ORIGINAL CONTRIBUTION



Biosorption of Chromium and Lead from Electroplating Industry Effluent Using Modified Cane Bagasse

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Abstract The biosorption capacity of cane bagasse for the discharge of chromium and lead from the Electroplating industry effluent was investigated. The batch biosorption method was applied to get the optimum initial ion concentration, dosage, agitation time, and pH for the adsorption of Cr and Pb metals. The maximum percentage removal of chromium was obtained with the optimum conditions of initial metal ion concentration—5 mg/l, dosage—0.5 g, agitation time - 40 min. and pH-5. Similarly, for lead, the optimum conditions were initial metal ion concentration-5 mg/l, dosage—0.6 g, agitation time - 50 min. and pH—6. The temperature effect on biosorption was carried out and found to be 30 °C. The experimental data were validated with the Freundlich and Langmuir isotherms. It was observed that the Langmuir model was well-suited compared to the Freundlich model. The kinetics for the biosorption of chromium and lead was assessed using first-order and second-order models. The correlation coefficient (R^2) value for chromium and lead was 0.955 and 0.974, respectively, for first-order kinetics but for second order the correlation coefficient of chromium and lead was 0.993 and 0.989 obtained, respectively, and concluded that the given data were well explained by secondorder kinetics compared to first order. The thermodynamic parameters ΔG° , ΔH° , and ΔS° were also examined and found that a positive value of ΔH° , indicated biosorption was endothermic and a negative value of the free energy (ΔG°) stated that spontaneous nature of the biosorption. The biosorbent characteristics were also analyzed using SEM and FTIR analysis. The maximum biosorption of chromium

Bangaraiah Pagala pbangaraiah79@gmail.com and lead was found to be 97.12% and 98.8%, respectively. A desorption study was also conducted and found 95.2% of absorbed metals were removed from the sorbent. From these findings, it was concluded that chemically modified cane bagasse is a potential biosorbent for chromium and lead biosorption from the Electroplating industry wastewater.

Keywords Cane bagasse · Chromium · Lead · Biosorption · Isotherm · Kinetics

Introduction

Toxic metal contamination is treated to be one of the most hazardous pollutions. Generally, metal pollution occurs due to mining, tanning, electroplating processing, and discharging of industrial wastes. These effluents without treatment, if discharged into water bodies cause threats to human life and ecological systems. The presence of both essential and non-essential metals such as Cobalt, potassium, magnesium, iron, chromium, lead, nickel, etc., induce multiple organ damage and health issues even at low concentrations [1]. If these metals' concentration exceeds the threshold limit could become poisonous to man and the environment. So, there is a need for a new technique for the discharge of heavy metals before release into the surface water bodies to protect the ecosystem [2].

The chromium and lead-containing effluents are discharged from metal plating, mining, and electroplating industries. There are many health issues like liver damage, cancer, immunity problem, and diarrhea in human beings if the concentration of chromium and lead enters the human body through water and food more than 0.05 mg/L and 0.01 mg/L respectively as per WHO [3]. Several physicochemical methods are available for the removal of toxic metals from effluent like ion

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exchange, reverse osmosis, electrodialysis, and precipitation. But these traditional techniques have certain disadvantages like partial removal, sludge formation, and high cost. These techniques lack technical sophistication and ineffective for the removal of toxic metals [4]. In this context, a safer, cheaper, and more efficient method, biosorption has been developed for Cr and Pb removal using cane bagasse.

In the biosorption of chromium and lead metals from the effluent, biosorbent plays a key role. The selected biosorbent must have the characteristics of being capable of degrading waste, morphological structure, and functional groups for accumulating heavy metals [5].

The cane bagasse comes from the sugar industry after sugar production and also from juice factories. Bagasse is an easily available agricultural waste product. If bagasse was thrown as waste, leads to environmental pollution. So, it is very much essential to make it a useful one. Many researchers have done work on bagasse for the removal of heavy metals. So, in the present work bagasse was utilized for the removal of chromium and lead from electroplating industrial effluent [5].

Many sorbents were investigated for Cr and Pb removal from industrial discharges. Spurthi et.al investigated rice husk for Cr removal and found it to be 91% [6]. Sunil et.al researched groundnut, neem leaf powder, and wheat bran for chromium removal and found 69%, 87.3%, and 83.35%, respectively. Casuarina leaf powder removed 94.73% of lead from wastewater [7]. Rice straw removed 94% of lead from wastewater [8]. From the observation of previous literature, the present biosorbent cane bagasse was tested for better results.

In the present investigation, the cane bagasse was applied for the treatment of real effluent, i.e., electroplating industry effluent collected from an industry located in Vijayawada, India. The biomaterial was modified by acid treatment with HNO_3 to increase the active surface and eliminate soluble components. Because of using chemically modified bagasse the percentage removal of metals was increased. The biomaterial analyzed in this work had high surface area, high porosity, and excellent metal ion selectivity.

The present work focuses on investigating the efficacy of chemically modified cane bagasse for the removal of chromium and lead ions from electroplating industrial effluent. The process variables such as agitation time, dosage, metal ion concentration, pH, and temperature were estimated. Kinetic, equilibrium, and thermodynamic studies were also analyzed.

Materials and Method

Biosorbent Preparation

The cane bagasse was taken from the sugar industry located in Vijayawada of Andhra Pradesh in India. The cane bagasse was scrubbed with distilled water to clean dust particles. Then bagasse was harvested under sunlight for two days [9]. The dried cane bagasse was grounded and sieved using a standard sieve analysis procedure for different-size fractions. The biomaterial was modified by acid treatment with HNO₃ to increase the active surface and eliminate soluble components. Because of using chemically modified bagasse the percentage removal of metal was increased. The biomaterial analyzed in this work had high surface area, high porosity, and excellent metal ion selectivity. The present biomaterial gave a good percentage removal of both chromium and lead metals. The surface area of the bagasse was estimated using a BET analyzer and found 0.824 m²/g.

Sample Solution

The industry effluent containing chromium and lead, generated from the electroplating industry after the primary treatment was taken as a sample for the present investigation. The preliminary treatment was conducted to remove coarse solids and other large materials from the sample. Preliminary treatments include screening, grit removal, and sedimentation [10]. The effluent was collected from the Electroplating industry located in the Vijayawada of Andhra Pradesh state in India. The effluent characteristics were chromium-8.42 mg/l, lead-9.61 mg/l, total suspended solids-195 mg/l, BOD-18 mg/l and COD- 125 mg/l measured using analytical testing kit [11]. The concentration of metals present in the effluent was estimated using Atomic Absorption Spectrophotometer [AAS].

Experimental Procedure

Biosorption

Batch biosorption was studied by taking 150 ml of effluent and 0.4 g of biomass in a 500 ml conical flask. The sample pH, dosage, and initial concentration were maintained at a constant for determining the optimum agitation time. The solution was mixed with an agitator for 55 min at room temperature and 150 rpm [12]. At different time intervals (1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 min) samples were collected from the agitator and kept aside for 5 min for settlement. Then the sample was filtered using a membrane filter. The final concentration of the sample was estimated using Atomic absorption spectroscopy [SAMUZO]. A similar procedure was followed to get the remaining parameters. The % removal of chromium/lead was determined from the following equation.

The percentage removal of $Cr/Pb = (C_1 - C_0)/C_1 * 100$.

The C_{I} -initial concentration of the sample. C_{o} -Final concentration of sample after adsorption.

Desorption Study

The saturated biosorbent with lead and chromium was poured in contact with 100 ml of 0.1 M HCl for 5 h in a shaker at a temperature of 30 °C and 250 rpm. The liquid phases were filtered and analyzed by atomic absorption spectrophotometer. The performance of HCl in the biosorbent regeneration was estimated in four cycles for metal ions to determine the biosorbent regeneration.

Results and Discussion

Agitation Time

with % removal

The biosorption experiments were conducted to achieve the equilibrium agitation time required to get the maximum percentage removal of chromium and lead by keeping the initial metal ion concentration—5 mg/l, dosage—0.5 g, and pH—5 for chromium and initial metal ion concentration-5 mg/l, dosage—0.6 g, and pH—6 at constant for lead. The change in percentage removal with agitation time (1-55 min.) was identified by plotting % removal with agitation time shown in Fig. 1. From Fig. 1 it is noticed that percentage removal was increased with an increase in agitation time. The % removal of chromium and lead was high at the early step since the binding sites available at starting stage were high and also more interactions between metal ions and cane bagasse. At a later stage rate of removal was slower since deposited metal ions were at an earlier stage [13]. The same trend was also followed in lead removal. The equilibrium time attained for chromium and lead was 40 min and 50 min. respectively. So, the optimum agitation time of 40 min for chromium and 50 min for the lead was required to get 97.1% and 98.8% removal of chromium and lead respectively from the effluent.

Biomass Dosage

The biomass dosage is a key variable in the adsorption of metal ions by controlling the accessibility of the adsorption site. The variation in % removal of chromium and lead with dosage [0.1-1 g] is plotted in Fig. 2. The increase in chromium and lead removal was observed with an increase in the amount of biomass added. The adsorption capacity was increased because more binding sites onto the biosorbent were available for attracting the metal ions [14]. Once the equilibrium stage was reached, i.e., metal ions adsorbed equal to binding sites present on the sorbent surface, no variation in percentage removal though adding more amount of biomass [15]. The same trend was observed in the case of lead removal also. So, the optimum dosages were observed at 0.5 g and 0.6 g for both chromium and lead, respectively.

Initial Metal Ion Concentration

Figure 3 Shows, the change in metal ion concentration on the removal of chromium and lead. To understand the variation of percentage removal, different concentrations ranging from 5-60 mg/l were considered while keeping dosage, agitation time, and pH at a constant level and plotted. The chromium and lead removal declined with an increase in initial concentration. It was attributed to the less surface area available to accommodate more ions. The binding sites present on the bagasse were not sufficient for competing for metal ions [16]. At higher concentrations presence of metal ions was more but the amount of biomass was unchanged, and the available binding sites were fewer [17]. At lower concentrations all the ions interacted with active sites; hence, the percentage of removal was more. So, the optimum metal ion concentration attained was 5 mg/l for both chromium and lead.



Agitation time(Min.)





concentration with % removal

Fig. 3 Change of initial ion

Solution pH

The change in pH on the removal of chromium and lead using cane bagasse was significant. The solution pH could affect the protonation of the functional groups present on the biomaterial and also the metals present in the sample. As the pH of the solution increases, the functional groups are negatively charged, favoring the adsorption of metal ions.

The pH range from 1–9 was examined to find the influence of pH on the biosorption of chromium and lead using bagasse biomass as shown in Fig. 4. In the figure percentage removal of metal ions was increased with an increase in pH, but at the early stage rate of chromium and lead removal was low because of protonation of functional groups present on the surface of biomass, after this increase in pH was observed from 3–5. The functional groups present on sorbent are positively charged when protonated at low pH and are negatively charged at higher pH. Because of this at low pH, the binding of chromium and lead to active sites of biosorbent was restricted [18]. So, the removal was less at low pH. With the increase in pH, there was an increase in ligands with negative charges, which resulted in increased binding of chromium and lead. After pH 5 for chromium and 6 for lead, the percentage removal of metals was decreased because of the diminution of free ions due to the formation of hydroxyl complexes at the higher pH values and the subsequent precipitation of metal ions. Hence the percentage removal of chromium and lead was high. The optimum pH value determined for chromium and lead was 5 and 6, respectively [19].

The point of zero charges of cane bagasse was estimated by the addition of the salt method. The sample of 0.4 gm and 150 ml of 0.01 M NaCl solution were added in conical flasks at room temperature. The pH of the solutions was adjusted to an initial pH (pH_i) value of 1, 2, 3, 4, 5, 6, 7, 8 and 9 by adding NaOH (0.1 M) solution. The content in each flask was





then stirred in a shaker at 150 rpm for 24 h and the final pH (pH_f) of each sample was measured. The difference between the initial and final pH (pH_f-pH_i) of each solution was determined. The plot of $(pH_f - pH_i)$ versus pH_i is shown in Fig. 5.

From Fig. 5, the net zero charges were obtained at pH 4.8 for chromium and 5.9 for lead. At pH below PZC, the biosorbent surface was positively charged, representing a strong interaction between the anion and the functional groups. However, at pH above PZC, biosorbent is dominated by the hydroxyl group, which restricts attraction between the anions and the sorbent surface, lowering the metal uptake [20].

Temperature

The temperature effect on the biosorption of chromium and lead was not significant. However, there was an increase in biosorption with an increase in temperature (10-30 °C),



since surface activity and kinetic energy were increased. After 30 °C, no change in the percentage removal of chromium and lead was observed, respectively [21]. But at higher temperatures, there was damage to the biosorbent. So, generally, biosorption is conducted at a room temperature of 30 °C. Presented in Fig. 6.

Adsorption Isotherms

The mechanism involved in the adsorption of chromium and lead was tested by using adsorption isotherms. The most appropriate equation was developed for the equilibrium data. In this work two isotherms namely Langmuir and Freundlich have been used to test the given data. The Langmuir isotherm was applied based on the assumption of monolayer adsorption onto the surface of the sorbent and a limited number of active sites [22]. Also considering the uniform



distribution of energy of biosorption over the surface. The expression is given by

$$1/q_{\rm eq} = 1/(b C_{\rm eq}) + 1/q_{\rm m}$$

 $q_{\rm eq}$ -biosorption rate at equilibrium[mg/g], $C_{\rm eq}$ - metal ion concentration at equilibrium[mg/l], $q_{\rm m}$ -maximum uptake rate. The plot is shown in Fig. 7A, B. From Table 1, the R^2 value for chromium was 0.983, and for lead 0.982.

Fig. 6 Temperature effect

The separation factor (RL) was calculated and also included to find whether the adsorption is favorable or not.

$$RL = 1 / (1 + KL * Co)$$

where KL is the Langmuir constant and C_o -is the initial concentration. The RL value indicates whether the type of the isotherm is linear (RL=1), favorable (0 < RL < 1), unfavorable (RL>1), or irreversible (RL=0). In the present



Effect of temperature

Fig. 7 Langmuir isotherms A chromium B lead

Table 1 Adsorption isotherm constants	Metal		Langmuir model			Freundlich model		
		B [l/mg]	$q_{\rm max}$ [mg/g]	R _L	R^2	n	K_{f}	R^2
	Chromium	0.075	28.44	0.037	0.983	1.091	2.36	0.959
	Lead	0.316	16.83	0.021	0.982	1.210	2.54	0.940

investigation, RL obtained was 0.016, which was under the favorable range [23].

Freundlich isotherm assumes a heterogeneous surface and is not strict in the formation of a monolayer. This model was developed by assuming multilayer adsorption. It was also considered interactions between molecules adsorbed and non-uniform energy of adsorption over the surface of the biosorbent [24]. The equation is presented as

$$q_{\rm eq} = KC_{\rm eq}^{1/n}$$

Here *K*, *n* –biosorption capacity and intensity, respectively. The plot is drawn and presented in Fig. 8A, B. The equilibrium constants are calculated and listed in Table.1. The R^2 value for chromium was 0.959 and for lead 0.940. So, it was clear that the given data were well followed by the Langmuir model.

Kinetic Study

The biosorbent performance was estimated by doing kinetic analysis. It also determines the controlling mechanism involved in the biosorption of chromium and lead using cane bagasse. Pseudo first-order and second-order kinetic equations are considered for testing the mechanism involved in biosorption [25]

The Pseudo first-order kinetic model is given by

 $\log(q_e - q) = \log q_e - K_1 t.$

Here, K_1 - rate constant for first order, qe & q- quantity of solute sorbed [mg/g] at equilibrium and it was observed that the coefficient of determination [R^2] value was 0.955 and 0,974 for chromium and lead respectively as listed in Table 2 at any time, respectively [26]. The plot was drawn and shown in Fig. 9A, B.

The second-order kinetic model is given by

$$t/q = (1/K_2q_e^2) + t(1/q_e)$$

 K_2 —second order constant. The plot is drawn and shown in Fig. 10A, B. The kinetic parameters are evaluated and shown in Table. 2. It was observed the coefficient of determination [R^2] value was 0.993 for chromium and lead 0.989. These R^2 values were very close to one compared to the first order; hence, the data are most suitable for second-order kinetics.

Intra Particle Diffusion

0.5

^в -0.5 Бод

B)

Intra-particle diffusion: the mechanisms that explain the transfer of a solute from a solution to the sorbent are bulk diffusion, film diffusion, pore diffusion, and surface diffusion. Intra-particle diffusion model was applied to find the rate-controlling process. The intra-particle diffusion was estimated by using the following equation.

LogC_e Vs Log q_e

Log C_e

 $R^2 = 0.940$

0.5

1.5

Log q_=0.421Logc_-0.531

2.0



Fig. 8 Freundlich isotherms **A** chromium **B** lead

Table 2 Kinetic study

Metal	Pseudo first o	order		Second order			
	$q_{\rm e} [{\rm mg/g}]$	K_1 [Min ⁻¹]	R^2	$q_{\rm e} [{\rm mg/g}]$	$K_2 [{ m Min}^{-1}]$	R^2	
Chromium	3.41	0.041	0.955	6.52	0.003	0.993	
Lead	0.52	0.063	0.974	11.81	0.121	0.989	

-1.0



Fig. 9 First-order kinetics A chromium B lead



Fig. 10 Second-order kinetics A chromium B lead

$qt = Kpt^{1}/_{2} + C$

Figure 11, the plot of intra-particle diffusion showed multi-linearity, indicating that three stages have taken place. The first portion was attributed to the diffusion of sorbate through the solution to the external surface of the adsorbent. The second portion describes the ion stage, where intra-particle diffusion was rate limiting. The third portion was attributed to the final equilibrium stage. The curve is not passing through the origin, intra-particle diffusion is not a rate-controlling step, the slow movement of the solute from the boundary layer to the surface represents film diffusion, the movement of the solute into the pores states pore diffusion and fast attachment of solute on the active sites shows surface diffusion but not consider during the design of kinetics. Finally, film diffusion is the rate-controlling process [27].

Thermodynamics

The thermodynamic behavior of biosorption was evaluated by using thermodynamic parameters. The changes in Gibbs energy change (Δ G), enthalpy (Δ H), and entropy [Δ S] for different temperatures were calculated. Gibbs free energy change was determined by

$\Delta G = -RT \ln K$

 Δ G- Gibbs energy change in KJ/mol, *R*- Gas Constant, *T*-absolute temperature in oK, *K*-equilibrium Constant. The relationship among the three energy changes was given by





$\Delta G = \Delta H - T \, \Delta S$

Changes in entropy and change in enthalpy were obtained using

$Ln K = (\Delta S/R) - (\Delta H/R) X 1/T$

Plot 1/T vs lnk and $\Delta S \& \Delta H$ were evaluated from the intercept and slope of the line, respectively [28]. From Table.3, the results stated that biosorption of chromium and lead was endothermic. The Gibbs free energy change (ΔG°) had negative values indicating that the biosorption is spontaneous. From Table.3, it was also noticed that the negative values of free energy change, and increased with increasing temperature. This may be due to the activation of more sites on the surface of the biosorbent with a rise in temperature or that the energy of biosorption sites had an exponential distribution band at higher temperatures enabling the energy barrier of biosorption to be overcome. When the free energy change (Δ Go) ranges between -20and 0 kJ/mol, adsorption is classified as physical adsorption, while in chemical adsorption values of free energy change range from -80 to -400 kJ/mol. In the present investigation, free energy change for Chromium and lead biosorption onto cane bagasse was in the range of (-4.9 to -15.5) kJ/mol. So, the biosorption was physical adsorption. The results

obtained from Freundlich isotherm, the constant n value lay between one and ten indicated that the biosorption process was physisorption. From the kinetic study, it was concluded that the second-order kinetics is well-suited to explain the adsorption kinetics of the cane bagasse biosorbent. This suggested that the rate-limiting step in this biosorption process may be chemisorption involving valency forces through the exchange of electrons between sorbent and sorbate [29].

Scanning Electronic Microscopic Analysis

A new SEM image was incorporated for better clarity. The SEM images of sugarcane bagasse powder before and after the biosorption of chromium and lead ions are shown in Fig. 12. Figure 12a showed the presence of pores and rough surfaces with narrow thicknesses between fibers which were responsible for conducting the mass transfer of metal ions toward the surface. It was observed that the surface morphology of cane bagasse before metal uptake had larger pore sizes than the after metal uptake with few pores (Fig. 12b). This was due to the pores being occupied by the metals. After biosorption of chromium and lead, it was observed that a smooth structure with narrow thickness. The microcavities observed on the surface of cane bagasse were between 15 and 41 μ m diameter (Fig. 12b, c) which facilitates adsorption. The particle size of the biosorbent was

S. No	ΔH , J/mol	$\Delta SJ/mol-K$	ΔG at different temperatures J/mol				
			293 K	303 K	313 K	323 K	333 K
1	21.195	45.57	- 13330.8	- 13786.5	- 14242.2	- 14698	- 15154
2	21.176	41.434	-12119	-12533.3	- 12947.7	-13362	-13776
3	23.225	46.91	-13721.4	- 14190.5	- 14659.6	-15129	- 15598
4	19.549	32.416	-9478.34	-9802.5	- 10126.7	-10451	-10775
5	15.241	17.06	-4983.34	- 5153.94	- 5324.54	- 5495.1	- 5665.7

Table 3 Thermodynamic study



Fig. 12 SEM Analysis of bagasse A without loading B chromium loading C lead metal loading

also an important factor to be considered in biosorption. The particles size of 50 μ m performed better sorption compared to 150, 200, and 250 μ m. The surface area of biosorption increases with a decrease in particle size. The surface area of cane bagasse 0.824 m2/g was obtained [30].

FTIR Analysis of Bagasse

The FTIR analysis of cane bagasse before and after biosorption of chromium and lead is carried out and shown in Fig. 13. Before adsorption the peak observed at 1382 cm^{-1} corresponds to O–H stretching and NH stretching presenting amino group. The peak 1135 cm^{-1} was assigned

to alkynes with stretches of C=C. The sharp peak at 708 cm⁻¹ indicated carbonyl group (C=O) stretching from aldehydes and ketones. The presence of O–H, C≡C, and carbonyl groups confirms the presence of carboxylic acid groups in the biosorbent. The bonds C–H and C–O were identified at 584 cm⁻¹ and 465 cm⁻¹, respectively. It was observed that after biosorption of Chromium and lead the peaks were shifted to a new position in the biosorbent and noticed O–H stretching and NH stretching at 1355 cm⁻¹ and 1385 cm⁻¹ due to metal ions deposit. The bond C=C occupied new peaks at 1114 cm⁻¹ and 1140 cm⁻¹ for chromium and lead ions sorption. The O–H, N–H, and carbonyl and carboxylic functional groups were found on cane bagasse





Fig. 14 Desorption study



after chromium and lead biosorption were at 596 cm⁻¹ and 602 cm⁻¹, respectively [31].

Desorption Study

A desorption study was needed to recover metals from the waste and for regeneration of the biosorbent to find its potential as a sorbent for commercial usage. The percentage of lead desorbed from cane bagasse using HCl could decrease from 95.2 to 62.6% within the four cycles as per Fig. 14. A small amount of sorbed metal that could not be recovered due to that amount was strongly bonded to the sorbent. After three cycles the decrease in biosorption efficacy of cane bagasse is very nominal. Hence it is viable to use cane bagasse as a biosorbent for the removal of chromium and lead [32].

Conclusions

The one-parameter model was applied to know the potential of sugar cane bagasse for biosorption of chromium and lead from electroplating industry effluent. The optimum process variables obtained were initial metal ion concentration 5 mg/l, dosage 0.5 g, agitation time 40 min, and pH 5 for chromium sorption. For lead sorption initial metal ion concentration—5 mg/l, dosage—0.6 g, agitation time – 50 min, and pH—6. The kinetic and equilibrium analysis were also analyzed. The equilibrium data were well-fitted to the Langmuir model and the kinetic data followed second-order kinetics. The Gibbs free energy change showed a negative value, which indicates that the biosorption process of chromium and lead onto the cane bagasse occurred spontaneously in operating conditions. The percentage biosorption was estimated as 97.12 and 98.8 for chromium and lead respectively. The cane bagasse biosorbent has the benefits of being cheap, easily available, no sludge formation, can be regenerated, technically feasible, and having the affinity for heavy metal removal. Industrial effluents contain not only a single pollutant but also contains a large mixture of pollutants that may influence sorption systems and selectivity. As a result, enough measures should be taken to develop and apply novel biomaterials. In the future, a composite biosorbent may be prepared for the removal of multiple metals from industrial effluent. The results revealed that sugar cane bagasse could be effectively applied for the removal of chromium and lead from the industrial effluent.

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Author Contributions The only author contributed to the study's conception and design. Material preparation, data collection, and analysis were performed.

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Declarations

Conflict of interests The authors have no relevant financial or non-financial interests to disclose.

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