solvent-based, and dry (powder) paints. The major constituents of the wastewater generated in the paint industry are from the cleaning of vessels and various unit operations [1]. The direct release of this effluent into the aquatic environment spoils aquatic life imposes health risks and the accumulation could result in toxicity to both human and aquatic life. It can also contribute to respiratory problems, irritation to eyes, skin, lungs and cause headache, muscle weakness, damage to liver, and kidney. Legal restrictions in organized industrial zone and environment conservation make it mandatory that the effluent is treated before it is discharged into the environment [2].

Various technologies have been developed to remove the pollutant from the effluent, among which, coagulation is an appropriate technology for the treatment of paint effluent [3]. Many coagulants such as alum, ferric chloride, polyaluminium chloride (PACl),

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and calcium carbonate have been used in the removal of pollutants from the wastewater. In concern with human health like Alzheimer's disease [4] and toxicity present in the sludge, it is the time to develop the alternate coagulant [5].

The successful treatment process, not only depends on the pollutant removal ability of the coagulant, but also in abundance of the material for the treatment processes everywhere. So the coagulant should either be an industrial waste or available plenty in nature [6]. Environmental researchers identified several plant types, like *Moringa oleifera*, *Stryconus potatorum*, *Cactus* species, *Phaseolus vulgaris*, surjana seed, maize seed, tannin, gum arabic, *Prosopis juliflora*, and *Ipomoea dasysperma* seed gum, as coagulants [7].

Keeping this in view, an attempt has been made to evaluate the treatability of crab shells as a coagulant in the pollutant removal from paint effluent. Crab shells are the huge quantity of the natural waste product from the seafood processing industries. Millions of tons of crab shells are being generated annually all over the world. Due to high costs and strict environmental regulations, landfills are becoming less popular for waste disposal. Proper reuse of this material can be the better solution and also generates possible revenue to the industries [8].

Crab shells have been used as an adsorbent in the removal of heavy metals such as lead, copper, manganese(II), zinc(II), cerium, europium [6,9,10], and in the treatment of electro-plating industrial effluents [11]. The chemical composition of crab shell was $CaCO_3$ 40–66%, $MgCO_3$ 3–5%, protein 11–29%, chitin 20–27%, lipid 1.35%, and <2% others on dry basis [8].

Chitosan in crab shell waste has the advantage of low cost and high biocompatibility. Chitosan, a linear cationic polymer of high-molecular weight 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]. About 100 g of crab shell powder yielded 6.83 g raw chitin after demineralization, deproteinization, and 4.65 g of chitosan [13]. Chitosan was used as a coagulant in the removal from natural water and milk processing plant wastewater [14,15].

The focus of this study is to evaluate the ability of *Portunus sanguinolentus* as a coagulant for the treatment of water-based paint industrial effluent. The leverage of variables such as time, eluent type and concentration, crab shell dose, coagulant volume, initial pH, and initial concentration were investigated in terms of color, chemical oxygen demand (COD), and turbidity.

2. Materials and methods

2.1. Simulated effluent

All the chemicals used in this study were of analytical reagent grade branded by Merck, India. The simulated industrial water-based paint effluent was prepared by varying the composition of white primer- and acrylic-based blue colorant (5% (v/v)) using double-distilled water [16]. Five different samples were prepared and named as sample number 1–5 (Table 1). The physico-chemical properties of the simulated sample (sample 5), which resembled the real effluent from paint industry was listed in Table 2.

2.2. Coagulant and preparation of coagulant extract

The wasted biomaterial crab shells were identified as a coagulant and it was collected from local sea foods markets of Pudukottai, Tamil Nadu, India. The crabs are from the east coast of the Bay of Bengal. This three red-spotted crab shells, named *P. sanguinolentus*, were washed thoroughly with deionised water to remove the soft tissues, sun dried for four hours, powdered, sieved through a 0.5 mm sieve, and used as animal based coagulant.

The known weight of crab shell powder was added in 100 mL of solvent named as eluent. This was kept in the shaker for 15 min at 200 rpm, to extract the chitosan which is responsible for coagulation. The resultant solution was then allowed to settle for 10 min. The known volume of the supernatant liquid named as eluate, was used as a coagulant.

2.3. Experimental setup

A commonly used six stirrer arrangement jar test apparatus with base floc illuminator (Deep Vision, India) was taken as equipment for coagulation process. Experiments were conducted in six numbers of equal volume (2,000 mL) beakers. About 1,000 mL of simulated effluent was taken in each study to evaluate the leverage of variables such as time (min), eluent type (deionized water, NaCl, and $BaCl_2$), and concentration (1–5 N), crab shell dose (g), coagulant volume (20–100 mL), initial pH (5–10), and initial concentration (3,100, 4,224, 5,650, 6,258, and 7,693 mg/L named as sample number 1–5, respectively) were investigated. The known volume of coagulant was added in each beaker. After the addition of coagulant into the effluent, the jar test apparatus was maintained with the rapid mixing for 5 min at 200 rpm and slow mixing for 20 min at 80 rpm, and was allowed to settle for 15 min. About 50 mL of the supernatant of treated

Table 1
Concentration of simulated samples (made upto 1,000 mL)

Sample number	White primer (mL)	Blue colorant (mL)	Initial COD (mg/L)
1	48	2	3,100
2	46	4	4,224
3	44	6	5,650
4	42	8	6,258
5	40	10	7,693

Table 2
Physico-chemical characteristics of the simulated industrial wastewater (sample number 5)

Parameters	Concentration in mg/L (except for pH)
pH at 25°C	7.6
Total dissolved solids (mg/L)	304
Total suspended solids (mg/L)	6,880
Oil and grease (mg/L)	19
Chloride as Cl (mg/L)	68
Chemical oxygen demand (COD) (mg/L)	7,693
Sulfate as SO_4 (mg/L)	24
Biochemical oxygen demand (mg/L; 3 d incubated at 27°C)	2,648
Iron as Fe (mg/L)	0.05
Turbidity (NTU)	7,760

effluent was centrifuged at 10,000 rpm for 5 min and used for analysis.

All the experiments were repeated at least thrice for consistency and the results averaged. The plot was made for the averaged value with the reproducibility less than 2%.

2.4. Performance evaluation

The coagulation activity of wasted crab shell was assessed in terms of color, COD, and turbidity. All the parameters mentioned in Table 2 were measured using standard methods [17]. Color was measured using SL 218 double UV visible spectrophotometer (Elico—India) at λ_{max} 612 nm. COD was calculated using the dichromate method [17]. Turbidity was measured using digital nephelo-turbidity meter 132 (Elico —India) and it was expressed in nephelometric turbidity units (NTU). pH is adjusted using digital pH meter MK. V.I (Elico—India).

3. Results and discussion

3.1. Characterization of P. sanguinolentus

Chitin is the most important natural polysaccharide found in cretaceous shells or in the cell walls of fungi. Its principal derivative is chitosan obtained by deacelylation of chitin. Due to the presence of amino group, it is soluble in aqueous acidic medium [18]. The samples of chitosan produced were characterized in KBr pellets by using an infrared spectrophotometer in the range of 400–4,000 cm^{-1} (ABB MB 3000).

The FTIR spectrum of the standard chitin contains 14 major peaks, whereas the FTIR spectrum of the *P. sanguinolentus* was obtained and the effective peaks were compared with that of the standard chitin. The wavelengths of the main bands observed in the infrared of the alpha–chitin in the present study are depicted in Table 3a [19].

The FTIR spectrum of the standard chitosan displayed several peaks at the ranges of 893, 1,021, 1,255, 1,420, 1,581, and 3,404 cm^{-1}; whereas the *P. sanguinolentus* sample also showed major peaks (Fig. 1 and Table 3b). In general, chitosan from *P. sanguinolentus* shows bands at 3,000–3,500 cm^{-1} (NH bond) and at 1,400–1,650 cm^{-1} (C=O bond). The spectra of chitosan showed a broad absorption band in the range 3,000–3,500 cm^{-1} attributed to O–H stretching vibrations. The peaks around 2,885, 1,650, 1,589, 1,326, and 1,080 cm^{-1} in the FTIR spectrum of Chitosan are due to the stretching vibrations of aliphatic C–H, Amide I (–NH deformation of –$NHCOCH_3$), Amide II, Amide III, and C–O–C bonds, respectively. These are the characteristics of the chitosan polysaccharide [20].

Table 3a
Wavelength of the main bands obtained for the standard chitin and eluate of crab shells

Vibration modes	Standard-α-chitin (cm^{-1}) [19]	Crab shell-α-chitin (cm^{-1})
OH out of plane bending	690	709.36
NH out of plane bending	752	750
CH_3 wagging along chain	952	1,000
CO stretching	1,026	1,024
CO stretching	1,073	1,069
CH_2 bending and CH_3 deformation	1,418	1,420
Amide I band	1,661	1,663
CH stretching	2,878	2,862
Symmetric CH_3 stretching and asymmetric CH_2 stretching	2,930	2,958
NH stretching	3,268	3,252
OH stretching	3,439	3,438.17

Table 3b
Wavelength of the main bands obtained for the standard chitosan and eluate of crab shells

Vibration modes	Standard-chitosan (cm^{-1}) [20]	Crab shell-chitosan (cm^{-1})
HPO_4^{2-}	891.41	912
PO_4^{3-}	1,026.63	1,031
PO_3^4	1,259.54	1,249
H group (monomer)	1,422.73	1,420.78
($–NH_2$) Amide II	1,587.94	1,575
Structural unit	3,377.95	3,438.17

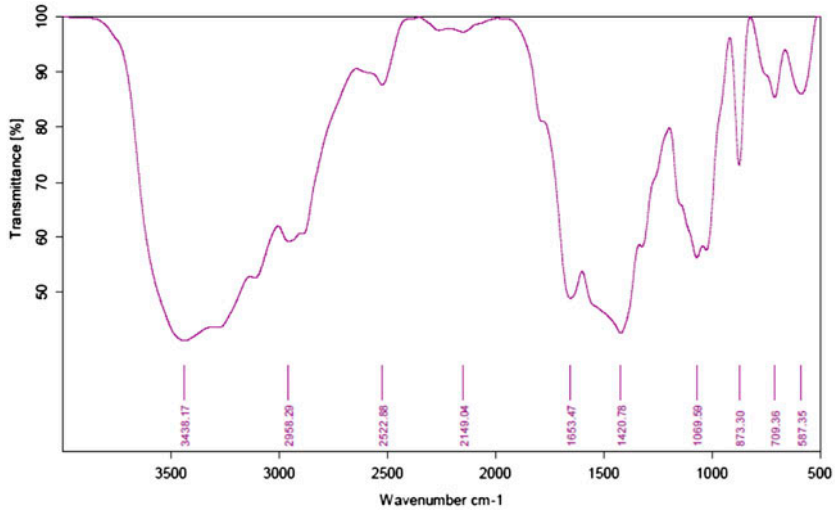

Fig. 1. FTIR spectrum of crab shells (*P. sanguinolentus*).

3.2. Influence of time

In coagulation process, the influence of the length of the slow mixing and the settling period was an important factor in terms of treatment efficiency. The slow mixing time varied from 10 to 30 min. While extending the slow mixing period, it was noticed that the size of the macro-flocs was expanded, due to which the settling was strengthened. The equilibrium, maximum removal of color, and turbidity was marked at 20 min of slow mixing after 5 min of rapid mixing.

In order to get the clarified, treated effluent in the form of supernatant, the settling period ranged from 15 to 60 min. It was observed that the residual color and turbidity was decreased when the treated effluent was allowed to settle for the long period. Based on the removal efficiency, 81.8% for color, 80.73% for turbidity (Figs. 2a and 2b), the equilibrium, and the optimum settling period were concluded as 15 min, and there was no apparent variance in the removal efficiency after 15 min.

These results were supported in the treatment of wastewater from milk processing plant, using chitosan as a coagulant [15] and optimization of micro-algae coagulation processes using chitosan [21]. The removal percentage remained at the maximum even at the highest value of 60 min. But the reverse trend was noticed when alum and the PAC were used as a coagulant for the treatment of palm oil mill effluent. The prolonged mixing time break up the flocs formed and become re dispersed in the suspension [22]. In this case, the aggregated flocs remained intact even up to 60 min of settling and 30 min of slow mixing. The results confirmed that the coagulant forms strong bonds with the pollutant bridging the flocs strongly than chemical coagulants.

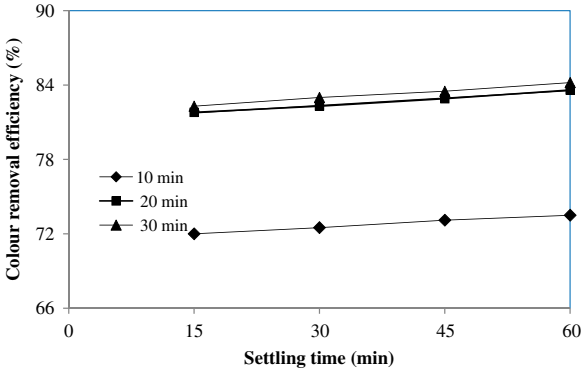

Fig. 2a. Effect of time on color removal efficiency.
Note: pH = actual effluent pH (7.2–7.8); coagulant: extragens = 5 g of crab shell powder: 100 mL of 3 N NaCl; coagulant volume = 100 mL; sample number 1.

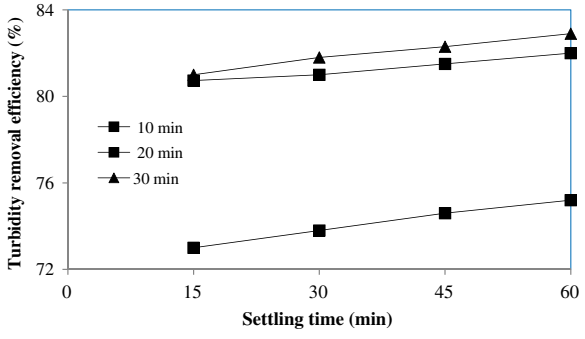

Fig. 2b. Effect of time on turbidity removal efficiency.
Note: pH = actual effluent pH (7.2–7.8); coagulant: extragens = 5 g of crab shell powder: 100 mL of 3 N NaCl; coagulant volume = 100 mL; sample number 1.

3.3. Influence of eluent type and concentration

The coagulant was prepared by suspending 6 g of crab shells in different eluents like water and 1–5 N of NaCl and $BaCl_2$. The prepared coagulants were added in 1 L of effluent each. It was noticed that lowest removal was attained when water was an eluent and the values are 6.37% removal of coloring matter and 9.39% of turbidity removal. The reason is chitosan; a main component in the crab shell, which is liable for the coagulation process, is insoluble in water. Further, the treatment was done using the eluates prepared from 1 to 5 M of NaCl and $BaCl_2$. The removal of color, COD, and turbidity was in increasing order when the concentration increased up to 3 N. Beyond that the treatment efficiency decreased till 5 M. The optimum results at 3 N NaCl was 81.80% for color, 70% COD, and 80.73% for turbidity (Figs. 3a–3c).

The believed reason for this result is that 3 N NaCl might extract the maximum possible amount of chitosan from a known amount of crab shells. Identical results were highlighted in the treatment of olive oil wastewater using chitosan [23]. The consumption of coagulant was varied by varying the strength of the ionic solutions. It was affirmed in the extraction of protein from common bean seed by stepwise raise in NaCl concentration [24].

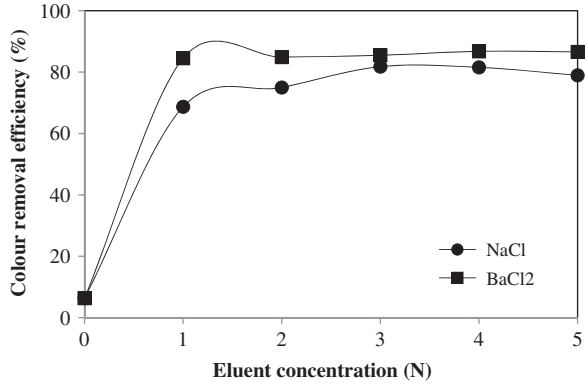

Fig. 3a. Effect of eluent concentration on color removal efficiency.
Note: pH = actual effluent pH (7.2–7.8); coagulant: extragens = 5 g of crab shell powder: 100 mL of water and 1–5 N of NaCl, $BaCl_2$; coagulant volume = 100 mL; sample number 1.

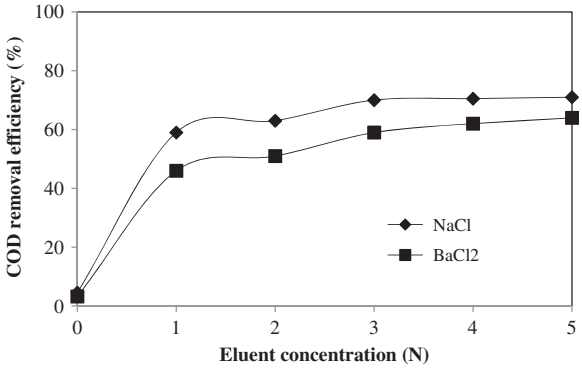

Fig. 3b. Effect of eluent concentration on COD removal efficiency.
Note: pH = actual effluent pH (7.2–7.8); coagulant: extragens = 5 g of crab shell powder: 100 mL of water and 1–5 N of NaCl, $BaCl_2$; coagulant volume = 100 mL; sample number 1.

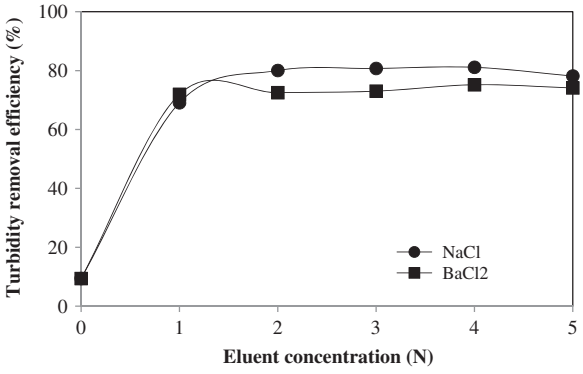

Fig. 3c. Effect of eluent concentration on turbidity removal efficiency.
Note: pH = actual effluent pH (7.2–7.8); coagulant: extragens = 5 g of crab shell powder: 100 mL of water and 1–5 N of NaCl, $BaCl_2$; coagulant volume = 100 mL; sample number 1.

3.4. Influence of crab shell dose

The crab shell powder amount varied from 1 to 6 g. The eluate prepared with the different doses of coagulant by using 3 N NaCl was applied in paint effluent. The optimum result was identified for 3 g of crab shells and the values are 53.99% for color, 55% for COD, and 90.49% for turbidity removal (Fig. 4). The removal was swelled when the doses increased from 1 to 3 g, after that decline in trend was observed. The assumed reason is that though the coagulant dose increased, the volume of eluent used to extract the chitosan, from the source crab shell was maintained as constant volume. Due to an inadequate quantity of the

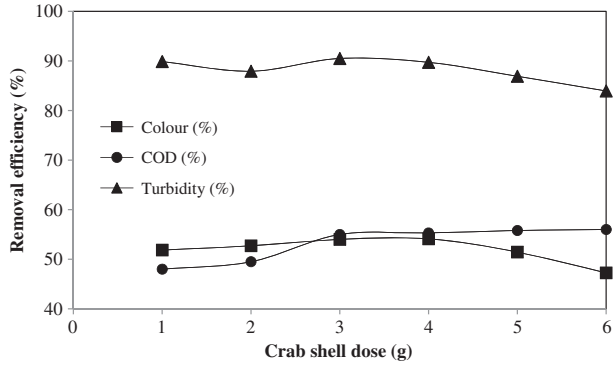

Fig. 4. Effect of coagulant dose on removal efficiency.
Note: pH = actual effluent pH(7.2–7.8); coagulant: extragens = 1–6 g of crab shell powder: 100 mL of 3 N NaCl; coagulant volume = 100 mL; sample number 1.

eluent, all the available chitosan could not be extracted and utilized for the treatment.

This result is in agreement with previous studies [12,15]. When the dosage increased continuously, the surface charge reversal occurred and the removal of color, COD, and turbidity decreased. The effluent pH is close to neutral (7.2–7.8), the charge reversal from negative to positive happened in a high dosage of crab shell that means chitosan, and then the colloidal destabilization occurred which is not favored the coagulation reaction. An agnate trend was grasped in the removal of Congo red dye from its aqueous solution using natural coagulants [25].

3.5. Influence of coagulant volume

Different volumes (20–100 mL) of 3 g crab shell eluated in 100 mL of 3 N NaCl were applied to the paint effluent. The removal efficiency gradually increased with the volume of the coagulant. The equilibrium efficiency was noticed for 100 mL of the coagulant solution and the results are 83.28% for color, 67% for COD, and 73.5% for turbidity (Fig. 5). The reason may be that the amount of available chitosan for the coagulation is in increasing order when the volume increased (Table 4). The coincidence in the results was identified in the removal of turbidity from water by natural coagulant [26].

3.6. Influence of initial pH

The influence of pH was examined in the range of 5–11 (beyond which precipitate was formed). The removal was in increasing order from acidic to basic region. At basic pH 8–9, it shows the maximum

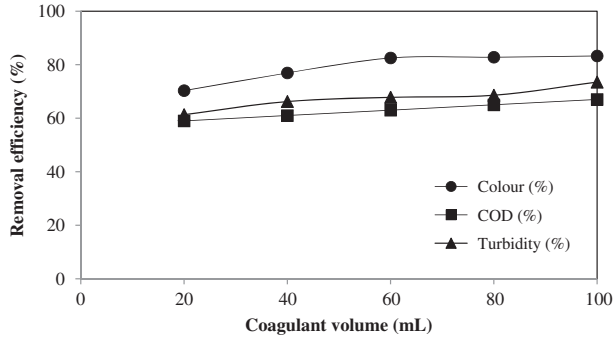

Fig. 5. Effect of coagulant volume on removal efficiency.
Note: pH = actual effluent pH (7.2–7.8); coagulant: extragens = 3 g of crab shell powder: 100 mL of 3 N NaCl; coagulant volume = 20–100 mL; sample number 1.

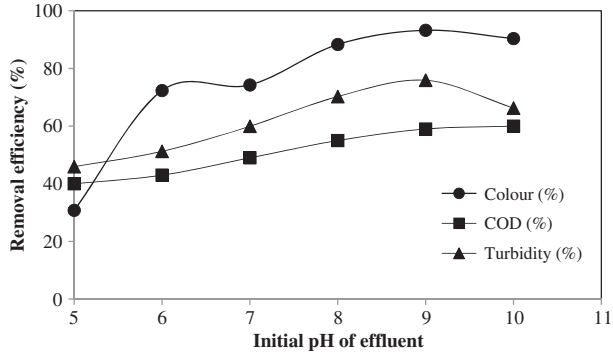

Fig. 6. Effect of initial pH of effluent on removal efficiency.
Note: pH = 5–11; coagulant: extragens = 3 g of crab shell powder: 100 mL of 3 N NaCl; coagulant volume = 100 mL; sample number 1.

Table 4
Concentration of crab shell in jars

Jar number	Volume of coagulant (mL) (prepared using 3 g of crab shell powder eluted in 100 mL of 3 N of NaCl)	Concentration of crab shell (g/L)
1	20	0.588
2	40	1.154
3	60	1.698
4	80	2.222
5	100	2.727

efficiency of 93.23% for color, 59% for COD, and 75.90% for turbidity (Fig. 6).

$CaCO_3$ a major constituent of crab shell favors micro-precipitation of pollutant ions as $CaCO_3$ dissociated to Ca^{2+} and CO_3^{2-}. But the solubility of $CaCO_3$ varies with solution pH. The speciation of carbonate ions are,

$$\text{Crab shell } (CaCO_3 + \text{chitin, protein})\ H_2O \cdot \text{Crab shell (chitin, protein)} + Ca^{2+} + Co_3^{2-}$$

$$CO_3^{2-} + H_2O \cdot HCO_3^- + OH^-$$

$$M^{2+} + CO_3^{2-} \cdot MCO_{3(S)}$$

$$MCO_{3(S)} + \text{Crab shell (chitin, protein)} \cdot \text{Crab shell (chitin, protein)} + MCO_{3(S)}$$

At basic pH 8, the insoluble hydroxides formed which simulates the sludge formation and reduces the toxicity by means color and turbidity, beyond which the removal decreased due to the formation of soluble carbonates. The believed mechanism involved in the coagulation was adsorption and charge neutralization. Opposite-charged particles adsorb and because of charge neutralization, settling of flocs happened. The pollutants are separated by means of biodegradable sludge. An identical trend was executed in the removal of Mn(2) and Zn(2) from aqueous solution using crab shell particles as adsorbent [9].

3.7. Influence of initial concentration

Five different initial concentrations of simulated samples such as 3,100, 4,224, 5,650, 6,258, and 7,693 mg/L were prepared and named as sample number 1–5, respectively. The observed removal was increased from sample number 1 to 5. The crab shells were exhibited the maximum coagulation behavior of

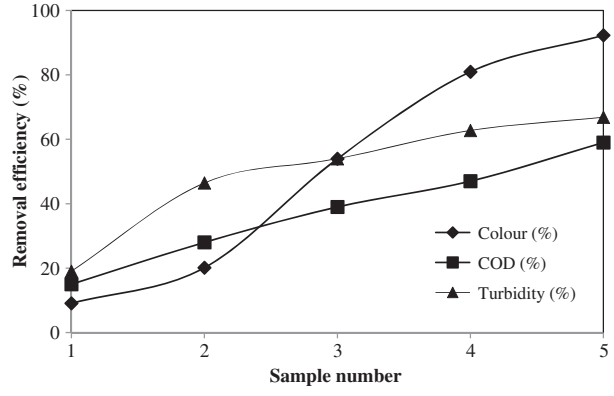

Fig. 7. Effect of initial concentration of effluent on removal efficiency.
Note: pH = actual effluent pH (7.2–7.8); coagulant: extragens = 3 g of crab shell powder: 100 mL of 3 N NaCl; coagulant volume = 100 mL; sample number 1–5.

Table 5
Comparison of the characteristics between raw effluent and treated effluents under optimum conditions

Parameters	Raw effluent (sample number 5)	Treated effluent using crab shells as a coagulant	Treated effluent using alum as a coagulant [28]	Treated effluent using $FeCl_3$ as a coagulant [29]
pH at 25°C	7.2–7.6	7.71	6.96	7.52
Color (nm)	0.4583	0.0353	0	0.0488
COD (mg/L)	7,693	2,693	571	1,277
Turbidity (NTU)	7,760	1,036	7	890

the higher concentration solution sample number 5 and the removal efficiencies were 92.29% for color, 59% COD, and 66.85% for turbidity (Fig. 7). The pollutant removal was boosted with the increase in the initial concentration of effluent from sample number 1 to 5. A more efficient utilization of the coagulant is expected due to a greater driving force by a higher concentration gradient. Akin studies were carried out while decolorizing the brilliant green from aqueous solution using cactus fruit peel [27].

The characteristics of the raw effluent and effluent treated using animal-based coagulant *P. sanguinolentus*, chemical-based conventional coagulants alum, and ferric chloride from previous study [28,29] were compared in Table 5. It was observed from the table, that the removal was found to be more when conventional chemical coagulant alum, ferric chloride was used, to treat a liter of effluent. But *P. sanguinolentus*, was also performed well in color, COD, and turbidity removal and the availability of this material is universally abundant. In environmental aspect, the wasted biomaterial *P. sanguinolentus* could be the better replacement for the chemical coagulant.

4. Conclusions

The coagulation ability of the wasted biomaterial crab shells, *P. sanguinolentus* was assessed and confirmed in the treatment of simulated water-based paint effluent through color COD and turbidity removal. The FTIR spectrum values certified the existence of chitosan, chitin in *P. sanguinolentus,* which is answerable for the coagulation property. Concurrently, the wasted biomaterial was managed and the treatment of paint effluent was also succeeded. Being a universally available, low cost, and abundant, wasted biomaterial, and based on its removal efficacy, this study concludes that *P. sanguinolentus* could be an alternate solution for the treatment of water-based paint effluent. The distinct conclusions derived from the studies are as follows:

The proposed results are that the chitosan magnitude extracted from *P. sanguinolentus* was magnificent using 3 N NaCl eluent. Eluate from 3 g crab shells under basic pH showed maximum removal efficiency, and it was identified for higher initial concentration effluent, sample 5. For the coagulation process, the optimized time was 20 min of slow mixing followed with 15 min of settling span. The results were compared with conventional coagulant alum and ferric chloride. The wasted biomaterial crab shells could act as propitious surrogate for conventional coagulants.

References

[1] B.K. Körbahti, N. Aktaş, A. Tanyolaç, Optimization of electrochemical treatment of industrial paint wastewater with response surface methodology, J. Hazard. Mater. 148 (2007) 83–90.
[2] A. Akyol, Treatment of paint manufacturing wastewater by electrocoagulation, Desalination 285(31) (2012) 91–99.
[3] M.A.E.L. Shazly, H.E.A. Hassanin, M.M. Kamel, Appropriate technology for industrial wastewater treatment of paint industry, Am. Eurasian J. Agric. Environ. Sci. 8(5) (2010) 597–601.
[4] T.P. Flaten, Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water, Brain. Res. Bull. 55 (2001) 187–196.
[5] Y.Y. Chun, Emerging usage of plant based coagulants for water and wastewater treatment, Process Biochem. 45(9) (2010) 1437–1444.
[6] S. Dahiya, R.M. Tripathi, A.G. Hegde, Biosorption of lead and copper from aqueous solutions by pretreated crab and arca shell biomass, Bioresour. Technol. 99(1) (2008) 179–187.
[7] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters, J. Environ. Manage. 93(1) (2012) 154–168.
[8] L. Shuguang, S.W. Gibb, E. Cochrane, Effective removal of zinc ions from aqueous solutions using crab carapace biosorbent, J. Hazard. Mater. 149(1) (2007) 208–217.
[9] K. Vijayaraghavan, H.Y.N. Winnie, R. Balasubramanian, Biosorption characteristics of crab shell particles for the removal of manganese(II) and zinc(II) from aqueous solutions, Desalination 266(1–3) (2011) 195–200.
[10] K. Vijayaraghavan, R. Balasubramanian, Single and binary biosorption of cerium and europium onto crab shell particles, Chem. Eng. J. 163 (2010) 337–343.

[11] K. Vijayaraghavan, K. Palanivelu, M. Velan, Crab shell-based biosorption technology for the treatment of nickel-bearing electroplating industrial effluents, J. Hazard. Mater. 119 (2005) 251–254.
[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 (1) (2008) 79–85.
[13] Y. Bolat, S. Bilgin, A. Gunlu, L. Izci, S.B. Koca, S. Cetinkaya, H.U. Koca, Chitin-chitosan yield of freshwater crab (*Potamon potamios, Olivier* 1804) shell, Pak. Vet. J. 30(4) (2010) 227–231.
[14] H. Zemmouri, M. Drouiche, A. Sayeh, H. Lounici, N. Mameri, Coagulation flocculation test of keddara's water dam using chitosan and sulfate aluminum, 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(4) (2006) 411–417.
[16] B.K. Körbahti, A. Tanyolaç, Electrochemical treatment of simulated industrial paint wastewater in a continuous tubular reactor, Chem. Eng. J. 148(2–3) (2009) 444–451.
[17] APHA, Standard Methods for the Examination of Waste and Wastewater, 16th ed., American Public Health Associations, New York, NY, 1995.
[18] J. Brugnerotto, J. Lizardi, F.M. Goycoolea, W. Argüelles-Monal, J. Desbrières, M. Rinaudo, An infrared investigation in relation with chitin and chitosan characterization, J. Polym. 42 (2001) 3569–3580.
[19] C. Palpandi, S. Vairamani, S. Annaian, Extraction of chitin and chitosan from shell and operculum of mangrove gastropod Nertia (dostia) crepidularia Lamarck, Int. J. Med. Med. Sci. 1(5) (2009) 198–205.
[20] T.S. George, K. Senthil Guru, N.S. Vasanthi, K.P. Kannan, Extraction, purification and characterization of chitosan from endophytic fungi isolated from medicinal plants, World J. Sci. Technol. 1(4) (2011) 3–48.
[21] A.L. Ahmad, N.H.M. Yasin, C.J.C. Derek, J.K. Lim, Optimization of microalgae coagulation process using chitosan, Chem. Eng. J. 173(3) (2011) 879–882.
[22] A.L. Ahmad, S. Sumathi, B.H. Hameed, Coagulation of residue oil and suspended solid in palm oil mill effluent by Chitosan, alum and PAC, Chem. Eng. J. 118 (2006) 9–105.
[23] 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.
[24] M.B. Sciban, M.G. Antov, M.T. Klasnja, Extraction and partial purification of coagulation active components from common bean seed, APTEFF 37 (2006) 1–192.
[25] H. Patel, R.T. Vashi, Removal of Congo red dye from its aqueous solution using natural coagulants, J. Saudi Chem. Soc. 16 (2012) 131–136.
[26] M. Sciban, M. Klasnja, M. Antov, B. Skrbic, Removal of water turbidity by natural coagulants obtained from chestnut and acorn. Bioresour. Technol. 100 (2009) 6639–6643.
[27] R. Kumar, M.A. Barakat, Decolourization of hazardous brilliant green from aqueous solution using binary oxidized cactus fruit peel, Bioresour. Technol. 226(15) (2013) 377–383.
[28] S. Vishali, R. Karthikeyan, A comparative study of *Strychnos potatorum* and chemical coagulants in the treatment of paint and industrial effluents: An alternate solution, Separ. Sci. Technol. 49 (2014) 2510–2517.
[29] S. Vishali, R. Karthikeyan, *Cactus opuntia (ficus-indica):* An eco-friendly alternative coagulant in the treatment of paint effluent, Desalin. Water Treat. (2014) 1–9, doi: 10.1080/19443994.2014.945487.