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# Removal of heavy metals from tannery effluent using chitosan-g-poly(butyl acrylate)/bentonite nanocomposite as an adsorbent

R. Nithya and P. N. Sudha\*

## Abstract

In the present era, due to industrial revolution in the developing countries like India, the ground water system has been largely polluted. Tannery effluent is a major source of aquatic pollution, and a large number of tanneries are scattered all over India particularly in Tamilnadu, Uttar Pradesh and West Bengal. This work deals with the removal of heavy metals chromium and lead and the reduction of the important physicochemical parameters like total dissolved solid (TDS), total suspended solid (TSS), total solids (TS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total hardness, salinity, turbidity and electrical conductivity from the tannery wastewater by using chitosan-g-poly(butyl acrylate)/bentonite nanocomposite as an adsorbent. The batch system was used to conduct the biosorption experiments. The influence of different experimental parameters, such as contact time, pH and amount of adsorbent, was evaluated. The results showed that the prepared nanocomposite can be used efficiently for the treatment of tannery wastewater containing heavy metals.

**Keywords:** Tannery effluent, Physicochemical parameters, Heavy metal, Chromium, Lead

## Background

Due to the rapid growth of tannery industries and pollution-provoking factories, it has become mandatory to realise the perilous reactions of toxic organic compounds and heavy metal ions in the water resources and take drastic steps to remove such pollutions from water to save mankind and environment. It was found that the pollutions caused by Lead and Chromium are found to be very crucial and need to be removed, failure of which would cause very baneful effects. Hexavalent chromium, due to the presence of mutagenic and carcinogenic properties, causes liver damage, pulmonary congestion, edema and skin irritation, resulting in ulcer formation (Raji and Anirudhan 1998). The World Health Organization (WHO) has recommended a maximum level of 0.05 mg/l of Cr (VI) in drinking water (Bhaumik et al. 2011) and 0.1 mg/l in surface water (Guidelines for Drinking-Water Quality 2006). The liver, kidney and

reproductive system are affected severely by the toxic effect of lead, so also, the basic cellular processes and functions of the brain get negatively affected (Kushwaha et al. 2012). According to the WHO, the maximum permissible limit of lead for drinking water is 3–10 µg/l (Needleman 1999) and 0.1 mg/l for inland surface water.

Currently, biopolymers are industrially attractive because of their capacity to bind transition metal ions and are environmentally safe. One among the biopolymers is chitosan, a linear polysaccharide, composed of glucosamine and *N*-acetyl glucosamine units linked by  $\beta$  (1–4) glycosidic linkage. It has emerged as one of the low-cost adsorbents for the removal of heavy metals and dyes. Though it is affordable in terms of cost and is non toxic, it is strongly pH dependent and very much susceptible to biodegradation (Mi et al. 2002; Ravi Kumar 2000), thus limiting its practical use as adsorbent. Hence, chemical modification by grafting (Mishra et al. 2008; Srivastava et al. 2009) is one of the promising techniques to improve the physicochemical properties and stability of chitosan.

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**Table 1** Initial parameters of tannery wastewater

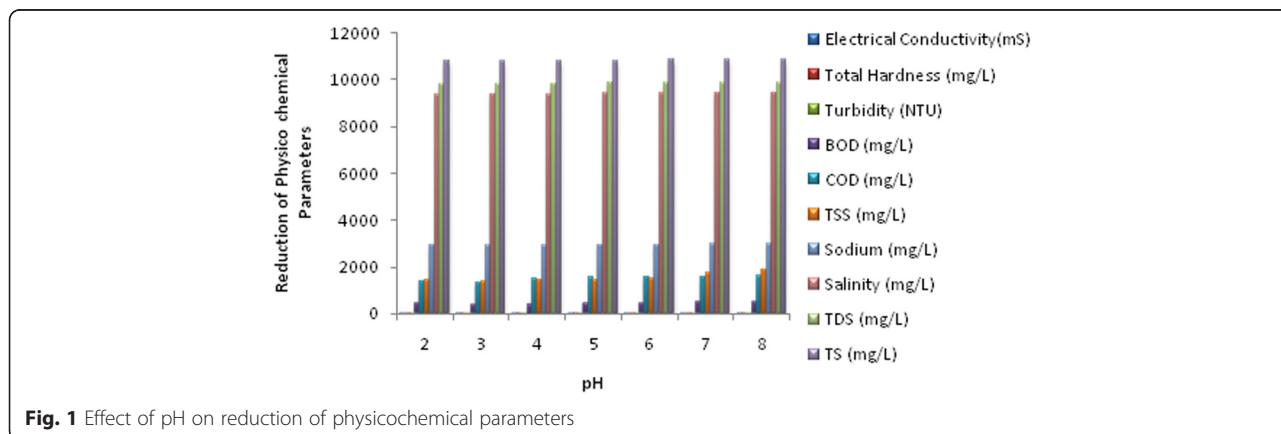
Parameters	Raw effluent collected	Maximum tolerance limits for industrial effluents discharged (mg/l)	
		Into inland surface water	Into public sewers
<b>Physical parameters</b>			
Colour	Blackish colour	Colourless	–
Odour	Disagreeable smell	Odourless	Unobjectionable
pH	7.43	5.5–9.0	5.5–9.0
<b>Chemical parameters</b>			
Electrical conductivity (EC) (mS/cm)	27.3	0.288	–
Biochemical oxygen demand (BOD) (mg/l)	1250	30	350
Chemical oxygen demand (COD) (mg/l)	4210	250	–
Total dissolved solids (TDS) (mg/l)	15,900	2100	2100
Total solids (TS) (mg/l)	31,740	2200	–
Total hardness (TH) (mg/l)	923	600	300
Turbidity (NTU)	453	10	5
Sodium (mg/l)	5000	–	60
Chromium (Cr) (mg/l)	1055	0.1	2.0
Lead (Pb) (mg/l)	0.43	0.1	1.0

Values expressed are as per the regulations given by (1) ISI standards for disposal of industrial wastewater. BIS (IS: 10500: 1991) and (2) Central Pollution Control Board. (1986), *Pollution Control Acts, Rules, and Notifications* issued there under. Fourth edition pp. 358–359. New Delhi, CPCB, Ministry of Environment and Forests. 897 pp

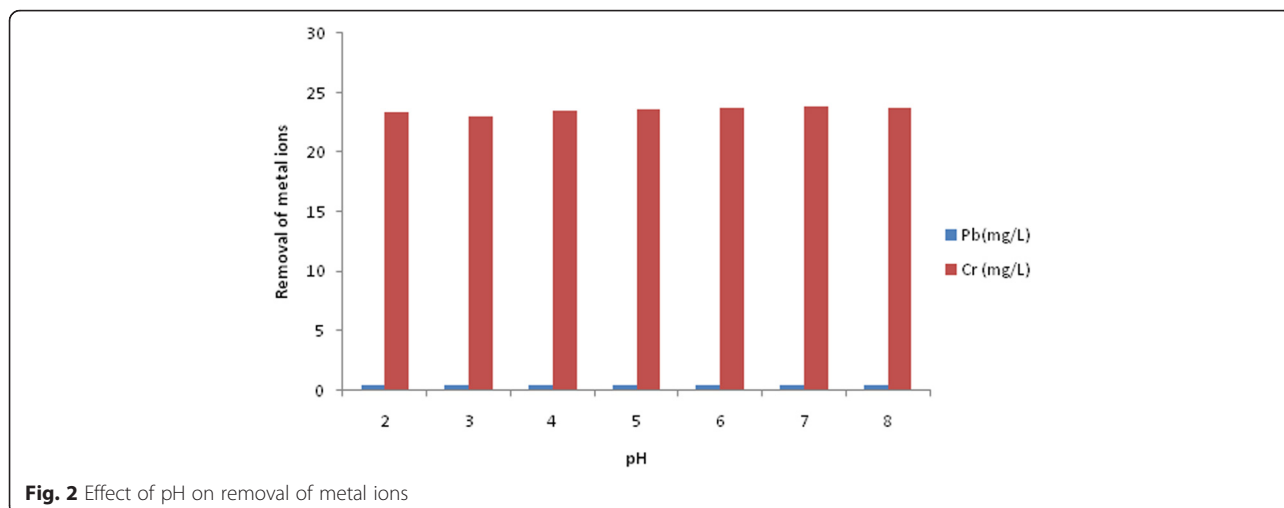
The syntheses of organic–inorganic polymeric materials have gained much attention recently for the removal of heavy metals from the wastewater because of their low cost, high mechanical resistance (Thambiannan et al. 2013; Junping et al. 2007) and effective adsorption of dyes (Mouzdahir et al. 2010). Bentonite is one of the most popular clay rocks with exceptional adsorption properties due to its large surface area (Schütz et al. 2013). It is a type of alumino silicate in the ratio of 2:1; its unit layer consists of one Al<sup>3+</sup> octahedral sheet between two Si<sup>4+</sup> tetrahedral sheets. However, negatively charged surface and large amount of exchangeable cations make natural bentonite highly hydrophilic, and its surface is covered with a layer of water, blocking, in part, its adsorption capability for organic pollutants. Moreover, it swells and form very stable colloidal suspension when it comes into contact with

water, which causes the solid–liquid separation very difficult after adsorption (Wang et al. 2014). Hence, bentonite can be used as fillers in various polymer matrices to prepare nanocomposites because the functional groups of bentonite such as SiAOASi can interact strongly with functional groups in polymer matrices such as AOH, ANH<sub>2</sub>, ACOOH and *N*-acetyl glucosamine units (Darder et al. 2005). A different composite with chitosan has been done by several researchers (Vanamudan et al. 2014; Abdel Khalek et al. 2012; Thayyath Sreenivasan Anirudhan et al. 2010).

The objective of this work is to use the novel adsorbent, chitosan-grafted-poly(butyl acrylate)/bentonite nanocomposite (Cs-g-PBA/bent) which is so far not known as reported for the removal of heavy metal Cr(VI) and Pb(II) ions from the industrial effluent rather than other



**Fig. 1** Effect of pH on reduction of physicochemical parameters



**Fig. 2** Effect of pH on removal of metal ions

physicochemical parameters. But, the other physicochemical parameters are used to check the validity of Cs-g-PBA/bent nanocomposite for the removal of Cr(VI) and Pb(II) in a tannery industry wastewater.

## Methods

### Materials

Chitosan (CS) (degree of deacetylation = 95 % determined by <sup>1</sup>H-NMR and molecular weight 13.45 × 10<sup>4</sup> Da) was purchased from India Sea Foods, Kerela, India. Ceric ammonium nitrate was purchased from Thomas Baker pvt Ltd. Acetic acid and glutaraldehyde was purchased from Sisco Research laboratories Pvt Ltd. Bentonite was purchased from Aryem chemicals, Chennai.

### Methods

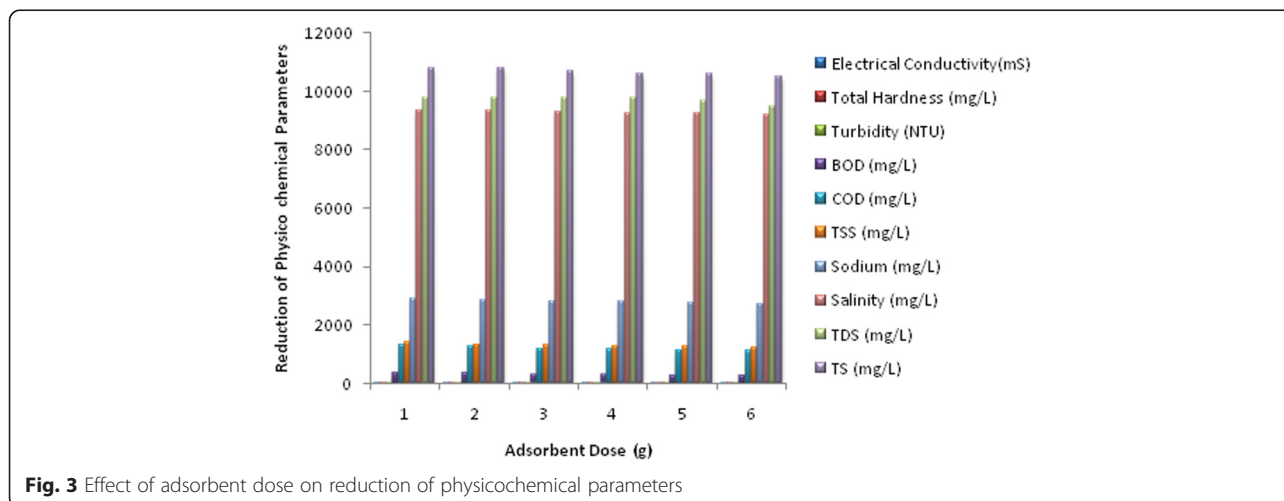
#### Preparation of chitosan-g-poly(butyl acrylate)

A known amount of chitosan (0.5 g) was dissolved in a known volume (30 ml) of 2 % aqueous acetic acid. *N*-

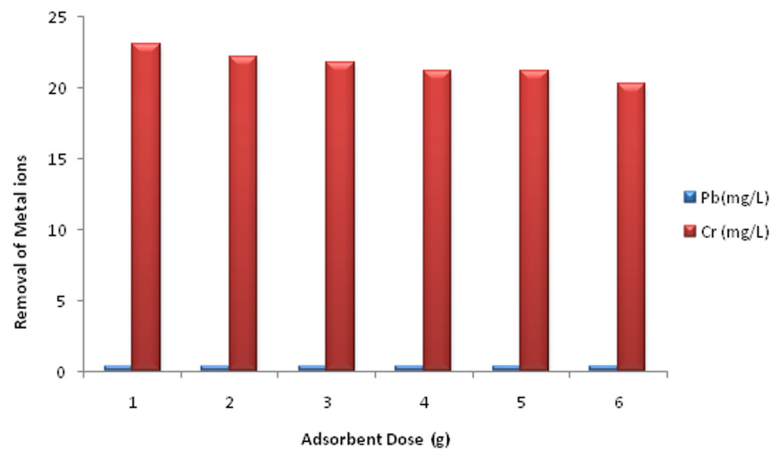
Butyl acrylate (0.6 ml dissolved in 20 ml ethanol) was added, and then, a freshly prepared solution of ceric ammonium nitrate (CAN) in 1 N nitric acid was added drop by drop with continuous stirring for 30 min. The reaction was stopped, and the product was precipitated using 2 N sodium hydroxide solution with vigorous stirring. The precipitate was washed with distilled water for several times and filtered.

#### Synthesis of chitosan-grafted poly (butyl acrylate)/bentonite (Cs-g-PBA/bent) nanocomposites

Bentonite powder (bent) was heated at 110 °C for 1 h to activate the surface. A known amount of bentonite (1 g) was immersed in distilled water to make a slurry. About 1 g of poly(butyl acrylate) grafted chitosan was dissolved in (5 %, v/v) acetic acid. This solution was then added to the slurry and the mixture was stirred for 30 min. Five millilitres of 25 % glutaraldehyde was then added and stirred vigorously for 5 min. The mixture was stirred and soaked in an ultrasonic bath for 30 min. The



**Fig. 3** Effect of adsorbent dose on reduction of physicochemical parameters



**Fig. 4** Effect of adsorbent dose on removal of metal ions

temperature of the dispersion was at room temperature (25 °C). This mixture was then washed with water and dried in oven at 50 °C to get Cs-g-PBA/bent powder. By analysing the powder with DLS method, the particle size was found to be 679.3 nm, and hence, this powder would be more suitable for sorption studies.

**Batch adsorption experiments**

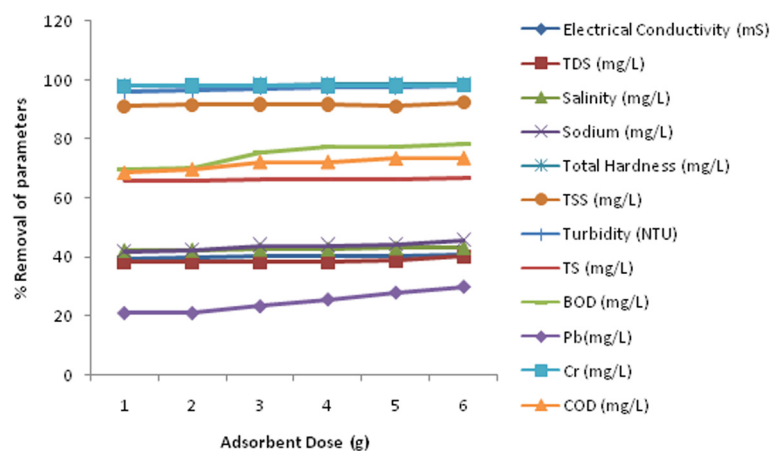
The batch adsorption experiments were conducted in 250-ml conical flasks containing 100 ml of tannery wastewater using 1 g of Cs-g-PBA/bent nanocomposite adsorbent. The flasks were agitated in an orbit shaker at room temperature. Effect of initial pH was studied by varying solution pH from 2 to 8 at the sorbent dosage of 1 g/100 ml for 1 h contact time. The pH of wastewater was adjusted by using 0.1 N HCl or 0.1 N NaOH. The effect of contact time and adsorbent dose on the sorption capacity of sorbent was studied in the range 1–6 h and 1–6 g. After the period, the solution was filtered using Whatman filter paper no. 42 and the filtrate was

analysed for physicochemical parameters and heavy metals chromium and lead. The adsorption removal percentage of various physicochemical parameters and heavy metals in a tannery industry wastewater was calculated by using the following formula:

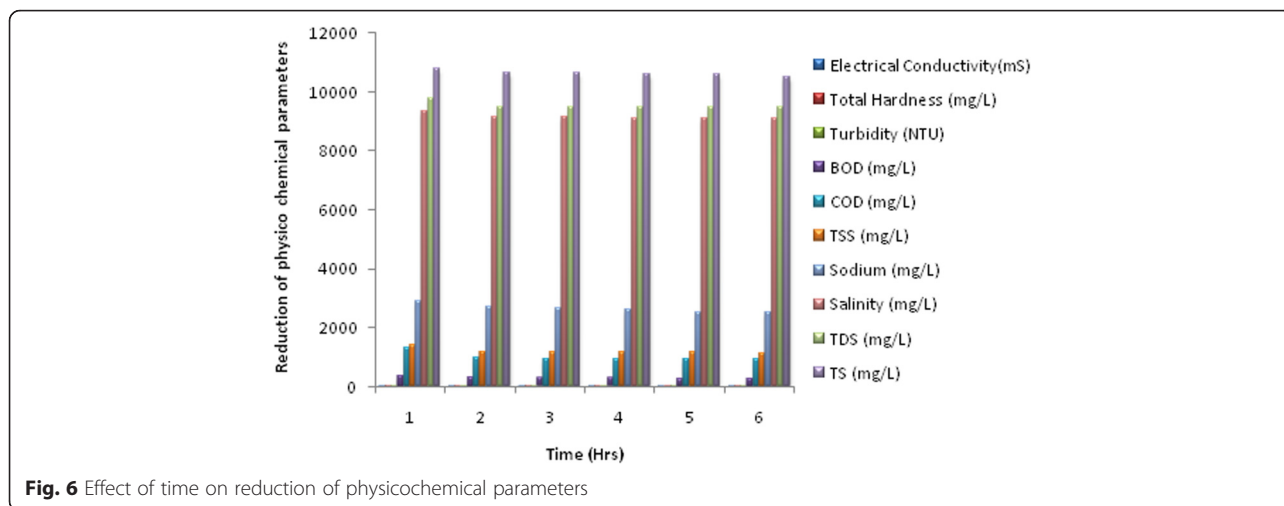
$$\% \text{Removal} = \frac{\text{initial concentration} - \text{final concentration}}{\text{initial concentration}} \times 100 \tag{1}$$

**Collection of sample**

The sample was collected from Ranipet (Ranipettai) a suburban town, which is a major industrial area located in Wallajah taluk, Vellore district, Tamil Nadu, at 79° 19'–79° 22' E longitude and 12° 53'–12° 57' N latitude and is situated 114 km west of Chennai. More than 200 tannery industrial units were located in and around this town. It is one of the biggest exporting centres of tanned leather in India and discharging their effluents on the



**Fig. 5** Effect of adsorbent dose on removal percentage (%) of some physicochemical parameters



open land and surrounding water bodies (Govil et al. 2004). This sample was collected in a plastic container and kept in the refrigerator at 4 °C, and the effluent was used for the experiment for the next day of sample collection.

**Physicochemical study**

The samples thus collected were analysed for total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total hardness, salinity, turbidity, electrical conductivity and presence of heavy metals like chromium and lead. The techniques and methods followed for analysis and interpretation of physicochemical parameters are those given by APHA (1995) and heavy metals by atomic absorption spectroscopy.

**Results and discussion**

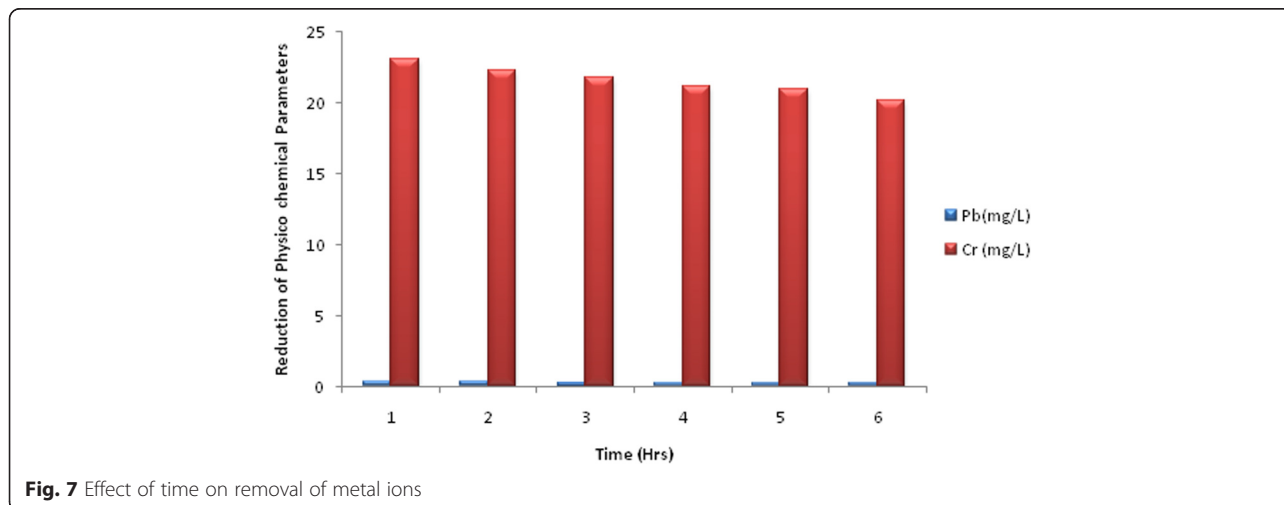
The mean values for each parameter of the wastewater revealed that most of them were beyond the standard

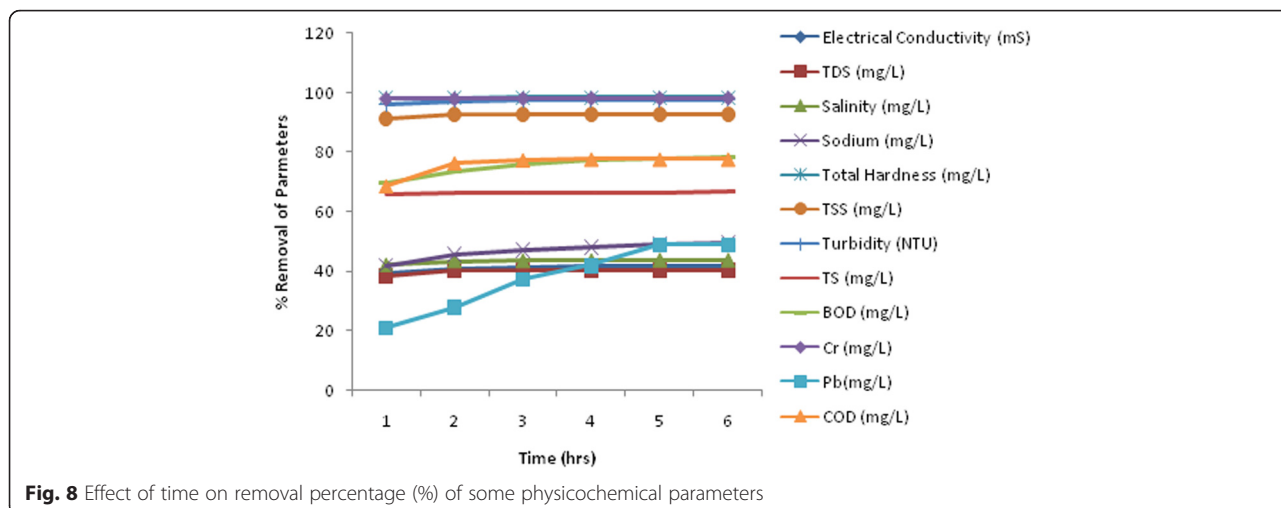
provisional limit provided by ISI (1991), CPCB as shown in Table 1.

**Effect of pH**

pH is the most important factor that affects the adsorption process. The effect of pH of tannery effluent on adsorption was investigated from pH 2–8 (Figs. 1 and 2). It was found that the reduction of physicochemical parameters and heavy metal ions were higher at low pH. This was due to the fact that low pH causes surface OH<sup>-</sup> groups to accept protons, facilitating ligand exchange since H<sub>2</sub>O is an easier ligand than OH<sup>-</sup> to get displaced from metal bonding sites, and hence, low pH promotes anion adsorption (Dessalew D. Alemayehu et al. 2012).

In other words, at low pH, a large number of hydrogen ions can neutralise the oppositely charged surface and thus enhance the electrostatic attraction between the adsorbent and adsorbate overcoming electrostatic repulsion between them (Vasanthy and Lakshmana Perumalsamy 1995). Moreover from the literature, at low pH, the





spontaneous reduction of Cr(VI) into Cr(III) also occurred due to high redox potential (1.3 V), and hence, chromium(VI) has been removed up to 97 % (Bhaumik et al. 2012; Karthik and Meenakshi 2014). Lead showed a minimal of 21 % removal efficiency, and this may be due to intervention of other ions which were also present in the effluent. The optimum pH 3 was selected for further experiments.

**Effect of adsorbent dose**

The effect of adsorbent dose was studied by varying dosage from 1–6 g with the optimum pH 3 (Figs. 3 and 4). With the increase of adsorbent dose, the reduction of physicochemical parameters and the removal of heavy metal ions increased up to 5 g. This was due to the increased available binding sites in the nanocomposite for the complexation of metal ions (Saravanan et al. 2013). Equilibrium was almost attained after 5 g of adsorbent dosage as a result of decrease in available sites in the adsorbent. The maximum removal percentage (%) obtained in 5 g of dose for all parameters is shown in Fig. 5. The highest removal efficiencies for different chemical parameters achieved were 78 % (BOD), 73 % (COD), 91 % (TSS), 39 % (TDS), 98 % (Cr), 99 % (total hardness), and 28 % (Pb), 40 % (electrical conductivity), 43 % (salinity), 45 % (sodium), 66 % (TS) and 98 % (turbidity).

**Effect of time**

The effect of contact time on the reduction of physicochemical parameters was determined by varying time from 1–6 h (Figs. 6 and 7) at pH 3. The dependency of removal efficiency of some physicochemical parameters on reaction time is shown in Fig. 8. The highest removal efficiencies for different chemical parameters achieved were 77 % (BOD), 78 % (COD), 93 % (TSS), 41 % (TDS), 98 % (Cr), 98 % (total hardness), and 42 % (Pb), 42 %

(electrical conductivity), 44 % (salinity), 48 % (sodium), 67 % (TS) and 98 % (turbidity).

The reduction efficiency increased rapidly till 240 min. There was no significant change in equilibrium concentration after 240–360 min since the adsorption phase reached equilibrium. A faster initial removal rate was possibly due to the availability of sufficient vacant adsorbing sites in the adsorbent. Afterwards, the rate of removal decreased significantly due to availability of limited vacant adsorption sites (Sivakami et al. 2013).

**Table 2** Physical and chemical characteristics of the untreated and treated effluent

Parameters	Untreated effluent	Treated at pH 3
Physical parameters		
Colour	Blackish colour	Colourless
Odour	Disagreeable smell	Odourless
Chemical parameters		
Electrical conductivity (mS/cm)	27.3	16.6
Biochemical oxygen demand (BOD) (mg/l)	1250	380
Chemical oxygen demand (COD) (mg/l)	4210	1320
Total dissolved solids (TDS) (mg/l)	15,900	9800
Total solids (TS) (mg/l)	31,740	10,800
Total hardness (TH) (mg/l)	923	16
Salinity (mg/l)	16,200	9360
Turbidity (NTU)	453	18
Sodium (mg/l)	5000	2900
Chromium (Cr) (mg/l)	1055	23.05
Lead (Pb) (mg/l)	0.43	0.34

### Comparison of treated effluent with the raw effluent

The comparative study for some effluent quality parameters of the raw effluent and the treated effluent is presented in Table 2 where the treated effluent was mentioned at pH 3. The concentration of total chromium drops down from 1055 to 23.05 mg/l with a removal of 97.81 % of chromium, and hence, it is obvious that a chromium concentration has been reduced to a large extent by using Cs-g-PBA/bent nanocomposite. The concentration of lead was reduced from 0.43 to 0.34 mg/l with a removal percentage of 20.93 %. Electrical conductivity was also decreased to 39.19 % and cannot be reduced to a greater extent as observed in the case of chromium concentration. This might be due to some ionic species which do not get precipitated (Sabur et al. 2013). The initial value of COD was 4210 mg/l, and after treatment, it was decreased to 1320 and the percentage removed is 68.64 %. BOD was reduced from 1250 to 380 mg/l. TSS was removed to 91.16 % and TS to 65.97 %. Turbidity was removed from 453 to 18 NTU.

### Conclusions

Though tannery is an indispensable industry for the economic and social growth of a country, the fact that the wastewater generated by these industries gets directly discharged into the nearby water body with insufficient treatment is alarming. Most of the physicochemical parameters investigated in this study showed that almost all the effluent characteristics were above the provisional discharge limit set by ISI. In the present study, experiments have been conducted for the removal of Cr(VI) and Pb(II) from the tannery industrial wastewater using Cs-g-PBA/bent nanocomposite as an adsorbent. To know the ability of Cs-g-PBA/bent, the experiments were conducted with varying adsorbent dosage, contact time and pH.

The results showed that the maximum removal percentage of Cr(VI) in the tannery industrial wastewater at an optimum adsorbent dosage of 5 g, contact time of 240 min and pH of 3 was 97.81 %. Also, the resultant maximum removal percentage of Cr(VI) in tannery industry wastewater with optimum processing parameters was verified with the other physicochemical parameters of BOD, COD, total hardness, TDS, TSS, TS, salinity, turbidity, electrical conductivity and sodium in the tannery industry wastewater. Further, it was understood that the various pollutants of tannery wastewater like hexavalent chromium, total hardness, TSS and turbidity were reduced to the maximum extent of satisfaction with a comparatively economical absorption process. As this process is promising, it can be concluded that chitosan-g-poly (butyl acrylate)/bentonite nanocomposite is more effective for removal of heavy metals and reduction of concentration of physicochemical parameters from the tannery effluent.

### Competing interests

The authors declare that they have no competing interests.

### Authors' contributions

PNS and RN contributed to the conception and design of the study. RN carried out the experiments, analysed the data and drafted the manuscript, and PNS supervised the works. Both authors read and approved the final manuscript.

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