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ORIGINAL PAPER

Zero residual heavy metals in aqueous media using composite coagulant converted from bauxite residue

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Abstract

In this study, an iron–aluminum composite (IAC) coagulant was synthesized from bauxite residue, and its applicability was investigated by harvesting biomass of *Chlorella vulgaris* (*C. vulgaris*). Bauxite residue is not environmentally friendly due to its high alkalinity that could pose a risk for living organisms. In this study, the conversion of the bauxite residue into IAC coagulant was done, which delivered safe utilization of bauxite residue to reduce its deteriorating impact on the environment. The prepared IAC coagulant was characterized by scanning electron microscope, Fourier transform infrared spectroscopy, and ICP-MS (inductively coupled plasma mass spectrometer). Concurrently, the applicability of the IAC was examined by harvesting the biomass of a freshwater microalgae: *C. vulgaris* from culture media. Several parameters (dosage, settling time, pH, biomass concentration, and age of culture) were also optimized to achieve the maximum efficiency of IAC coagulant. It was found that the 0.92 g biomass of *C. vulgaris* can be effectively removed from a liter of culture media by using 0.2 g of IAC in 120 min of contact time, leaving no residual metals (aluminum and iron) in aqueous media. This study showed that IAC coagulant is an efficient coagulant due to simple steps of synthesis, its high efficacy, low dose requirements, relatively short settling time, its integrity with cells, and generating no secondary pollutions.

Keywords Iron–aluminum composite coagulant · Microalgal harvest · Cell integrity · Hazardous waste · Red mud · Secondary pollution

Introduction

Microalgae have received worldwide attention for their potential applications in the production of value-added products, such as pharmaceuticals, steroids, pigments, and biofuels (Skjånes et al. 2012). Besides, microalgae are efficient pollutant scavengers for a broad category of chemicals generated from domestic, industrial, and agricultural sectors through assimilation and breakdown of recalcitrant molecules, e.g., hydrocarbons, antibiotics, hormones, and PPCPs (Hena et al. 2020; Delrue et al. 2016). Remarkably, microalgal technology in wastewater treatment plants, pharmaceutical, cosmetic, food, and biofuels industries is expected to attract more attention in the future. However, the harvesting costs of microalgae remain high due to high energy consumption and expensive and large amounts of coagulant needed (Uduman et al. 2010).

Their small cell size (i.e., ranging from 5 to 50 µm) with negative surface charge enables microalgae to remain stable suspension in culture media, thus preventing an efficient biomass harvesting (Brennan and Owende 2010). Several methods have been developed for harvesting microalgae, all showing advantages and limitations. Centrifugation processes are not advantageous due to the relatively low concentration of biomass (Park et al. 2011). Also, the simultaneous high gravitational and shear forces compromise the cell integrity; therefore, impacting the downstream process

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(Chen et al. 2011). Interestingly, sedimentation under gravitational force is highly energy efficient; however, it is a slow process. Filtration is a promising technology for separating biomass from liquid media; however, processing large volumes of culture is time-consuming and expensive (Harun et al. 2010).

Remarkably, coagulation–sedimentation processes allow microalgae cells to agglomerate via charge neutralization mechanisms, thus forming flocs that induce cells to settle (Chen et al. 2011). The cationic polymers and polyvalent cation coagulants are used to neutralize the negative charges of the microalgae cells. Additionally, low acidic pH and high dosages of costly coagulants are required in most microalgae cell harvesting systems to achieve satisfactory recoveries (Pragya et al. 2013). However, heavy metal salts (i.e., especially aluminum salts) cause cell lysis (Papazi et al. 2009). Regardless of these technical issues associated with coagulation–sedimentation processes, the usage of coagulants is still the most popular due to easy handling and reasonably good performance.

Bauxite residue is a solid waste of aluminum refinery industries generated during the alkaline extraction of alumina from bauxite using Bayer process (Najar et al. 2011). Every 1 ton of alumina generates 1–1.5 ton of bauxite residue, depending upon the origin of bauxite ores (Poulin et al. 2008).

Due to the highly alkaline and corrosive nature of bauxite residue, a lot of research has been conducted globally to find its potential utilization and dealkalization (Luo et al. 2016). Bauxite residue is rich in iron, silicon, aluminum, and calcium (Najar et al. 2011), which are important elements for the production of coagulants.

Nevertheless, an integrated approach to minimize cost, energy consumption, and settling time of commercial coagulants during coagulation–sedimentation processes and reduction in environmental and health-related issues of bauxite residue is of great significance. In this study, the concept of circular economy in waste management is followed. The bauxite residue, which is a hazardous waste to the environment, is proposed as a coagulant source. As a result, iron–aluminum composite coagulant, an efficient coagulant from bauxite residue, has been synthesized, and parameters (dosage, settling time, pH, biomass concentration, and age of culture) for harvesting microalgal biomass from culture media were optimized.

Residual heavy metals in treated water is a serious health concern. Tzoupanos and Zouboulis., 2011 reported 140 µg L^{-1} aluminum in treated water and 1.86 mg aluminum in sludge. The composite coagulant (IAC) prepared in this study caused zero additional Fe and Al in water while 1.83 µg Al and 3.68 µg Fe in 1 g of microalgal biomass. To the best of our knowledge, coagulant causing zero secondary pollution in water has not yet been reported.

It is anticipated that this article would grab the interest of the researchers for further studies over harvestation of different microalgae as a feedstock for biofuel production or pharmaceutical uses due to its low metal residue.

Materials and methods

KBr and HCl were purchased from Sigma-Aldrich, UK. NaOH was purchased from Qrec, New Zealand. All chemicals were analytical-grade reagents.

Pre-treatment of bauxite residue and preparation of aluminum–iron composite coagulant

In this study, the bauxite residue used as the source material to synthesize IAC coagulant was received from the Environment Group, Bauxite Division JNARDDC India, and was supplied by the National Aluminium Company Ltd., Damanjodi, Orissa, India. The bauxite residue showed an alkaline pH of 10 and was pre-treated by crushing and grinding to decrease its grain size into a fine powder (≤ 50 µm). The powdered bauxite residue was washed and dried in an oven at 110 ± 2 °C and kept in a desiccator (Samal et al. 2015). The IAC coagulant from bauxite residue was synthesized by a three-step process (Fig. 1), which included acid leaching, hydrolysis, and polymerization, as follows (Lu et al. 2013).

(a) Acid leaching process: IAC coagulant was prepared by the acid leaching method (Liu et al. 2007), which involves treating 100 mg bauxite residue with 200 mL of HCl (1:2 w/v) of different concentrations, i.e., 1, 2, and 3M, for 5 h. The mixture of bauxite residue and

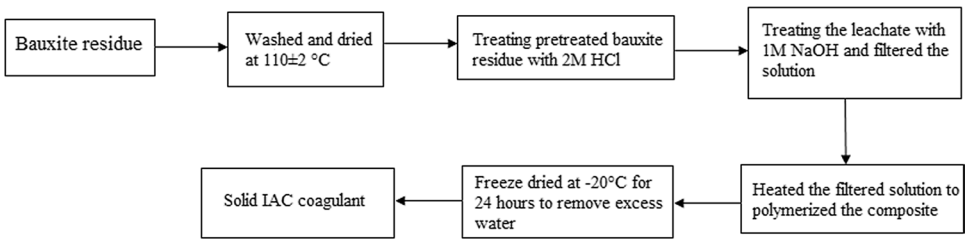

Fig. 1 Flowchart of IAC coagulant production using bauxite residue as a source material

HCl was heated in a water bath at 95 °C, followed by filtration through a 0.45 µm pore size membrane.

(b) Hydrolysis process: A 1M NaOH solution was added dropwise into 4 × 100 mL of filtered liquor (product from step "a") until reaching pH 1.5, 2.0, 2.5, and 3.0, respectively. The resultant solutions were filtered using 0.45 µm pore size membrane (Lu et al. 2013).

(c) Polymerization process: The hydrolysis was followed by polymerization to obtain the IAC coagulant. The chemical equation of the final step was summarized as follows (Zhao et al. 2011):

$$\mathrm{m\ Al_2(OH)_yCl^-_{6-y} + n\ Fe_2(OH)_xCl^-_{6-x}} \rightarrow \mathrm{Al_{2m}Fe_{2n}(OH)_{my+nx}Cl^-_{6m-6y+6n-nx}} \quad (1)$$

The solutions of pH 1.5, 2.0, 2.5, and 3.0 obtained through hydrolysis process were heated in a water bath at 95 °C for 5 h, followed by heating the samples on a hot plate until precipitates were formed. These precipitates (i.e., composite coagulants) were cooled down in a freezer at − 20 °C overnight (~ 14 h) and then freeze-dried for 24 h to ensure the removal of excess water (Lu et al. 2013).

The parameters for IAC coagulant synthesis were optimized based on the efficiency of the synthesized coagulant to coagulate microalgal cells. These efficiencies were calculated by the recovery (%) of *C. vulgaris* biomass, as described in "Coagulation–sedimentation jar experiments" section.

Characterization of bauxite residue and IAC coagulant

XRF (X-ray fluorescence spectrometry) analysis of bauxite residue and IAC coagulant

The elemental compositions of pre-treated bauxite residue before and after the acid leaching process were analyzed by standard test method ASTM E1621-21 using XRF.

SEM analysis of bauxite residue and IAC coagulant

The morphology of bauxite residue samples (before and after the acid leaching process) and IAC coagulant were determined through scanning electron microscopy (SEM, Zeiss EVO/MA 10, Germany). Samples were heated overnight (~ 14 h) at 110 °C in an oven (Binder hot air oven, USA) to completely remove moisture from the samples (Feng and Yang 2018). A small portion of each sample was mounted onto an SEM specimen stub and then coated with gold in a sputter coater (Quorum SC7620, UK) for 10 min to reduce charging effects.

FTIR analysis of IAC and poly-aluminum chloride coagulants

The functional groups of the IAC and poly-aluminum chloride coagulants were determined using Fourier transform infrared spectroscopy (FTIR, Nicolet, Thermo Fisher Scientific, US). The KBr pellet method was used (Castaldi et al. 2008). One milligram of sample was mixed with 99 mg of KBr. The pellet of the mixture was prepared under vacuum applying a force of 7 tons. The resulting pellet was inserted in a standard magnetic pellet holder, followed by the spectra measurement.

ICP-MS analysis of elements (Al and Fe) analysis in IAC and culture media

The elements (Al and Fe) in samples were analyzed by the standard test method ASTM D5673-16 using ICP-MS as described in elsewhere (Alisha et al. 2015).

Microalgae cultivation

A freshwater microalgae *C. vulgaris* UTEX2714 was obtained from the University of Texas at Austin, USA, and maintained in 500 mL flasks containing 250 mL BG11 culture medium (Table 1) at 28 °C. BG11 culture medium was prepared as mentioned earlier by Hena et al. (2020). The culture was exposed to an irradiance of 120 µmol photon m^{-2} s^{-1} and L:D cycle of 12:12 h for 14 days under 1.5% (v/v) CO_2 enriched air at a flow rate of 100 mL min^{-1} with a continuous stirring at 120 rpm in the photo-bioreactor (Model: INFORS HT Minitron). However, the duration of

Table 1 Compositions of BG-11 media in 1L Milli-Q

Chemicals	Weight (mg)
K_2HPO_4	75
KH_2PO_4	175
$MgSO4{\cdot}7H_2O$	75
$NaNO_3$	250
$CaCl_2{\cdot}2H_2O$	25
NaCl	25
$Na_2EDTA{\cdot}2H_2O$	50
$FeSO_47H_2O$ in 0.1 mL H_2SO_4	4.9
H_3BO_3	11.42
$ZnSO_4{\cdot}7H_2O$	1.412
$MnCl_2{\cdot}4H_2O$	0.232
$CuSO_4{\cdot}5H_2O$	0.252
$Co(NO_3)_2{\cdot}6H_2O$	0.08
$Na_2MoO_4{\cdot}2H_2O$	0.192

the culture was longer (i.e., 20 days) to study the effect of the age of the culture on the coagulant efficiency (as mentioned in "Effect of biomass and age of the culture" section). The cultivation was started by inoculating 10% v/v inoculums into media, which corresponded to 0.1 g L^{-1} dry cell weight (DCW) of microalgae. The final maximum microalgal biomass concentration of the replicas was in between 1.50 and 1.55 gL^{-1} DCW for *C. vulgaris* in 14 days. The 14 day-old microalgae cultures were poured in 3 × 50 mL centrifuge tubes and centrifuged (Kuboto 6500, Japan) at 6000 g for 10 min to separate supernatant and pellet. The supernatants were discarded, while serial dilution was performed on the pellets using Milli-Q water (Salim et al. 2011). The optical density (OD) of all the diluted pellets was measured using a UV–Vis spectrophotometer (Hitachi Model U-900). The diluted pellets were separately transferred into 3 × 1.5 mL Eppendorf tubes and allowed to centrifuge at 6000 g for 10 min. The supernatants were discarded, and the pellets in the Eppendorf tubes were dried overnight at 50 °C. The readings of dried pellets were recorded until constant weights were obtained. The absorbance spectra at 680 nm versus DCW were plotted to obtain a biomass standard curve (Supplementary Information S1).

Coagulation–sedimentation jar experiments

The coagulation and sedimentation experiments were conducted by jar test with a 14 day-old culture of microalgae. The beakers were filled with 500 mL of microalgal suspensions of a defined biomass concentration (DCW = 1.0 g L^{-1}). Different amounts of the IAC coagulant were added to the microalgae culture and mixed by stirring at 120 rpm for 2–3 min following by slow mixing (40 rpm) for 10 min and left undisturbed for sedimentation for 120 min. Biomass recoveries were calculated from the absorbance ratio of the clarified solution against the absorbance of a homogenous culture determined at the beginning of the experiment using Eq. (2) (Rashid et al. 2013);

$$\text{Recovery}\% = \frac{\text{ODt0} - \text{Odt}}{\text{Odt0}} \times 100 \quad (2)$$

where Odt_0 and Odt are the optical densities of the sample at time zero and at time *t,* respectively. The absorbance of the supernatant was measured at 680 nm. All experiments were performed in duplicate. The results were presented as mean values with standard deviation. Several parameters were optimized to increase the efficiency of the IAC coagulant, as discussed in the sections below.

Effect of dosage and settling time

The effect of the dosage of IAC coagulant (ranging from 0.1 to 1.0 g L^{-1}) and time of sedimentation (1–150 min) of microalgal biomass during the coagulation–sedimentation process were investigated (Guo et al. 2013) for constant biomass concentration (DCW = 1.0 g L^{-1}) of *C. vulgaris* suspension in 500 mL of volume in a temperature-controlled shaker (25 °C).

Effect of pH

The optimization of the pH based on the efficiency of the coagulant was conducted in two stages, as depicted in Supplementary Information S2. The first stage of the study was performed to estimate the optimum pH of the culture within the range of 1.2–7.6. After adding a fixed amount of IAC coagulant, i.e., 0.9 g L^{-1} (this value was obtained from the experimental section "Effect of dosage and settling time"), the pH of the cultures was adjusted using 0.1M HCl or NaOH. In the second stage of the study, the pH of the culture was maintained at 6.8 using 0.1M HCl or NaOH (Kim et al. 2011; Vandamme et al. 2012) based on the results of stage one. IAC coagulant was added at varied dosages in the range of 0.5–0.1 g L^{-1}. The final pH of the culture was 6.8 (i.e., pH after the coagulation–sedimentation process), where maximum biomass recoveries were attained. Both stages of the study were performed using 500 mL of *C. vulgaris* suspension allowing 120 min for a complete coagulation–sedimentation process.

Effect of biomass and age of the culture

The effect of biomass content on the coagulant efficiency was studied at different biomass concentrations ranging from 2.0 to 0.1 g L^{-1} as DCW. These experiments were conducted using 14 day-old culture of 250 mL of *C. vulgaris* suspension with an optimum IAC coagulant dosage of 0.2 g L^{-1} for 120 min of incubation time at controlled pH 6.8. The age effect of the culture on the efficiency of coagulant was studied using 250 mL culture with the same DCW (1.0 g L^{-1}) of different ages (day 1–20). The cultures of different ages were treated with the same dosage of coagulant (0.2 g L^{-1}) for 120 min of incubation time at controlled pH 6.8 (Granados et al. 2012).

Concentration factor

The concentration factors were determined using 250 mL of microalgal suspensions of defined biomass concentration (DCW = 1.0 g L^{-1}) in 8 × 500 mL beakers. A different amount of IAC coagulant was added in microalgae cultures

and mixed by stirring at 120 rpm for 2–3 min and left for coagulation–sedimentation (Salim et al. 2012). The concentration factors were calculated as the ratio of the heights of the total solution to the interphase (i.e., defined as the interphase between settled biomass and clear solution) as earlier mention in our previous work (Hena et al. 2015).

Integrity status of microalgae cells

The integrity of microalgae cells was determined by the Evans blue (Papazi et al. 2009) method with little modification (Hena et al. 2015). Approximately 1.0 mg of settled biomass of microalgae after the coagulation–sedimentation process was directly treated with 0.1M NaOH solution and centrifuged at 4500 rpm for 10 min to remove the attached IAC particles (if any) and re-suspended the pellets. The process was repeated twice. The final cells' pellet was treated with 100 µL of 1% Evans blue solution and incubated for 10 min at room temperature, then washed twice with Milli-Q water using centrifugation process, and observed under a light microscope.

Comparison of IAC with commercial coagulants

A comparison of efficiencies between IAC coagulant and five commercial coagulants was conducted. The efficiencies were measured in terms of coagulant dosage and settling time. The conditions (pH 6.8, DCW 1.0 g L^{-1}) were kept constant for all five commercial coagulants.

Statistical analysis

All data were analyzed statistically using SPSS Inc. software 20.0 (SPSS Inc, Illinois, USA). Statistical differences between samples were analyzed using one-way analysis of variance. All data presented were means value of duplicate unless stated otherwise. Differences were considered significant at $P < 0.001$ (Supplementary Information S3).

Result and discussion

Despite the intense research and remarkable efforts to reduce the harvesting costs of microalgae, which is very high due to the excess consumption of energy and using large amount of expensive coagulants (Uduman et al. 2010), IAC coagulant was prepared from bauxite residue: an industrial waste is a practical and environmental friendly approach to reduce the costs of microalgae production and processing; simultaneously, this research proposes a strategy of minerals recovery.

Synthesis of IAC coagulant

The IAC coagulant was synthesized from bauxite residue according to the procedures reported on metal leaching from minerals or mineral waste (Piga et al. 1993). The polyvalent metals, such as chloride and sulfate of iron and aluminum, are more effective because of their ability to form multi-charged poly-nuclear complexes (Georgantas and Grigoropoulou 2007). However, the coagulants of polyvalent metals rapidly were hydrolyzed when added to water, and the production of hydrolyzed species from a coagulant in water depends upon the hydrolysis steps of the coagulant during synthesis (Bratby 2006). In this research, leaching–hydrolysis–polymerization method of coagulant synthesis from mineral waste was followed (Zhao et al. 2011). IAC has a positive charge on its hydrolysis species, which attract the negative charge surrounding *C. vulgaris* and eventually form stable flocs. It is anticipated that IAC coagulant dissociates into their poly-hydrated ions forms, such as $Al(H_2O)_6^{+3}$ and $Fe(H_2O)_6^{+3}$ in culture or aqueous media (Lu et al. 2013). The nature of the IAC coagulant produced depends on the pH condition established during the hydrolysis process (Zhao et al. 2011). Besides the hydrolysis step, optimum HCl concentration for maximum heavy metals removal is required during the acid leaching step to improve the coagulation performance of the produced IAC. Therefore, two steps were taken into consideration to optimize the conditions during the synthesis of the IAC coagulant:

i. Alternating HCl concentration during leaching process while keeping the pH of the hydrolysis process constant (Fig. 2)
ii. Varying pH of the hydrolysis process while keeping the HCl concentration constant during the leaching process (Fig. 3)

The effect of different concentrations of (1–3M) HCl on the performance (i.e., biomass recovery) of the synthesized IAC was studied during the acid leaching step while maintaining the hydrolysis pH at pH 2.2.

The IAC prepared using 1M HCl treatment showed lower *Chlorella vulgaris* biomass recovery (i.e., 43.62%) than those of 2M and 3M HCl (i.e., 76.02% and 75.9% biomass recovery, respectively) (Fig. 2). The lower recovery at 1M HCl might be caused by the production of a composite coagulant containing a lower amount of cations to react with

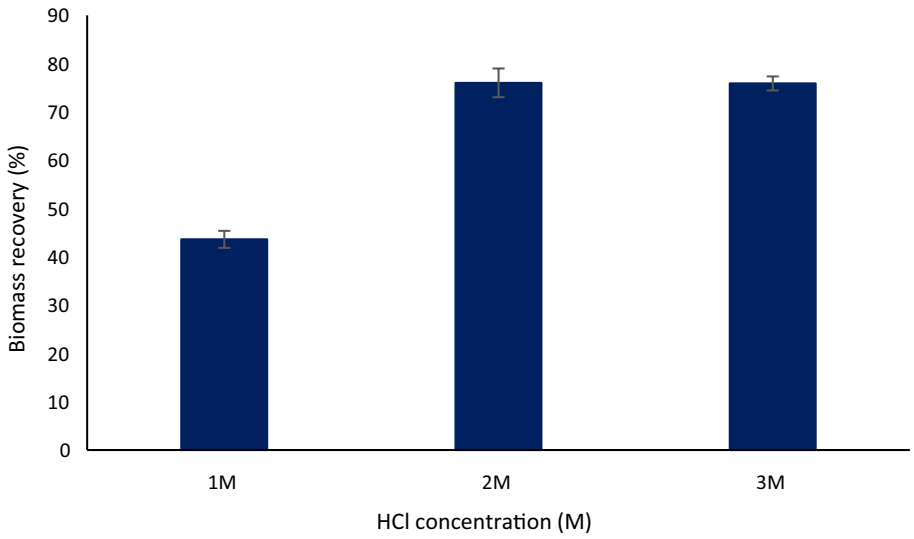

Fig. 2 Effect of HCl concentration during acid leaching step on biomass recovery efficiency of *C. vulgaris*. ANOVA test confirmed that concentration of HCl used during acid leaching step has a significant effect on biomass recovery efficiency as $P < 0.001$

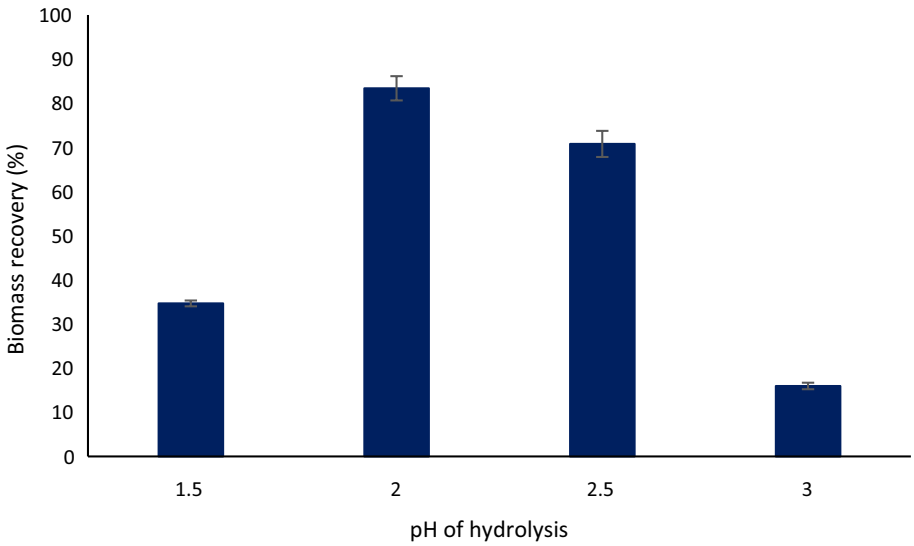

Fig. 3 Effect of pH of hydrolysis during the synthesis of IAC coagulant on biomass recovery efficiency of *C. vulgaris.* ANOVA test showed that pH of hydrolysis used during composite synthesis step has a significant effect on biomass recovery efficiency as $P < 0.001$

Table 2 X-ray fluorescence spectrometry (XRF) analysis of bauxite residue before and after the leaching process

Major compounds	Concentration bauxite residue (% w/w)	
	Before leaching	After leaching
SiO_2	7.10	7.26
TiO_2	4.99	19.14
Al_2O_3	15.45	38.02
Fe_2O_3	52.96	12.45
MnO	0.11	0.11
MgO	0.13	0.28
CaO	2.13	0.06
Na_2O	4.36	0.10
K_2O	0.12	0.34
P_2O_5	0.23	0.08
Cl	–	1.21
Total	87.58	79.05

negatively charged cells through charge neutralization during coagulation. The biomass recovery efficiencies of IAC coagulants produced by treating bauxite residue with 2M and 3M HCl showed no significant difference. Therefore, 2M HCl was selected for the acid leaching step. Almost every metal detected by XRF, as shown in Table 2, has been leached out using HCl. Since aluminum and iron (III) were the most abundant elements in bauxite residue (Song et al. 2010), aluminum chloride and iron chloride were expected as the most abundant in the leachate and the IAC coagulant. The extracted amount of Fe and Al in liquor from red mud were reported as 31.54 /100 mg red mud and 0.07 /100 mg red mud, respectively. The analysis showed that 40.27% w/w of the red mud was undissolved using 2M HCl for leaching process.

The leached liquor containing heavy metals was highly acidic. Therefore, for the hydrolysis process, 1M NaOH

(~0.92M) was added to the leached liquor to increase the initial pH value. The hydrolysis reactions for metal chloride species were represented by iron and aluminum only (Eqs. 3 and 4) since they were present in the highest amount.

$$2FeCl_3 + xH_2O \rightarrow Fe_2(OH)_xCl^-_{6-x} \quad (3)$$

$$2AlCl_3 + yH_2O \rightarrow Al_2(OH)_yCl^-_{6-y} \quad (4)$$

The effects of four different pH values were studied during the hydrolysis step of the IAC coagulant synthesis. Figure 3 shows that increasing the pH of hydrolysis decreased the biomass recovery efficiency of *C. vulgaris*. However, at pH 1.5, the lower efficiency of the IAC coagulant revealed the possibility of incomplete hydrolysis. At pH 2.0, biomass recovery efficiency was the highest at 83.39%, followed by pH 2.5, showing an efficiency of 70.79%. Nevertheless, pH 3.0 showed the lowest biomass recovery efficiency at 15.96%. Thus, pH 2.0 was selected to synthesize the IAC at a large scale.

Instrumental analysis and characterization of bauxite residue and IAC coagulant

Bauxite residue is classified as a complex material due to the variation of its chemical composition. The common major elements found in bauxite residue are oxides of iron, aluminum, silicon, calcium, titanium, and sodium; however, the % of the composition always varies depending upon the origin of the bauxite residue. The Indian bauxite residue contained 52.96% w/w Fe_2O_3, followed by 15.45% w/w of aluminum oxide, which was slightly different from the material obtained from the Birac Alumina Industry (Eastern Bosnia, Serbia) with 48.5% w/w of Fe_2O_3 and 14.14% w/w Al_2O_3 (Cabllk 2007). The XRF and SEM analyses of the bauxite residue after pre-treatment and leaching processes were performed to identify their properties, composition (i.e., major elements), and the morphology of their surface structure.

XRF analysis of bauxite residue

Results for XRF analysis (Table 2) showed that the Indian bauxite residue consisted of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, CaO, Na_2O, MnO, MgO, K_2O, and P_2O_5. The data confirmed that iron oxide was predominant with 52.96% w/w, followed by 15.45% w/w of aluminum oxide. The total percentage of major elements found in the bauxite residue (before acid leaching) was 87.58%. Remarkably, the remaining minor elements could not be traced by this analysis. The XRF analysis of bauxite residue samples after the leaching process demonstrated the extraction of Fe_2O_3, CaO, Na_2O, and P_2O_5 from bauxite residue to acid liquor (Zhao et al. 2011).

SEM analysis of bauxite residue and IAC

The morphology of the bauxite residue before and after the leaching process was observed under SEM (7.5 mm focal distance × 2.00 K magnification, scale = 1 µm), as shown in Fig. 4a, b, respectively. The morphology of bauxite residue showed various shapes and surfaces. The brightness of the surface indicated that bauxite residue incorporated negative charges (Postek and Vladar 2015). Figure 4b shows that after the leaching process, the pretreated bauxite residue became

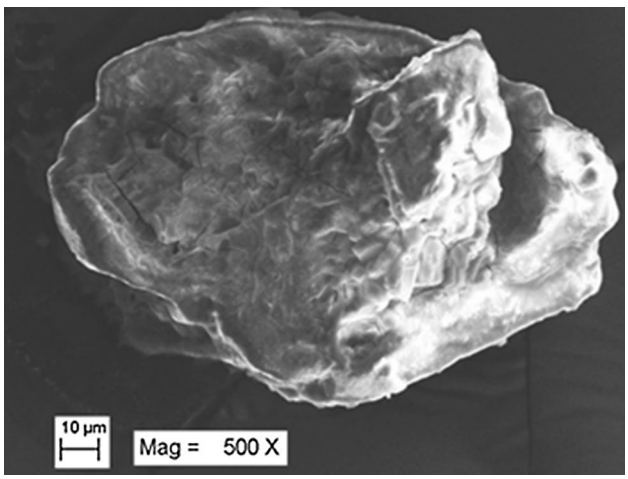

Fig. 5 Scanning electron micrograph of IAC coagulant

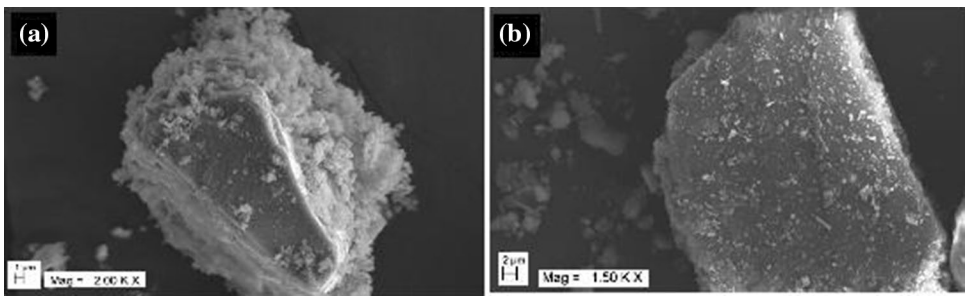

Fig. 4 Scanning electron micrograph of bauxite residue (**a**) before and (**b**) after leaching

darker with a smoother surface. This observation confirmed that the leaching process removed metals and induced charge neutralization (Postek and Vladar 2015).

The morphology of the synthesized IAC showed smoother surfaces compared to the bauxite residue (Fig. 5). The smoothness of the surface would be induced by the presence of hydroxyl groups generated during the hydrolysis process (Postek and Vladar 2015). The excess water was removed during the freeze–drying process as the structure showed cracks on the surface of the IAC coagulant.

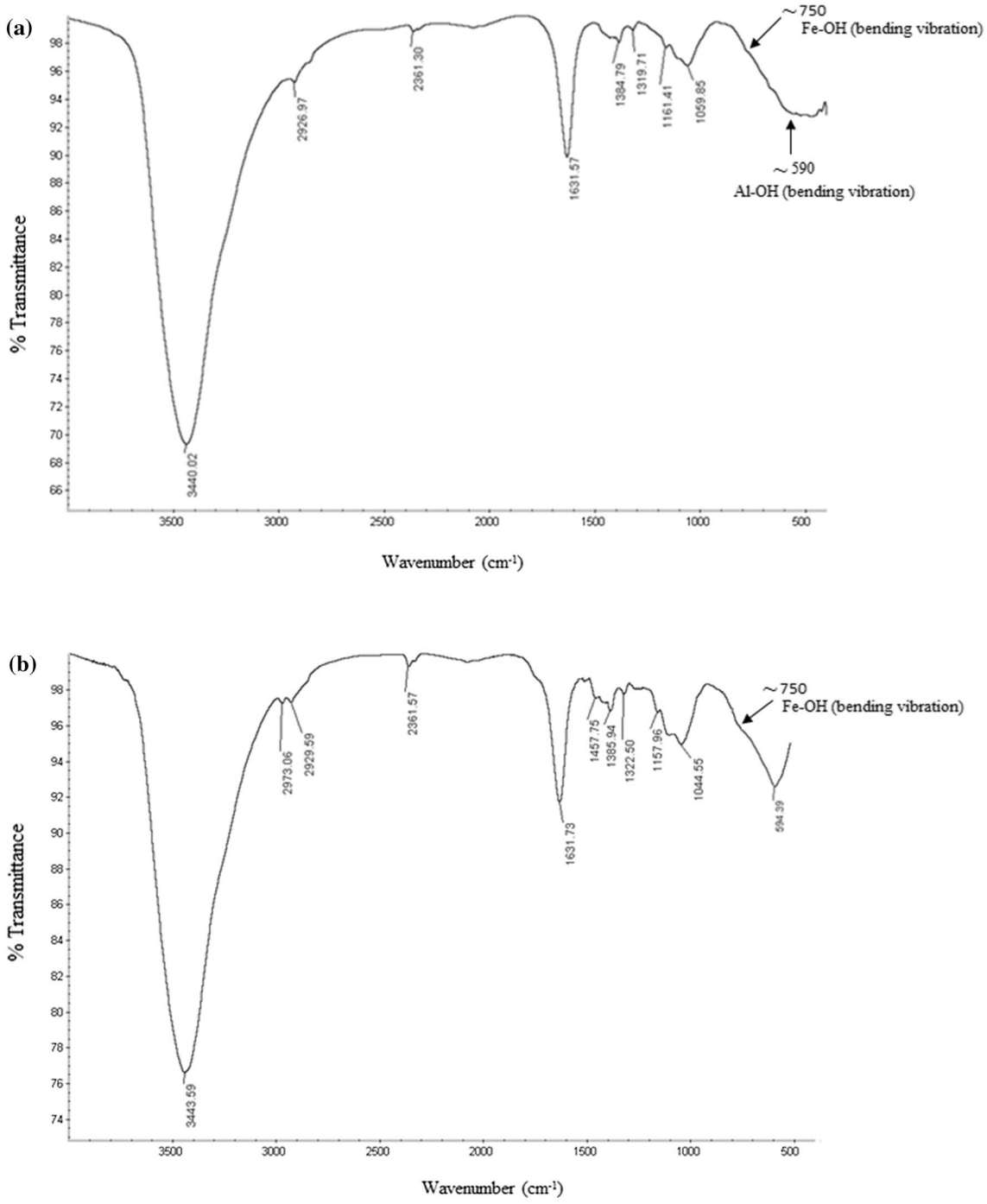

Fig. 6 FTIR spectra of (**a**) IAC and (**b**) PACl. A minute bending vibration peak of Fe–OH for IAC and PACl and a broad peak of Al–OH for IAC have been located manually, referring to the literature of Sun et al. (2011)

FTIR analysis of IAC and comparison with poly-aluminum chloride (PACl)

Fourier transform infrared spectroscopy (FTIR) was used to detect the functional groups present in the synthesized IAC and compare its composition with commercially available PACl. The FTIR spectrum of IAC and commercially available PACl are depicted in Fig. 6a, b, respectively. The broad and strong absorption peaks present at 3440.02 cm^{-1} and 3443.59 cm^{-1} were assigned to the O–H stretching vibration for IAC and PACl, respectively, indicating the presence of hydroxyl groups. The absorbance peak of the hydroxyl functional group (H-bonded) usually appears in the range of 3500–3200 cm^{-1}. The peak observed at 1631.57 cm^{-1} corresponds to the bending vibration of water absorbed during polymerization and crystallization process in IAC synthesis, while, in PACl, the same peak appeared at 1631.73 cm^{-1}. Meanwhile, the peak at 1059.85 cm^{-1} and 1044.55 cm^{-1} for IAC and PACl, respectively, was attributed to the asymmetric stretching vibration of Fe-OH-Fe or Al–OH-Al (Fang et al. 2007; Tzoupanos and Zouboulis et al. 2011). Peaks at ~ 750 cm^{-1} for IAC and PACl were attributed to bending vibrations of Fe–OH, which reflected that the commercial PACl contained iron as an impurity. A broad peak at ~ 590 cm^{-1} and 594.39 cm^{-1} for IAC and PACl was identified as bending vibrations of Al–OH.

ICP-MS analysis of heavy metals in IAC

The ICP-MS analysis confirmed that the proposed IAC coagulant contained only 8.4 ppm aluminum and 16.9 ppm iron as elements (Table 3).

Table 3 ICP-MS analysis of Al and Fe in IAC

Sample	Heavy metals	
	Al (ppm)	Fe (ppm)
IAC	8.44	16.99

Evaluation and optimization of parameters for harvesting microalgal biomass using IAC coagulant

In this section, the efficacy of IAC was evaluated by using it for harvesting the biomass of *C. vulgaris* from culture aqueous media. The coagulation process is one of the harvesting processes applied to recover microalgae biomass. The IAC coagulant synthesized in this research was studied for its coagulation/flocculation properties to remove microalgal cells. The positive charges on the IAC would attract the negative charges on the *C. vulgaris* surface and form stable flocs (Hena et al. 2020). Once charges were neutralized, electrostatic repulsion between cells is weakened, and thus, the inter-particle repulsion is reduced (Ahmad et al. 2011). Vandamme et al., (2013) reported that at high pH (i.e., above the isoelectric point), microalgae could also settle via sweeping flocs enmeshment.

Influence of the IAC dosage under uncontrolled pH condition

To obtain comparable results, all experiments were performed at the same initial biomass concentration of 1.0 g L^{-1} as DCW and the same sedimentation time (120 min). Experiments showed no sedimentation improvement above 120 min (Supplementary Information S4). The dosage of coagulant is one of the most important factors affecting the extent of biomass recovery. To identify the optimum dosage

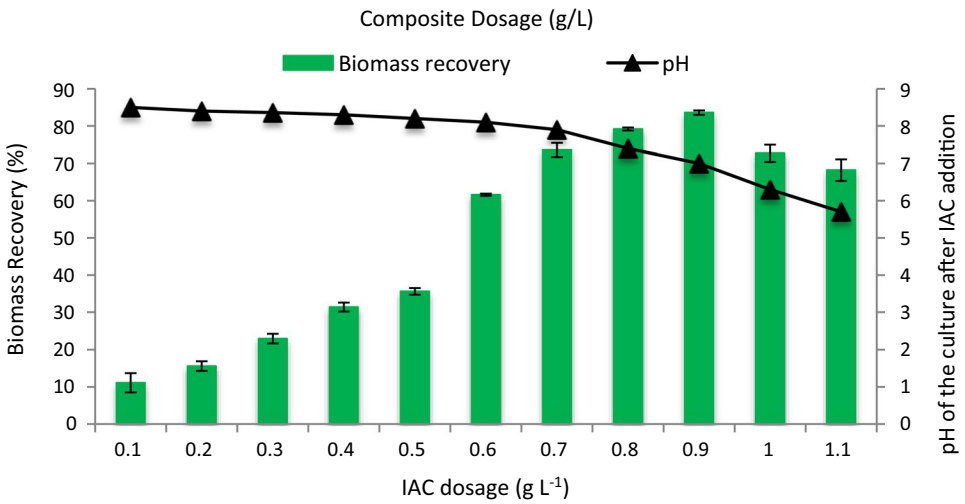

Fig. 7 Effect of different dosages of IAC on biomass recovery (%) of *C. vulgaris* with a defined biomass concentration weight of 1.0 g L^{-1}; 120 min sedimentation time. The culture of *C. vulgaris* was 14 days old. The final pH of the system varied with the IAC dosage, as shown on the secondary Y-axis

of IAC for *C. vulgaris* biomass recovery, experiments were conducted with doses ranging from 0.1 to 1.1 g L^{-1} IAC. The results plotted in Fig. 7 indicated that the optimum dosage of the IAC was 0.9 g L^{-1} with 83.6% of biomass recovery at pH 7. Coagulant dose and pH are the main parameters controlling the efficiency of the coagulation/flocculation process. In the case of IAC and other iron and aluminum salts, the addition of coagulant leads to a decrease in pH (Lewis acid); the higher the dose, the more pronounced the pH decrease (i.e., pH variation also depends on the buffer capacity of the treated solution). In Fig. 7, the lower biomass recovery at a dosage below 0.9 g L^{-1} might be caused by either insufficient amount of coagulant or high pH, while the low biomass recovery at a dosage above 0.9 g L^{-1} could be due to acidic pH or an excess coagulant dosage leading to charge re-stabilization and dispersion. To confirm the optimum pH condition for IAC, another set of experiments was conducted under constant IAC dosage, i.e., 0.9 g L^{-1} and varying coagulation pH ("Influence of the IAC coagulant dose for a fixed pH 6.8" Section).

Influence of pH for a fixed IAC coagulant dose (0.9 g L^{-1})

The efficiency of IAC for biomass recovery of *C. vulgaris* was tested under controlled pH conditions (pH 1.2–7.6) for a fixed coagulant dose (0.9 g L^{-1}) and a sedimentation time of 120 min (Fig. 8).

As expected, at low pH 1.2–3.6, biomass recovery efficiencies were relatively low (less than 20%) and slightly increased to 25.6% at pH 4.4. Significant improvements were recorded at higher pH 5.2–6.8, with biomass recoveries ranging from 83.7 to 87.7%. Lower biomass recovery (i.e., 69.1%) was observed at higher pH (i.e., 7.6). It is evident from Fig. 8 that the IAC coagulant can efficiently work under a wide range of pH, i.e., 5–7. Such optimum pH range (pH 5–7) is commonly observed for the coagulation/flocculation of dissolved natural organic matter and particles in water treatment processes operated using ferric and aluminum salts. Charge neutralization (i.e., neutralization of negatively charged microalgae cells by positively charged metal hydroxides) and adsorption onto the formed flocs are the two mechanisms involved in the removal process (Vandamme et al. 2013; Gonzalez-Torres et al. 2014). Aluminum sulfate was used for *Scenedesmus* sp. and *Chlorella* sp. harvesting via charge neutralization mechanism (Grima et al. 2003). Papazi et al. (2009) reported harvesting of *Chlorella minutissima* using ferric chloride and aluminum sulfate by surface charge neutralization mechanism. Gonzalez-Torres et al., (2014) recorded pH 6 and 7 as optimum pH conditions for harvesting *Microcystis aeruginosa* using aluminum sulfate and ferric chloride, respectively, which is comparable to the optimum pH of the current study.

Influence of the IAC coagulant dose for a fixed pH 6.8

From previous results, pH 6.8 was selected as the optimum coagulation/flocculation pH for harvesting *C. vulgaris* from the culture suspension. The optimization of the IAC coagulant dosage was studied under IAC doses ranging from 0.1 to 0.5 g L^{-1} and controlled pH 6.8 adjusted with 0.1M HCl during the coagulation step. The sedimentation time was maintained for 120 min. The results are depicted in Fig. 9. A maximum 0.92 g L^{-1} biomass of *C. vulgaris* was recovered (i.e., 92% of the total biomass), using 0.2 g L^{-1} IAC at pH 6.8 ± 0.1.

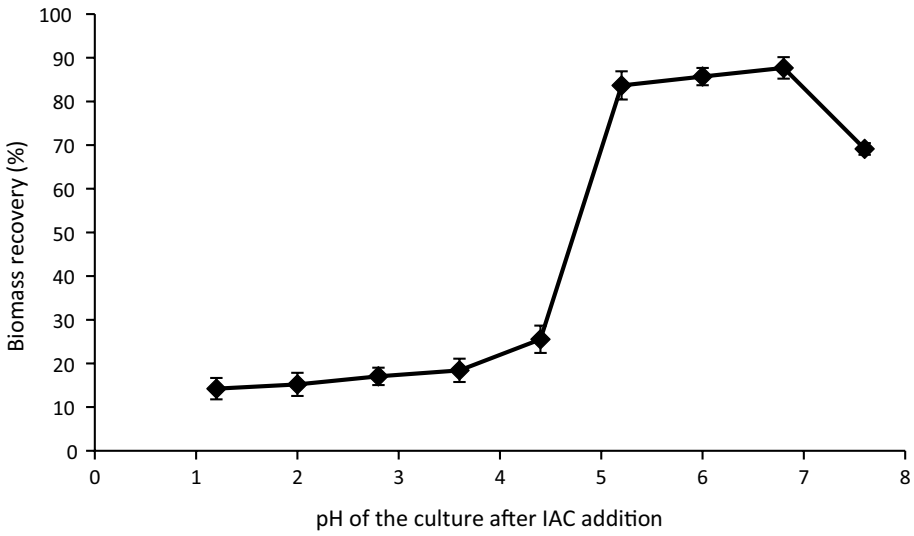

Fig. 8 Effect of the pH of the culture on biomass recovery (%) of *C. vulgaris* with 0.9 g L^{-1} IAC; 120 min sedimentation time. The final pH of the cultures was adjusted from 1.2 to 7.6 by adding 0.1 M HCl or 0.1 M NaOH after IAC addition

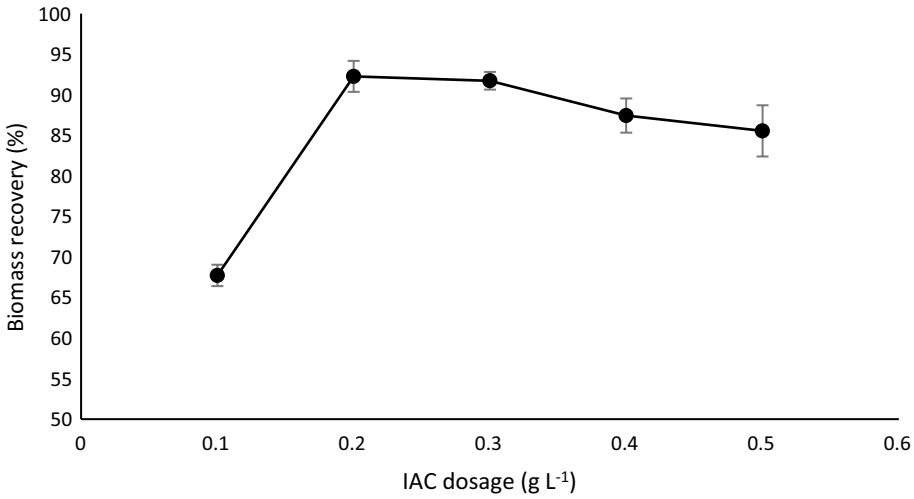

Fig. 9 Effect of the pH of the system (maintained at pH ~ 6.8) on the percentage of biomass recovery (%) of *C. vulgaris* with a defined biomass concentration weight of 1.0 g L^{-1}. The culture of *C. vulgaris* was 14 days old

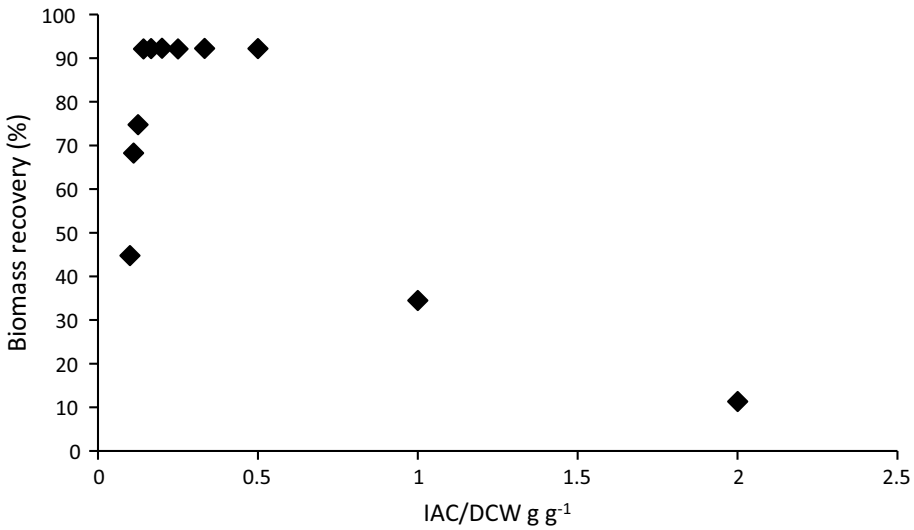

Fig. 10 Biomass recovery (%) of *C. vulgaris* as a function of relative applied IAC doses (IAC/DCW g g^{-1}) under predetermined optimum conditions (0.2 g L^{-1} IAC; 120 min sedimentation time; controlled pH 6.8). The culture of *C. vulgaris* was 14 days old

The pH of the pure culture on day 14 was 8.7, which was significantly higher than the optimum pH 6.8. The IAC was acidic in nature; hence, its addition caused a decrease in pH of the culture. Earlier, 0.9 g L^{-1} IAC was needed (Fig. 7), because the pH was uncontrolled (pH 8.7) and the optimum pH 6.8 was achieved by the acidic nature of the IAC. The IAC could only effectively coagulate the biomass once the optimum pH was attained by the additional IAC. While in controlled pH condition (optimum pH) the pH of the culture was maintained at 6.8 by adding 0.1M HCl in culture media, which cut off the additional dosage of IAC. It is anticipated that the main reason for the dosage to drop from 0.9 (Fig. 7) to 0.2 g L^{-1} (Fig. 9) was to attain the optimum pH of culture by using 0.1M HCl or 0.1M NaOH.

Effect of biomass content and age of the culture

Another set of experiments was performed at a fixed IAC dose of 0.2 g L^{-1} with varying biomass concentrations from 0.1 to 2.0 g L^{-1} DCW and under controlled pH 6.8 and 120 min sedimentation time. Biomass recoveries (%) as a function of relative IAC doses (IAC/DCW g g^{-1}) are provided in Fig. 10.

The biomass recovery was maximum at moderate relative IAC doses ranging from 0.14 to 0.5 g g^{-1} (IAC/DCW). However, at lower ($\leq$0.12 g g^{-1}) and higher ($\geq$ 1 g g^{-1}) relative IAC doses, the biomass recoveries (%) were lower than those of the moderate relative IAC doses. At lower relative IAC doses, the biomass recovery (%) was lower due to the

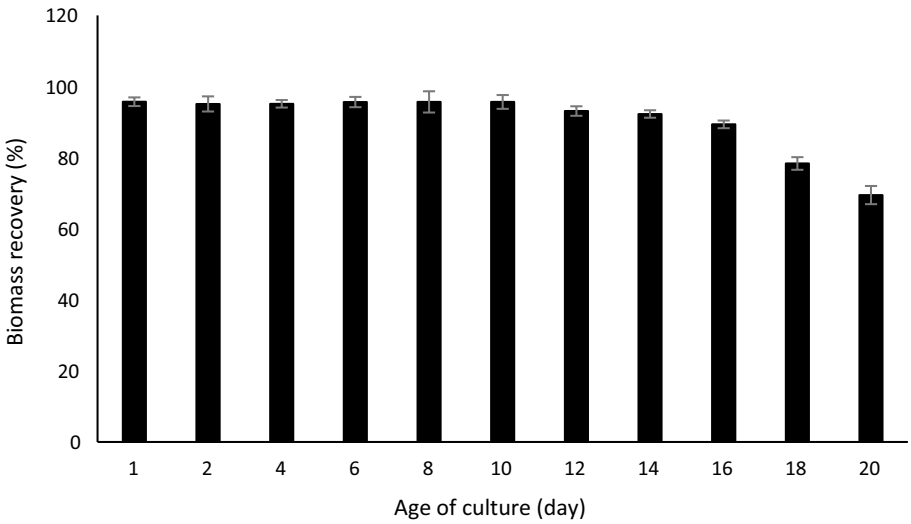

Fig. 11 Effect of the age of the culture on biomass recovery (%) of *C. vulgaris* under predetermined optimum conditions (0.2 g/L IAC; 120 min sedimentation time; controlled pH 6.8). The defined biomass concentration weight was 1.0 g L^{-1}

insufficient amount of IAC used to neutralize the negative charges of microalgae. Nevertheless, at higher relative IAC doses, the biomass recovery (%) was lower due to the excess of net positive charges of IAC, thus causing re-stabilization and dispersion among the microalgae cells. Normally, the coagulation–flocculation processes of most of the microalgal cultures are operated between 0.5 and 2.5 g L^{-1} (Granados et al. 2012); hence, no more major optimization would be required for IAC to harvest the microalgae.

In general, the production of biomass increased with the age of the microalgal culture until the stationary phase is reached. During the exponential growth and stationary phase of growth, the microalgae produce exo-polymeric substances (EPS). EPS are described as a matrix of biopolymer substances primarily incorporating polysaccharides, and a significant amount of proteins and lipids (Bellinger et al. 2010). EPS would also interact with the IAC coagulant to neutralize the charges. To test this hypothesis, the experiments were conducted by keeping the biomass constant (expressed as DCW) for cultures of different ages (days). Until day 16, the IAC (constant dosage) efficiency remained constant; this efficiency started to decrease significantly after day 16 and reached 69.5% on day 20 (Fig. 11). This decrease was due to the production of negatively charged EPS by *C. vulgaris*. Some of the IAC coagulants were consumed by the EPS, thus inducing a lower efficiency and a decrease in the biomass recovery (%) of *C. vulgaris*.

Concentration factor

The concentration factor is a parameter used to evaluate the degree of compactness of harvested biomass (Salim et al. 2012). This factor is expressed as the ratio of the

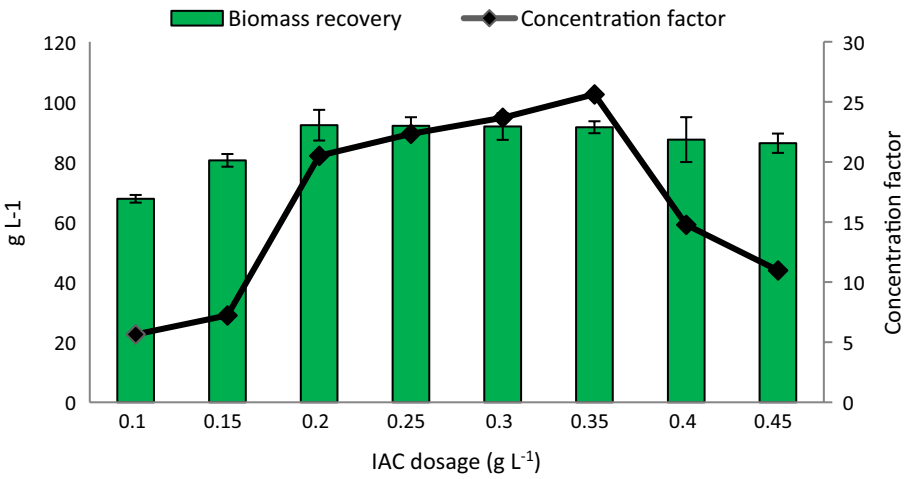

Fig. 12 Effect of different dosages of IAC on biomass recovery (%) and concentration factor of *C. vulgaris* under 120 min sedimentation time; controlled pH 6.8. The defined biomass concentration was 1.0 g L^{-1}

heights of the total solution to the interphase (i.e., defined as the interphase between settled cells and clear solution) after the coagulation–sedimentation process. Thus, the concentration factor allows a reduction in the equipment size necessary for biomass dewatering (Rashid et al. 2013). This parameter clearly depended on the IAC dose and was measured at various IAC dosages. Interestingly, before IAC addition, no interphase was observed in microalgae culture, and the concentrations were homogenous throughout the culture. When the IAC coagulant was added, flocs or aggregation of microalgal biomass started forming within 30 min, and interphase was clearly observed 100 min after the addition of the IAC coagulant. The interphase height decreased with time and became constant in 120 min after the addition of IAC. As depicted in Fig. 12, the variations in the height were directly proportional to the dosage of the coagulant. Data in Fig. 9 showed that for *C. vulgaris,* 0.2 g L^{-1} IAC coagulant was optimum to achieve the highest biomass recovery as 92.2%, while the concentration factor was reported as 20.5. The concentration factor further enhanced by almost 25% with an increase of coagulant (0.35 g L^{-1}), although the biomass recovery was almost the same compared to 0.2 g L^{-1} dosage (i.e., the decrease in biomass recovery was less than 1%). These results revealed that although the biomass was coagulated and settled down, the negative charges on microalgal cells were probably not completely neutralized by the IAC. Excess IAC (up to 0.35 g L^{-1}) compressed the settled biomass of *C.vulgaris* due to further neutralization of the negative charge. The successful settlement of microalgal biomass before complete neutralization of charges reflected the flocculation mechanism of the IAC coagulant, specifically, formed mesh-like structures binding to two or more negatively charged coagulated suspended particles which entrapped microalgal cells eventually increase their mass and settle down. Hence, IAC behaves as a flocculant-like PACl (Li et al. 2019). However, both biomass recovery and concentration factor decreased significantly when IAC dosage was increased above 0.35 g L^{-1}. The results indicated that overdosing of IAC coagulant resulted in dispersion and charge re-stabilization. Similar results were obtained by other researchers (Zheng et al. 2012). These analytical data reflected that IAC coagulants were attached or adsorbed onto the surface of the microalgae cells, thus resulting in surface charge neutralization and inducing a decrease in surface potential. Eventually, the adsorption of coagulant on the surface of microalgal cells beyond the point of charge neutralization caused charge reversal and re-stabilization or re-suspension of microalgae cells, as depicted in Fig. 13.

Integrity of the cell of *C. vulgaris* after application of IAC coagulant

In general, most of the microalgal cells get disrupted during the harvesting process and thus affected the downstream processing (Zheng et al. 2012; Hena et al. 2015). To assess the impact of IAC coagulant on *C. vulgaris* cells, the coagulated cells were observed using a light microscope. Supplementary Information S5 shows the integrity of the *C. vulgaris* cells after harvesting with IAC. Briefly, the broken cell wall of microalgae appeared blue because of the diffusion of Evans blue solution into the cytoplasm (Hena et al. 2015). However, in the current study, *C. vulgaris* did not show any blue stain, therefore supporting IAC as a safe and appropriate coagulant for microalgal biomass recovery.

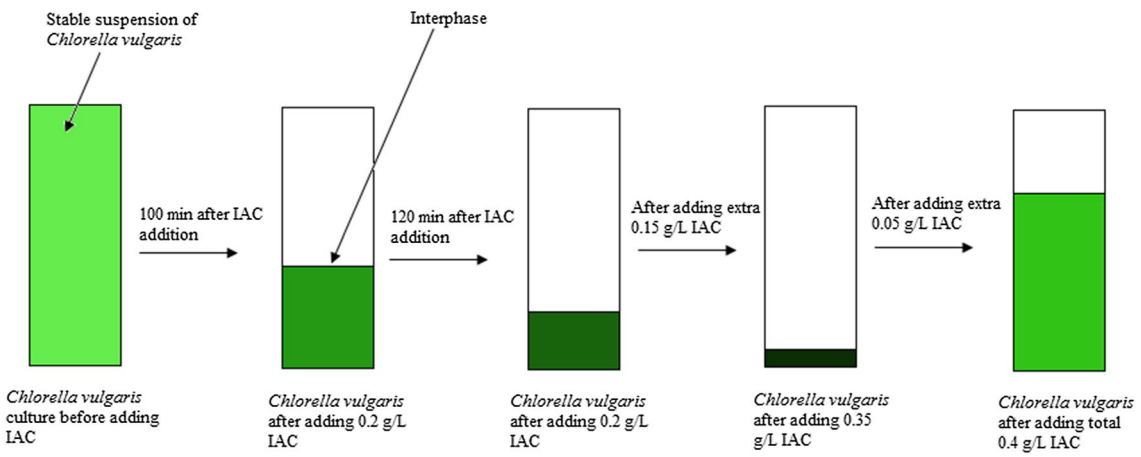

Fig. 13 Schematic diagram of the degree of compactness of harvested biomass of *C. vulgaris*

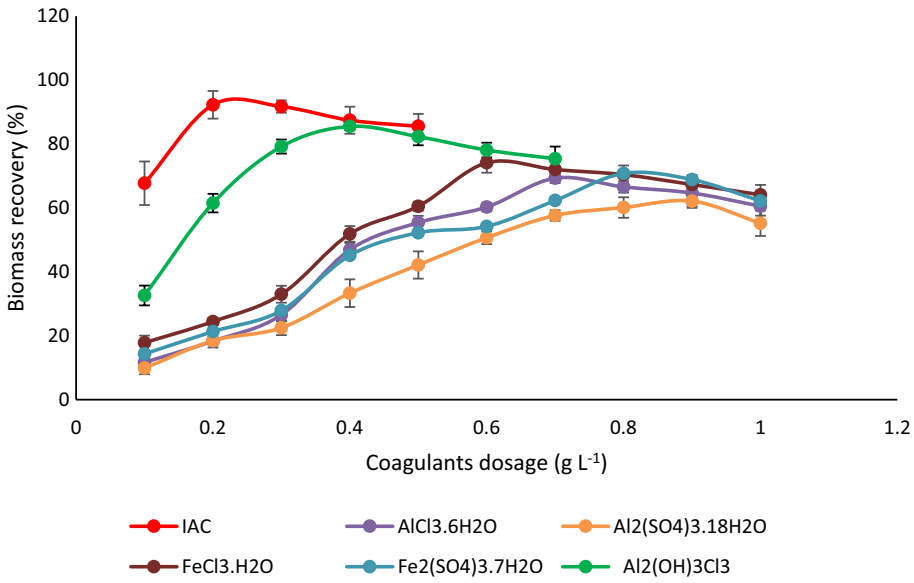

Fig. 14 Comparison of IAC and commercial coagulants on biomass recovery (%) of *C. vulgaris* under controlled pH 6.8. The defined biomass concentration weight was 1.0 g L^{-1}

Table 4 Metal residue in recovered biomass of *C. vulgaris* after the coagulant–sedimentation process

Coagulants	Residual metals
$AlCl_3{\cdot}6H_2O$	112.5 mg/g; (Al^{+3}/DCW)
$Al_2(SO_4)_3{\cdot}18H_2O$	117.7 mg/g; (Al^{+3}/DCW)
$Al_2(OH)_3Cl_3$	119.4 mg/g; (Al^{+3}/DCW)
$FeCl_3{\cdot}H_2O$	249 mg/g; (Fe^{+3}/DCW)
$Fe_2(SO_4)_3{\cdot}7H_2O$	240 mg/g; (Fe^{+3}/DCW)
IAC	1.83 µg/g; (Al^{+3}/DCW), and 3.68 µg/g; (Fe^{+3}/DCW)

$Al_2(OH)_3Cl_3$ is poly-aluminum chloride

Comparison between IAC and commercial coagulants

The performance of the synthesized IAC and five commercial coagulants ($FeCl_3{\cdot}H_2O$, $Fe_2(SO_4)_3{\cdot}7H_2O$, $AlCl_3{\cdot}6H_2O$, $Al_2(SO_4)_3{\cdot}18H_2O$ and $Al_2(OH)_3Cl_3$) was compared in terms of the recovery of *C. vulgaris* biomass at controlled pH 6.8 and the same initial biomass concentration of 1.0 g L^{-1} as DCW. The coagulation–sedimentation experiment for each coagulant was continued until the biomass recovery became stable. Among all tested coagulants, the synthesized IAC coagulant from bauxite residue exhibited the highest efficiency 92.3% (0.2 g L^{-1}) in terms of recovery of biomass in 120 min settling time, followed by ferric salts: $FeCl_3{\cdot}H_2O$ and $Fe_2(SO_4)_3{\cdot}7H_2O$ achieved 74.1% (0.6 g L^{-1}) and 70.8% (0.8 g L^{-1}) biomass recovery in 200 min settling time, while $AlCl_3{\cdot}6H_2O$, $Al_2(SO_4)_3{\cdot}18H_2O$ and $Al_2(OH)_3Cl_3$ (poly-aluminum chloride) showed 69.3% (0.7 g L^{-1}), 62.1% (0.9 g L^{-1}) and 85.5% (0.4 g L^{-1}) biomass recovery in 250 min, respectively (Fig. 14). The data within the parentheses represented the dosage of coagulants required to achieve the maximum biomass recovery. Ferric salts evidenced better efficiencies than aluminum salts; however, their usage is not recommended for harvesting microalgae because ferric salts interfere with the microalgal metabolites (Perreault et al. 2010). Generally, aluminum salts caused microalgal cell disruption, which affects downstream processing, especially if the purpose of harvesting is to obtain cellular metabolites (Zheng et al. 2012; Papazi et al. 2009). Aluminum salts are a risky option for recovering microalgal biomass after wastewater treatment due to their ability to damage the cell integrity. Besides, a large amount of commercial coagulants are needed for recovering microalgal biomass; their use causes a high concentration of residual metals (1–2 mg/g aluminum in *Nannochloropsis salina* biomass) concentrations in harvested biomass (Vandamme et al. 2013), which eventually hinders the extraction of metabolites. The comparison between the estimated metal residues of aluminum and iron in recovered biomass of *C. vulgaris* using IAC and commercial coagulants is shown in Table 4. The residual metals (aluminum and iron) in the recovered biomass of *C. vulgaris* using IAC was more than 60,000-fold lower than commercial coagulants (Table 4).

Table 5 Comparison between the biomass removal efficiency of IAC with other coagulants

Coagulant	Microalgae	Dosage	Sedimentation time (min)	Biomass removal (%)	References
Alkyl-grafted chitosan Fe_3O_4–SiO_2	*Chlorella vulgaris*	0.013 g L^{-1}		90	Tran et al. (2013)
Chitosan	*Thalassiosira pseudonana*	20 mg L^{-1}	10	90	Han et al. (2016)
Extracted *Moringa oleifera*	*Chlorella vulgaris*	8 mg L^{-1}		76	Behera and Balasubramanian (2019)
Tannin	*Oocystis* sp.	5 mg L^{-1}		80	Barrado-Moreno et al. (2016)
$Fe_2(SO_4)_3$	*Chlorella minutissima*	0.75 g L^{-1}	240	80	Papazi et al. (2009)
$Al_2(SO_4)_3$	*Chlorella minutissima*	0.75 g L^{-1}	120	80	Papazi et al. (2009)
AlCl3	*Chlorella minutissima*	0.5 g L^{-1}	60	80	Papazi et al. (2009)
FeCl3	*Chlorella minutissima*	0.5 g L^{-1}	180	80	Papazi et al. (2009)
$Al_2(SO_4)_3$	*Chlorella vulgaris*	2.5 g L^{-1}		91.9	Zhu et al. (2018)
Chitosan	*Chlorella vulgaris*	0.25 g L^{-1}		92.4	Zhu et al. (2018)
$Fe_2(SO_4)_3$	*Scenedesmus spinosus*	1.5 g L^{-1}		61.6	Reyes and Labra (2016)
IAC	*Chlorella vulgaris*	0.2 g L^{-1}	120	92	This study

After coagulation–sedimentation process, heavy metals leach out from settled biomass or sludge back into the water (Tzoupanos and Zouboulis 2011). Tzoupanos and Zouboulis (2011) reported 140 µg/L residual Al in treated water, which was within the range of recommended limit set by WHO (0.2 mg L^{-1} Al).

In this study, the concentrations of Fe and Al in culture aqueous media were analyzed before the addition of IAC and after the coagulation–sedimentation process was over using 0.2 g L^{-1} IAC in 120 min. The concentrations of Fe were 0.47 ± 0.02 mg/L and 0.46 ± 0.03 mg/L before the addition of IAC and after coagulation process, respectively, while Al was not detected before and after the process. This results attributed that IAC does not cause any secondary pollution, and its use is effectively safe for environment.

The FTIR study of IAC and PACl revealed the compositional similarity due to which IAC can be associated with the inorganic polymer coagulant. IAC recovered more biomass in half of the dosage of PACl. Simultaneously IAC has shown shorter settling time and lesser metal residue than PACl. It is attributed that the better performance of IAC over PACl is due to the presence of the polymers of both aluminum and iron (Lu et al. 2013). High dosage of commercial coagulants leads to higher amount of metal residue in recovered biomass and filtered culture media. The filtered culture media after biomass recovery either reused for microalgal culture or discharged into water bodies after proper treatment. Generally higher amount of residual metal in recovered biomass causes leaching of residual metal back in the culture media, which degrades the quality of water and imposed an extra step to be involved before discharging the treated culture media (Lu et al. 2013). The total aluminum and iron element present in IAC dosage used for 1 L of culture media to harvest microalgal biomass are far less (1.83 µg L^{-1} Al and 3.68 µg L^{-1} Fe) than the recommended limit set by WHO (0.2 mg L^{-1} Al and 10 mg L^{-1} Fe) for drinking water. Hence, IAC coagulant does not impose any significant threat to human health and living organisms. Concurrently, the lower concentration of aluminum and iron in IAC coagulant overcome the problems associated with ferric and aluminum salts coagulants such as metabolite interference and loss of cell integrity, respectively, without compromising the efficiency of coagulant.

The microalgal biomass removal capacity of IAC was compared with other coagulant reported in the literature and is shown in Table 5. Chitosan, extracted *Moringa oleifera* and Tannin are biopolymers that exhibit higher efficiency than inorganic coagulants (Beltrán-Heredia et al. 2012). Natural organic coagulants require less dosage to remove

biomass from aqueous media due to its excellent polymeric structure (Rashid et al. 2013). However, IAC is found to have a relatively lower dosage requirement comparing other inorganic coagulant to remove 92% of biomass, and this indicates that it can be considered a promising inorganic composite coagulant for the removal of biomass from aqueous media or for water treatment.

Conclusion

This study associated with the conversion of an industrial waste: bauxite residue into a coagulant, is a waste to worth paradigm. The IAC coagulant synthesized from bauxite residue showed a remarkable potential for high biomass recoveries from microalgae culture and caused no residual heavy metal in water, providing an environmentally friendly process for biomass recovery. The low dose requirements, relatively short settling time, high concentration factors, and cell integrity of microalgae are significant advantages of IAC over many other frequently used coagulants. The optimum conditions to harvest 0.92 g of biomass of *C. vulgaris* cells from its culture biomass concentration of 1 g/L (DCW) needed 0.2 g/L IAC at pH 6.8 in 120 min. This study showed that IAC could be a promising coagulant for removing microalgal biomass after phycoremediation of wastewater or even from eutrophic ponds.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s13762-022-04336-z.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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