Original Article

Efficiency of immobilized Zea mays biomass for the adsorption of chromium from simulated media and tannery wastewater

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ABSTRACT

In view of adsorption efficiency of modified agricultural biomasses, present study was conducted to appraise the chromium [Cr(III) and Cr(VI)] adsorption capacities of corn cob immobilized biomass. Corn cob biomass was immobilized in calcium alginate bead and process variables such as Cr ions initial concentrations, pH, dosage and contact time were optimized. The Cr(III) and Cr(VI) were adsorbed up to 277.57 mg/g and 208.6 mg/L onto corn cob immobilized biomass under optimized conditions of process variables. Both Cr ions followed Langmuir isotherm and the pseudo-second order kinetic model. Optimized conditions were employed for Cr adsorption from tannery effluents and up to 64.52% and 55.98% Cr(III) and Cr(VI) were removed, respectively. The immobilized corn cob biomass was run up to 5 repeated adsorption-desorption cycles and 98.0% and 1.51% adsorption efficiencies were reduced at the end of 5 adsorption-desorption cycles of Cr(III) and Cr(VI), respectively. NaOH (0.1 M) efficiently desorbed the Cr ions from corn cob immobilized adsorbent and up to 79.8% and 86.0% Cr(III) and Cr(VI) ions were recovered respectively. Results revealed that the immobilization is a viable technique for the modification of native agricultural biomass for efficient remediation/sequestration of metal ions from industrial effluents.

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1. Introduction

The waste agriculture biomasses have been extensively studied for adsorption and commercial adsorbents have been developed based on agricultural waste biomasses. More recently, the modification (immobilization/bio-composites preparation) attracted the attention of environmentalists in view of their excellent physico-chemical properties and adsorption efficiencies [1–14]. Native biomass have disadvantages such as un-even particle size, low density, poor mechanical strength, rigidity and instability under
variable conditions [6,15]. So far, the deficiencies of native biomass can be minimized by immobilizing the biomass with suitable matrix, which offer various advantages, i.e., occupy less volume, easier to handle during processing, stable for multiple cycles and stable under different conditions, i.e., salinity, metal toxicity, pH and temperature. In view of advantages of immobilization, the modification/immobilization has emerged an attractive alternative to produce efficient adsorbents [6,16]. Number of studies have been performed to study immobilized biomass performance and based on adsorption capacity, stability and recycling, the immobilized/modified materials found to be excellent versus native biomasses [17–25]. To date, alginate beads, carrageenan beads, polyurethane foam, agarose beads, agar beads, polyacrylamide gels, silica gel, capron fibers, ceramics material, cellex-T, anionexchange resin, amberlite, ionexchange resin, controlled-pore glass, Luffa cylindrical sponge, graphene nanosheets, chitosan nanofibers, polyvinyl foams, and filter paper have been used as a matrix and employed for the removal of metal ions (Ni, Cu, Cd, Zn, Au, Cr, Hg, U, Pb, Al, Co, Fe, Mn, Pd, Pt, Ag), inorganic ions (ammonium, phosphate, nitrate, nitrite, phosphorus, etc.) and other organic compound including dyes [6,13,14,16,26–32].

Maize (Zea mays L) is a Pakistan’s third most important cereal crops after wheat and rice. It is used as food, feed as well as wet milling industrial agent. Pakistan environmental conditions are very favorable and for domestic need, surplus amount of maize is produced [33]. Corn cob is produced as a waste material from maize during processing. Small amount of corn cob waste is used as a fuel (in kitchen for cooking purpose) and other is wasted in huge quantity [34]. In view of current scenario of heavy metals contamination of water bodies, there is need to explore alternate adsorbents for the remediation purposes. So far, the possibility to use modified corn cob waste biomass as adsorbent is of great interest, which has not been studied previously for Cr ions adsorption.

In the present investigation, corn cob powder was immobilized in Ca–alginate beads and adsorption efficiency of prepared adsorbent was evaluated for Cr ions. Various process variables such as Cr ions initial concentrations, contact time, pH and adsorbent dosage. Equilibrium and kinetic models were employed to evaluate the adsorption behavior of Cr(III) and Cr(VI) on to modified corn cob adsorbent. SEM and EDX techniques were employed as cationization techniques. The recycling ability of prepared adsorbent was also checked using NaOH as desorbing agent.

2. Material and methods

2.1. Chemical and reagents

The chemical used like K2Cr2O7 (99%), Cr(NO3)3 (99%), NaOH (97%), HCl (37%), acetone (99%), CaCl2 (97%), Na-alginate and Cr(III) and Cr(VI) standards were purchased from Sigma–Aldrich (Germany). Stock solutions of Cr(III) and Cr(VI) were prepared by dissolving salts of Cr(NO3)3 and K2Cr2O7 in ultra pure water and used to prepare working concentrations. Ultra pure water with a resistivity of 18.2 MΩ cm (Milli-Q system, Millipore) was used for the preparation of solution. The siever (OCT-DIGITAL 4527-OI), orbital shaker incubator (PA 250/25.H), analytical balance (Shimadzu, AW 220), pH meter (HI-8014 Hanna), grinder (Moulinex, France) and spectrophotometer (CE Cecil 7200, UK) were used throughout the study (otherwise stated).

2.2. Biomass preparation

Waste maize corn cob was collected from Rafhan Private limited, Faisalabad Pakistan. Corn cobs were washed extensively with water, dried in sunlight followed by oven dried at 60 °C for 72 h. The dried biomass was chopped, grinded and sieved through Octagon siever (OCT-DIGITAL 4527-01) to get even particles. The particle fraction of 0.25 mm was collected and used for adsorption and immobilization purpose.

2.3. Immobilization procedure

Na-alginate (2%, w/v) was dissolved in hot water (60 °C) with continuous stirring and slurry, thus produced was cooled down to room temperature and 1 g of corn cob powder was added and homogenized by agitation and extruded into 0.1 M CaCl2 solution with the help of a syringe. The beads thus formed (3 mm) were kept at 4 °C for 2 h, washed thoroughly with ultra-pure water and subjected to Cr(III) and Cr(VI) adsorption from aqueous solution as well as tannery effluents.

2.4. Adsorption procedure

Various process variables were optimized for maximum Cr ions adsorption. pH effect was studied in the range of 1–6 pH and other conditions of adsorbent dosage (0.1 g), contact time (24 h) and metal ions concentration (100 mg/L) were constant. The concentration of Cr ions 25–1000 mg/L was studied, whereas 0.1 g adsorbent dose, 24 h contact time and pH 5 (Cr(III)) and 2 (Cr(VI)) were constant. The contact time was studied in the range of 10–1440 using adsorbent dose 0.1 g, Cr ions initial concentration of 100 mg/L and pH (5 and 2 for Cr(III) and Cr(VI), respectively). For batch experiments, 100 mL solution, shaking speed 100 rpm and room temperature (25 °C ± 2) were constant. For adsorption experiments, respective amount of adsorbent was mixed with Cr solution and pH was adjusted using 0.1 M NaOH/HCl, then the flasks were placed in orbital shaker for stipulated time periods. The Cr(III) and Cr(VI) residual concentrations were determined by using Atomic absorption spectrophotometer (A Analyst 300, PerkinElmer). The adsorbent was separated by centrifugation and the Cr adsorbed/unit mass was calculated. The qe values both for native and immobilized adsorbents were estimated using relation shown in Eq. (1) [35].

\[
q_e = \frac{(C_0 - C) \times (V/1000)}{m}
\]  

(1)

where, C0 is the initial concentration of chromium (mg/L), C is the equilibrium concentration (mg/L), V is the volume of solution (mL) and m is the adsorbent dose (g).

All adsorption experiments were run in triplicate and data thus, obtained was reported as mean ± SD.
2.5. **SEM and EDX analysis**

The loaded and un-loaded corn cob adsorbents (native and immobilized) were characterized by SEM and EDX techniques as precisely reported elsewhere [36].

2.6. **Desorption study**

The corn cob immobilized adsorbent, desorption ability was checked in 0.1 M NaOH solution. The loaded biomass was dried and placed in contact with 0.1 M NaOH solution and stirred for 24 h at 100 rpm and dye desorbed was estimated (Eq. (2)). The adsorption–desorption was performed up to 5 cycles.

\[
q_d (\%) = \frac{D}{R} \times 100
\]

where \(q_d (\%)\), \(D\) and \(R\) are representing desorption capacity, dye adsorbed and dye recovered (desorbed), respectively.

3. **Results and discussion**

3.1. **Effect of pH**

Effect of pH on Cr adsorption is depicted in Fig. 1(A and B), which was studied in the range of pH 1–6 for Cr ions initial concentration of 100 mg/L, contact time 120 min and adsorbent dosage 0.1 g. Cr ions removal efficiency was found to be pH dependent. The Cr(VI) adsorption was higher at pH 2 (40.7 mg/g) and by increasing pH, the adsorption capacity decreased linearly until pH 6. Cr(III) adsorption increased constantly up to pH 5, which was maximum at pH 5 (45.97 mg/g). The behavior of corn cob native and immobilized adsorbent was similar, however, immobilized biomass showed higher adsorption capacity at all pH values versus native corn cob biomass. The variable behavior of Cr adsorption at different pH values was due to different surface charges at different pH values. It is well known that the HCrO\(_4^−\) ion is the dominant specie of Cr(VI) in the pH range of 2–3 and by increasing the pH, this dominant specie is converted in to CrO\(_2^{2−}\) ions. Secondly, the surface bears positive charges at lower pH [37] and resultantly, the Cr(VI) adsorption was higher at pH 2, which decreased by increasing the pH, so far, the electrostatic interactions were higher at pH 2 for Cr(VI) and vice versa. These findings are in line with previous studies that Cr(VI) adsorption was higher under acidic conditions and deceased as the pH moved toward neutral value [6,38]. Different adsorbents also showed similar behavior for Cr adsorption, i.e., *Rosa damascena*. This can be correlated this behavior of Cr(VI) adsorption with HCrO\(_4^−\) ions at lower pH and decreasing adsorption of Cr(VI) was correlated with change in surface charges, which led to repulsive forces between Cr(VI) ions and adsorbent surface and the Cr(VI) adsorption decreased. For Cr(III), maximum adsorption was observed at pH 5, which was due to the formation of Cr(OH)\(_3^+\), Cr(OH)\(_2^{+}\), Cr\(_2(OH)\(_2^{+}\), and Cr\(_3(OH)\(_2^{+}\) species [39]. At higher pH, these species are adsorbed favorably. The Cr(III) less adsorption at lower pH values was due to the competition of Cr ions with protons, repulsion between protonated adsorbent surface and ions [40,41]. At higher pH, the protonation decreased and resu-
3.2. Effect of metal ions initial concentration

The effect of Cr ions initial concentration was studied in the range of 25–1000 mg/L both for Cr(VI) and Cr(III) using adsorbent dose (0.1 g) and pH (5 and 2 for Cr(III) and Cr(VI), respectively) and 24 h contact time. The adsorption responses of both native and immobilized corn cob adsorbents are shown in Fig. 2 (A and B). As it can be seen from results, by increasing the Cr ions initial concentration, the adsorption capacities increased, whereas percentage removal decreased as the initial concentration increased (Fig. 3 (A and B)). In case of Cr(III), the adsorption capacities were recorded to be 13.77 and 277.57 (mg/g) for initial concentrations of 25 and 1000 (mg/L), respectively, and percentage removal of 55.08 and 27.76 (%) was recorded, which indicates that by increasing the Cr ions initial concentration, the adsorption capacity increased and percentage adsorption was decreased. For Cr(VI), similar trend was observed, however, the adsorption capacities and percentage removal was low versus Cr(III). The removal efficiency of 208.6 mg/L for Cr(VI) ions initial concentration of 1000 mg/L was recorded, which reduced to 12.61 mg/L for initial concentration of 25 mg/L in case of corn cob immobilized adsorbent. The enhanced adsorption at higher concentration was due to the driving forces to overcome mass transfer resistance between the liquid and solid phases [4,5,2,3]. At extremely higher initial concentration, the available binding sites were saturated and the adsorption depends on the initial concentration [35]. The probability of interaction of ions with binding sites was reduced, which restricted the adsorption process. Therefore, for effective adsorption, the ions in solution that interact with the binding sites are important. The possible reason for this behavior can be explained on the basis of unsaturation of bindings sites and at higher concentration...
the competition between ions and available binding sites was increased and hence, the complexation of ions was difficult, which slowed down the adsorption process [4,5,2]. Similar trend of Cr adsorption have also been reported previously as a function of Cr ions initial concentration for dead fungal biomass of Phane-rochaeta cryosporium [47], immobilized C. elegans [46] and Cyanobacterium Oscil [48].

3.3. Effect of contact time

Effect of contact time on Cr(III) and Cr(VI) was studied in the range of 10–1440 min and adsorption responses are shown in Fig. 4(A and B) for corn cob native and immobilized biomass, respectively. The Cr ions adsorption was rapid up to 240 min followed by slow adsorption up to 400 min and beyond this, the Cr ions adsorption stopped. The adsorption of Cr ions took place in two distinct steps, i.e., an initial fast step (shorter duration) followed by slower adsorption (longer duration).

Lower adsorption at latter stage may be due to the difficulty faced by metal ions to occupy the remaining vacant binding sites. Secondly, slow adsorption in second phase might be due to intraparticle diffusion process [49]. The fast adsorption of Cr ions was due to availability of binding sites, which exhausted as the adsorption process proceeded with time and resultantly, adsorption slowed down. Therefore, the concentration gradient between ions and adsorbent was changed with time [50,51]. The corn cob native and immobilized biomasses also showed variable behavior or Cr(III) and Cr(VI) ions. However, immobilized corn cob response was promising versus native corn cob biomass. The sorption capacity for Cr(III) was 46.99 mg/g (immobilized) >34.61 mg/g (native). The Cr(VI) adsorption was 42.93 mg/g (immobilized) >28.26 mg/g (native). Similar trend of chromium adsorption using different biomasses have been reported previously for different biomasses, i.e., sugarcane bagasse [6], R. damascena phytomass [42], Chlorella biomass [52], dead fungal biomass of P. cryosporium [47], pistachio hull [37], O. americanum seeds biomass [53], banana peel [54], orange (Citrus cinesis) waste biomass [39] and walnut hull [38].

3.4. Effect of adsorbent dose

Adsorbent dosage significantly affected the Cr ions adsorption, the adsorption capacities for both types of adsorbents

![Fig. 4 – Effect of contact time on chromium adsorption onto native and immobilized corn cob adsorbents (adsorbent dose 0.1 g, Cr ions initial concentration of 100 mg/L and pH (5 and 2 for Cr(III) and Cr(VI), respectively) and contact time 10–1400 min).](image1)

![Fig. 5 – Effect of adsorbent dose on chromium adsorption onto native and immobilized corn cob adsorbents (adsorbent dose 0.1–0.5 g, Cr ions initial concentration of 100 mg/L and pH (5 and 2 for Cr(III) and Cr(VI), respectively) and contact time 24 h).](image2)
were higher at low adsorbent dose, which decreased as the adsorbent dosage increased (Fig. 5(A and B)). The Cr(III) adsorption was higher versus Cr(IV) for both types of corn cob adsorbents. The adsorption capacities of the native and immobilized corn cobs biomass was found higher at 0.1 g dose and decreasing trend was observed at higher doses. This behavior of low adsorption at higher adsorbent dose was due to the availability of more adsorption sites at lower absorbent dose, which decreased as the dosage increased. This decreasing efficiency was due to overlapping or aggregation particle and resultantly, adsorption sites affected at higher adsorbent dose [5, 6, 49, 55]. The enhanced adsorption capacity at low dose can be attributed to higher surface area and availability of more binding sites. Similar trend have also been reported previously for Cr ions adsorption for different adsorbents, i.e., higher adsorption at low dose, which decreased at higher dose of adsorbent at constant ions concentration and volume of solution for R. bourbonia phyto-biomass [35], sugarcane bagasse [6], T. clypeatus biomass [44], immobilized C. elegans [46] and chlorella biomass [52].

3.5. Comparison of corn cob native versus immobilized adsorbents

In comparison, the maximum adsorption capacities of immobilized corn cob were found to be 46.99 mg/g for Cr(III) at pH 5 and 42.93 mg/g for Cr(VI) at pH 2, for the initial metal concentration of 100 mg/L, biomass dosage 0.1 g and contact time 24 h. The immobilized corn cob showed significantly higher adsorption efficiency versus native corn cob biomass, i.e., at different Cr ions initial concentration, contact time, pH and adsorbent dose, the immobilized corn cob efficiency was higher, however, overall adsorption trend was the same for both type of adsorbents. Earlier studies also highlighted that the immobilized biomass has more adsorption efficiency versus native biomass [6, 44, 46, 52] and similar behavior was observed in the present investigation for native and immobilized corn cob biomass. It is well known that adsorption efficiency of adsorbent depends upon various factors like pH, temperature and adsorbent stability [49, 55] and modified biomass offers more stability under variable conditions. Moreover, the surface area, [56], protonation/deprotonation, electrostatic attractions [57] and adsorbent physico-chemical properties define the activity of binding sites for effective ions entrapment, adsorption and ions retention capacity [58]. Therefore, the immobilized/modified adsorbent may offers higher adsorption capacities versus native biomass [59].

3.6. Kinetics modeling

The pseudo-first order and pseudo-second order kinetics models were tested to fit the Cr adsorption experimental data. The tested pseudo-first order (Eq. (2)) and pseudo-second order (Eq. (3)) kinetics models can be seen in Eqs. (2) and (3), respectively [60, 61],

$$\frac{t}{q_t} = \frac{1}{k_{1,ads}q_0} + \frac{t}{q_0}$$  \hspace{1cm} (4)$$

where \(q_t\) is the mass of metal ions adsorbed at equilibrium (mg/g), \(q_0\) is the mass of metal at time t (min), \(k_{1,ads}\) is the first order reaction rate constant of adsorption (min\(^{-1}\)) and \(k_{2,ads}\) is the pseudo-second order rate constant (mg/g/min\(^{-1}\)). A comparison between pseudo-first order and pseudo-second order kinetic models is given in Table 1 for Cr(III) and Cr(VI). The pseudo-second order kinetic model with higher value of regression coefficient \(R^2\) of 0.999 for Cr(III) and Cr(VI), respectively fitted well to the experimental data. The \(q_t\) values (both for native and immobilized corn cob adsorbents) in case of pseudo-second order kinetic model were in agreement with experimentally determined values. From this behavior of Cr(III) and Cr(VI) ions adsorption onto immobilized and native corn cob biomass, it can be concluded that pseudo-second order kinetic explained well the Cr ions adsorption.

### Table 1 – Pseudo-first-order and pseudo-second-order kinetic models for Cr(III) and Cr(VI) adsorption onto corn cob (native and immobilized) biomasses.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Adsorbents</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_r) (mg/g)</td>
<td>(k_{1,ads}) (mg/g)min(^{-1})</td>
<td>(R^2)</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>Native corn cob</td>
<td>80.72</td>
<td>2.303 \times 10(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Immobilized corn cob</td>
<td>77.45</td>
<td>2.308 \times 10(^{-1})</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Native corn cob</td>
<td>82.22</td>
<td>2.441 \times 10(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Immobilized corn cob</td>
<td>77.62</td>
<td>2.317 \times 10(^{-1})</td>
</tr>
</tbody>
</table>

### Table 2 – Langmuir and Freundlich isotherms for Cr(III) and Cr(VI) adsorption onto corn cob (native and immobilized) biomasses.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Adsorbents</th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K_L) (mg/g)</td>
<td>(X_M) (mg/g)</td>
<td>(R^2)</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>Native corn cob</td>
<td>0.0039</td>
<td>166.66</td>
</tr>
<tr>
<td></td>
<td>Immobilized corn cob</td>
<td>0.0047</td>
<td>250</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Native corn cob</td>
<td>0.0052</td>
<td>111.11</td>
</tr>
<tr>
<td></td>
<td>Immobilized corn cob</td>
<td>0.0057</td>
<td>166.67</td>
</tr>
</tbody>
</table>


\[ https://dx.doi.org/10.1016/j.jmrt.2017.05.015 \]
The kinetics results were in accordance with previous studies reported for Cr by rose waste biomass [42]. While studying the adsorption of metals ions onto pretreated red rose distillation sludge [62] also reported high metal ions uptake initially followed by low adsorption and author correlated this effect with adsorption of metals ions into intracellular spaces.

### 3.7. Adsorption Isotherms

The adsorption isotherms are characterized by definite parameters, whose values express the surface properties and affinity of adsorbent for metal ions adsorption [35]. In the present study, Langmuir and Freundlich isotherm models were employed and are represented in Eqs. (4) and (5), respectively [63,64].

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}K_L} + \frac{C_e}{q_{\text{max}}} \tag{5}
\]

\[
q_e = K_F C_e^{1/n} \tag{6}
\]

where \(q_e\) is the metal ion adsorbed (mg/g), \(C_e\) the equilibrium concentration of metal ions in solution, and \(K_L\) and \(K_F\) and 1/n are the Langmuir and Freundlich constants, respectively. Data fitted with Langmuir and Freundlich isotherms is given in Table 2 for Cr(III) and Cr(VI). The higher \(R^2\) and \(q_{\text{max}}\) values suggested that the Cr ions followed Langmuir isotherm. The Langmuir isotherm model presumes the formation of monolayer coverage of metal ions on the outer surface of adsorbent. The maximum adsorption capacity, which is a measure of the adsorption capacity to form a monolayer was found higher in case of Cr(III) as compared to Cr(VI) (Table 2).
The adsorption capacity of both Cr ions were found in accordance with studies for the adsorption of Cr ions for different adsorbents i.e., rose waste biomass [42], immobilized C. elegans [46], P. ostreatus biomass [65], Chlorella biomass [52], T. clupeatus biomass [44], O. americanum seeds [53], P. cryosporium dead mass [47] and banana peel [54]. Freundlich isotherm presumes the adsorption on heterogeneous surface and is not restricted to the formation of monolayer and the fractional values of 1/n suggest the heterogeneity of adsorbent surface and simultaneously indicate a favorable adsorption of Cr(III) and Cr(VI) ions onto corn cob adsorbent. However, the values of correlation coefficients ($R^2$) obtained in case...
of Freundlich isotherm model are lower than those obtained in case of Langmuir model, which indicate that the Freundlich model did not describe the adsorption of Cr(III) and Cr(VI) onto corn cob adsorbents (native and immobilized). According to Langmuir adsorption model, Cr ions adsorption occurred at homogeneous adsorption sites and intermolecular forces decreased rapidly with the distance from the adsorption surface [6,35,66]. The model further based on the assumption that all the adsorption sites are energetically identical and adsorption occurs on a structurally similar binding site.

3.8. Chromium adsorption from tannery wastewater

The conditions optimized for Cr ions adsorption from aqueous solution were employed for the adsorption of Cr from tannery wastewater. The wastewater sample was obtained from five local textile units, Kasur, Pakistan. For Cr(III) removal from tannery wastewater, the adsorption study was performed at pH 5, contact time 400 min and adsorbent dose 0.1 g, whereas for Cr(VI), pH 2.0 was adjusted and results thus obtained are shown in Fig. 5(A). Under these conditions, the Cr(III) and Cr(VI) percentage were absorbed 64.52% and 55.88% (average removal). The adsorption efficiency of immobilized was significantly higher versus native corn cob biomass for Cr ions removal from tannery wastewater, which indicates that corn cob immobilized could possibly be used for Cr sequestration from industrial effluents to avoid environmental pollution [1,67–96].

3.9. Recycling of the adsorbent

The recycling of adsorbent is important for practical applications. The reusability/recycling of corn cob immobilized biomass was estimated by running 5 adsorption–desorption cycles. Desorption of Cr ions was performed using 0.1 M NaOH solution. Cr loaded biomass was placed in contact with NaOH solution for 24 at 100 rpm shaking speed and adsorption–desorption capacities recorded are shown in Fig. 6(B and C), respectively. The Cr(VI) desorption was achieved up to 86%, whereas Cr(III) was desorbed 79.8% using 0.1 M NaOH. Then, adsorbent was again dried and subjected to next adsorption cycle and after 5 consecutive cycles, the adsorption capacity of corn cob immobilized adsorbent was reduced up to 0.98% for Cr(III) and 1.51% for Cr(VI), which revealed that corn cob immobilized biomass is stable and could be used for multiple adsorption cycles and NaOH was found to be efficient desorbing agent for Cr ions recovery.

3.10. SEM and EDX study of corn cob biomass

EDX analysis is commonly used to determine the elemental composition of the adsorbents, through which the change in the elemental composition can be overlooked of loaded and un-loaded adsorbents. The surface morphology of the loaded and un-loaded adsorbents was performed by SEM analysis. In the present study, both EDX and SEM technique was employed to monitor the elemental composition and surface morphology of loaded and un-loaded corn cob adsorbents and responses thus obtained are shown in Fig. 7. SEM anal-

Fig. 8 – EDX analysis of native and immobilized corn cob adsorbent; (A) native corn cob before adsorption, (B) immobilized corn cob biomass before adsorption, (C) immobilized corn cob after Cr(III) adsorption and (D) immobilized corn cob after Cr(VI) adsorption.
ysis clearly revealed more uniformity in loaded biomass in comparison to un-loaded biomass. It is also evident that the biomass before adsorption has an uneven surface; whereas Cr ions loaded adsorbent revealed strong crosslinking on surface cell wall matrix. Further confirmation of the adsorption of Cr ions onto corn cob biomass was done by EDX analysis and results are shown in Fig. 8 of loaded and un-loaded adsorbents. The EDX pattern before adsorption did not show the characteristic signal of chromium, whereas, after adsorption a clear signal of chromium can be observed. Based on the results, it is concluded that corn cob immobilized biomass is an efficient adsorbent and can be used for metal ions adsorption from industrial effluents.

4. Conclusions

The corn cob waste biomass was immobilized in Ca–alginate matrix and adsorption efficiency was evaluated for Cr ions adsorption. At optimized conditions of Cr ions initial concentrations, pH, dosage and contact time up to 277.57 mg/g and 208.6 mg/L Cr(III) and Cr(VI) were adsorbed onto immobilized corn cob biomass, respectively and up to 64.52% and 55.98% Cr(III) and Cr(VI) were removed from tannery effluents. NaOH (0.1 M) efficiently recovered both Cr ions and immobilized corn cob biomass showed considerable stability over five repeated adsorption–desorption cycles. Immobilization found to be a viable technique for the preparation of efficient adsorbents and could be potential adsorbents for metal ions sequestration from industrial effluents.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES

[26] Ramteke LP, Gogate PR. Removal of copper and hexavalent chromium using immobilized modified sludge biomass


