Characterization and physicochemical aspects of novel cellulose-based layered double hydroxide nanocomposite for removal of antimony and fluoride from aqueous solution

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A B S T R A C T
A series of novel adsorbents composed of cellulose (CL) with Ca/Al layered double hydroxide (CCxA; where x represent the Ca/Al molar ratio) were prepared for the adsorption of antimony (Sb(V)) and fluoride (F−) ions from aqueous solutions. The CCxA was characterized by Fourier-transform infrared spectroscopy (FTIR), Brunauer–Emmett–Teller (BET), elemental analysis (CHNS/O), thermogravimetric analysis (TGA-DTA), zeta potential, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) analysis. The effects of varying parameters such as dose, pH, contact time, temperature and initial concentration on the adsorption process were investigated. According to the obtained results, the adsorption processes were described by a pseudo-second-order kinetic model. Langmuir adsorption isotherm model provided the best fit for the experimental data and was used to describe isotherm constants. The maximum adsorption capacity was found to be 77.2 and 63.1 mg/g for Sb(V) and F−, respectively by CCa1 (experimental conditions: pH 5.5, time 60 min, dose 15 mg/10 mL, temperature 298 K). The CCa1 nanocomposite was able to reduce the Sb(V) and F− ions concentration in synthetic solutions.
solution to lower than 6 μg/L and 1.5 mg/L, respectively, which are maximum contaminant levels of these elements in drinking water according to WHO guidelines.

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Introduction

The co-existence of heavy metals, non-metals and metalloids such as fluoride, sulfate, antimony, selenium and nitrate in natural water has posed a global concern for many countries. Over the recent years, and according to World Health Organization (WHO), antimony and fluoride belong to the most significant groundwater pollutants which can cause many environmental and health problems, especially for human beings (He et al., 2014; Wu et al., 2010). Fluoride ions are introduced to groundwater mainly from natural sources. For example, the groundwater can react with the rock aquifer containing fluoride which can result in the enrichment of groundwater by fluoride ions (Bhatnagar et al., 2011). Industrial activities such as fire retardants, pigment, mining industry and ceramic can also contribute to the discharge of various toxic metals and metalloids into aquatic environments (Ayoob and Gupta, 2006; Leng et al., 2012; Li et al., 2016; Meenakshi and Maheshwari, 2006). Some areas such as China, India, Bangladesh, Mexico, Southern Tunisia, Egypt, New Zealand and Japan have suffered from high concentrations of Sb(V) and F− in groundwater (Du et al., 2014; Guissouma and Tahrhouni, 2015; Li et al., 2012; Tsering et al., 2019). However, a small amount of fluoride ions of less than 1.5 mg/L in drinking water is essential and beneficial for teeth and dental health. On the other hand, a high concentration of fluoride (> 1.5 mg/L) intake into the body causes many diseases such as skeleton fluorosis, non-skeletal fluorosis and teeth disintegration (Dayananda et al., 2014; Nell and Livanos, 1988). As for antimony, a concentration of more than 6 μg/L in drinking water poses even greater danger than fluoride due to its inherent toxic and possibly carcinogenic nature (Smichowski and Madrid, 1998; Wu et al., 2010; Zhong et al., 2020a, 2020b). The environmental behavior of Sb(V) is often similar to that of arsenic (As) (Wilson et al., 2010). Therefore, there is an urgent need for a suitable method for the removal and preconcentration of Sb(V) and F− from groundwater. Various treatment techniques such as electro-dialysis, chemical coagulation, chemical precipitation, membrane separation, photochemical degradation, ion exchange, neutralization, reverse osmosis, biological processes and adsorption have been applied for the separation of Sb(V) and F− ions from contaminated water (Bergmann and Kopolar, 2011; Chen et al., 2020; Dorjee et al., 2014; Qiusheng et al., 2015; Wang et al., 2020; Zhang et al., 2014).

Among these methods, the adsorption process has attracted the attention of researchers due to its easy operation, eco-friendliness, good selectivity, high removal efficiency and cost-effectiveness (Bessiaies et al., 2020; Iftekhar, 2019; Iftekhar et al., 2018a, 2017a, 2020; Jagtap et al., 2012; Mouelhi et al., 2016; Ramasamy et al., 2019). Different adsorbents such as activated carbon, multi-walled carbon nanotubes, bauxite, hematite, iron oxides and hydroxides, activated alumina, bone charcoal, bentonite and sodium montmorillonite have been investigated for Sb(V) and F− removal (Bhaumik et al., 2011; Das et al., 2005; Loganathan et al., 2013; Rashmi et al., 2011; Salam and Mohamed, 2013; Swain et al., 2009; Yu et al., 2014; Zhao et al., 2010). Several studies have therefore concentrated on finding an effective and low-cost sorbent with uniformly accessible pores, a bead shape, physical and chemical stability, a high surface area and high affinity for both fluoride and Sb(V).

In this context, the synthesis of nanocomposites has attracted a great deal of interest for the adsorption process because of their phenomenal electrical, barrier and mechanical properties (Iftekhar et al., 2018a; Srivastava et al., 2020). They are known as composite materials, which have at least one dimension in the nano-range (1–100 nm). Various nanocomposites have been synthesized based on inorganic and organic matrices like carbon nanotubes (Liao et al., 2017; Rashmi et al., 2011), cadmium sulfide nanoparticles (Mohamed et al., 2014), silica (Peng et al., 2006; Trivinho-Strixino et al., 2004), layered silicate (Kokabi et al., 2007) and cellulose (Zhou et al., 2013).

Cellulose is a well-known effective matrix due to its special properties: hydrophilicity, high surface area, renewability, porosity, biodegradability and low cost in removing toxic pollution (Zhou et al., 2013). Cellulose is a natural polysaccharide endowed with intramolecular hydrogen bonding and good stability and can be derivatized to yield various useful products (Mohanty et al., 2002). Layered double hydroxides (LDHs) have attracted a great deal of interest because of their features: high customization capacity and applications as catalysts, ceramic precursors, ion exchangers, absorbents, drugs, carriers, polymer stabilizers and pollution remediation sorbents. LDHs are bidimensional solids with a positive charge excess in their brucite (Mg(OH)2)-like layers and balanced with the presence of anions in the interlayer space (Borgioglio and Rojas, 2019; Hudcová et al., 2019; Kameda et al., 2015, 2017; Leroux and Besse, 2001). LDHs capacity as pollutant sorbents has been extensively reported both for inorganic (Park et al., 2007) and organic (Asif et al., 2017, 2016; Gao et al., 2018, 2017; Habib et al., 2017; Hamida et al., 2018; Hammouda et al., 2019, 2017; Koilraj and Srinivasan, 2013; Wang et al., 2019, 2018) anions. However, the application of these LDH-intercalated biopolymer nanocomposites as an adsorbent for the separation of heavy metals, non-metals and metalloids from groundwater is limited.

In this context, the goal of this study is to synthesize a series of nanocomposites (CCxA) with different molar ratio of Ca:Al and to evaluate their potential for removal of Sb(V) and F− from their aqueous solutions. The prepared nanocomposites were characterized by various techniques viz. Fourier-transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), elemental analysis (CHNS/O), thermogravimetric analysis (TGA-DTA), zeta potential, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy with
energy dispersive X-ray spectroscopy (SEM-EDX) analysis. After that, the adsorption kinetics for Sb(V) and F⁻ removal have been studied to assess the reaction rate constants. Equilibrium and thermodynamic data were also investigated to understand more about the adsorption mechanism. The stability and affinity of the sorbent were also investigated to establish the environmental application of the synthesized LDH. It should be mentioned that, up to now, CC₃A nanocomposite has not yet been used for Sb(V) and F⁻ ion removal.

1. Materials and methods

1.1. Reagents

Cotton linter cellulose (CL), urea (CH₂N₂O), sodium hydroxide (NaOH), calcium nitrate (CaCl₂), aluminum chloride hexahydrate (AlCl₃·6H₂O), hydrochloric acid (HCl), potassium hexahydroxoyantimonate(V) (KSb(OH)₆) and sodium fluoride (NaF) were obtained from Sigma Aldrich. All chemicals were of analytical grade. A 50 and 100 mg/L stock solution of Sb(V) and F⁻, respectively were prepared in 1 L of deionized water. The stock solutions were further diluted to the required concentration of Sb(V) (5 mg/L) and F⁻ (12 mg/L).

1.2. Synthesis of CC₃A nanocomposite

The solution of cellulose used was prepared by addition of NaOH:urea (7:12 V/V) with cellulose (3.24 g) in water (81 mL) for 30 min at −12°C (Solution A), according to the reported methods described elsewhere (Iftekhar et al., 2017b). Then a solution of CaCl₂ and AlCl₃·6H₂O (Ca:Al = 1:1, 2:1, 3:1, 4:1) was dissolved in 100 mL of bi-distilled water (nalloted: solution B₁, B₂, B₃ and B₄, respectively). Afterward, solution B₁ was added dropwise in solution A for 1 hr under constant stirring at 200 r/min. The mixture was stirred at 50°C for 12 hr. Finally, the suspension was cooled down to room temperature and collected by centrifugation at 4000 r/min for 10 min, washed in ethanol (50% V/V), then dried in a laboratory oven at 60°C overnight and ground to a fine powder (CC₃A) using a tube mill (IKA tube mill control). Nanocomposites with Ca/Al ratio equal (2:1, 3:1 and 4:1) were also prepared using the same method and denoted as CC₆A, CC₇A and CC₈A, respectively.

1.3. Characterization of CC₃A nanocomposite

TheFTIR spectra of the CC₃A nanocomposites were obtained using the FTIR, Vertex 70 model Bruker Optic (Germany) (4 cm⁻¹ resolution from 400 to 4000 cm⁻¹). The spectra were collected at a rate of 100 scans per sample to determine the surface functional groups. The specific surface area of CC₃A nanocomposites was evaluated using the BET from Micromeritics TriStar II plus (USA) with Vac Prep 061. The morphological characteristics of the CC₃A nanocomposites were recorded by SEM in a S-4800 Hitachi microscope (Japan) operating at 10 kV. Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were measured on a Mettler-Toledo TGA-DTA instrument (UK) under nitrogen flow in temperatures ranging from 50 to 500°C at a rate of 10°C/min. To study the surface charge potential of the CC₃A nanocomposites, zeta potential Nano zetasizer (ZEN3500, Malvern, UK) was used in the range of pH between 2 and 12. A pH meter (pH 1100 L, VWR, Germany) was used to record the initial and final pH of the solutions used.

1.4. Batch adsorption experiments

Batch adsorption experiments were carried out in order to optimize various operating parameters such as pH, nanocomposite dose, initial concentration of Sb(V) and F⁻ ion and contact time. For kinetic, isotherm and thermodynamic, experiments were performed by varying time (1 to 1440 min), concentration (5 to 85 mg/L) and temperature (298 to 318 K), respectively. The adsorption capacity of adsorbent and removal percentage (R, %) could be calculated by the following equations:

\[ q_e = \frac{(C_0 - C_e) \times V}{W} \]  
\[ R = \frac{C_0 - C_e}{C_0} \times 100\% \]

where \( q_e \) (mg/g) is adsorption amount at equilibrium, \( V \) (L) is the volume of the solute solution, \( W \) (g) is the mass of adsorbent used to perform the experiments and \( C_0 \) (mg/L) and \( C_e \) (mg/L) are the initial and equilibrium concentrations of Sb(V) and F⁻ in the solution, respectively.

1.5. Analytical methods

After Sb(V) and F⁻ adsorption equilibrium experiments, the samples were filtered using a 0.2 µm membrane filter. The samples containing Sb(V) were analyzed by inductively coupled plasma (ICP-OES) Agilent 5110 (Germany) and the analytical regression coefficient \( R^2 \) was greater than 0.998. Fluoride analysis was done by ion meter (model OR930, Orlab, India) coupled with a compatible fluoride ion-selective electrode (ISE). To prevent the interference of other ions in fluoride detection, TISAB (total ionic strength adjustment) buffer solution was used to remove the other ion interferences in fluoride analysis and was added to each aliquot at a volume ratio of 1:1. TISAB buffer solution contained 58 g sodium chloride, 57 mL glacial acetic acid and 4 g of 1.2-cyclohexylene diamine tetra acetic acid (Thakur and Mondal, 2017). The same ion meter coupled with a pH electrode was used to measure the pH of the solution and the pH of the solution was adjusted to 5.5 ± 0.1 by adding NaOH (0.5 mol/L).

2. Results and discussion

2.1. Characterization of CC₃A nanocomposite

Samples of CC₃A with different Ca/Al molar ratio were analyzed using XRD for estimating the purity and structure of the synthesized nanocomposite. The diffraction peaks (Fig. 1a) corresponding to the plane (002), (004) and (006) are the characteristic peaks of Ca/Al LDH (Granados-Reyes et al., 2016; Milagres et al., 2017). This not only confirmed that the synthesized nanocomposite was highly crystalline but also indicated the formation of hydrocalumite. In general, pure cellulose gives two diffraction peaks at the 2θ of 8.36° and 17.56°.
In this study, diffraction peaks corresponding to cellulose were not obtained (Fig. 1a), thereby indicating its intercalation in Ca/Al LDH. In a previous study by Iftekhar et al. (2017b), absence of cellulose peaks in the XRD plot was attributed to its inclusion in the structure of Zn/Al Layered double hydroxide. In addition to the hydrocalumite peaks, the XRD plot displays additional peaks (Fig. 1a) with intensity increasing with the increase in the Ca/Al molar ratio. Since CCxA cannot use or stabilize all calcium ions that were added during the synthesis process due its ionic size (i.e., 1.1 Å for Ca and 0.54 Å for Al), reaction of un-used calcium (in aqueous phase) with carbonate, which is produced following the solubilization of carbon dioxide from ambient air in water, results in the formation of calcium carbonate polymorphs (Chang et al., 2011; Milagres et al., 2017; Xu and Poduska, 2014). Based on the reasons presented above, the additional peaks in the XRD plot were detected probably due to the presence of calcium carbonate polymorphs such as aragonite and vaterite. It can be seen in Fig. 1a that such peaks are mainly found in CCxA samples, while the intensity of such peaks are quite low in other samples.

Fig. 1b illustrates the FTIR spectrum of the samples between 4000 and 400 cm⁻¹. The broad peaks in a range of 3300–3500 cm⁻¹ are likely associated to the presence of O–H stretching (Barathi et al., 2013; Wu et al., 2011), and that at 1660–1682 cm⁻¹ is attributed to the bending vibration of OH group (Biswas et al., 2007). The FTIR bands at 1440–1620 cm⁻¹ were related to the symmetrical and asymmetrical stretching vibrations of the carboxylate groups (Rosca et al., 2005). There were other absorption peaks at 1153 and 1163 cm⁻¹ for C–O–C from the glucosidic linkage of the cellulose biopolymer (Zhu et al., 2016). The peaks in the low-frequency region i.e. below 1000 cm⁻¹, except for carbonate peak that is observed in the region, was related to the M-OH vibrations and O-M-O stretching (where M = Ca and Al) (Iftekhar et al., 2018a; Wang et al., 2011).

The surface area of CCxA nanocomposites with different ratios of Ca/Al was measured using BET. It is evident from the results presented in Table 1 that increasing the Ca contents in CCxA leads to an increase in the surface area of nanocomposites which is probably due to increase in the replacement of Al ions in Al(OH)₃ by Ca ions. Further increase in Ca contents resulted is damaging the positively charged hydroxylated sheets developed by replacements of Al ions by Ca and thus the surface area decreased in CCxA nanocomposite. Likewise, increasing the Al contents though improve the net positive charge of the LDH layers, at some point, may lead to the disordering of LDH layers or the phase change due to radius difference between Ca and Al ions. Results also suggest that all samples show type III with H3 hysteretic loop isotherm, indi-
cating the presence of mesoporous materials comprising aggregates of plate-like particles. Chemical composition of the samples obtained by ICP and CNHS/O analyses is given in Table 1. It is clear that the obtained values Ca/Al molar ratio is in good agreement with the theoretical value.

The thermal analysis (TGA-DTA) was assessed to determine the thermal stability of the prepared material. It is obvious from Fig. 1c that similar observations were made for the TGA analysis of all different samples CC2A. The TGA-DTA curve of CC2A with different ratio (Fig. 1c) shows two steps of thermal decomposition, which occur as endothermic processes. The weight loss around 100°C was related to the physical evaporation of adsorbed water. The two mass losses register in the range of 290–520°C should correspond to the decomposition of the interlayer CO3²⁻ anions with dihydroxylation of the LDH sheets. These results obtained are similar to the previous study reported by Elmoubarki et al. (Elmoubarki et al., 2017). The weight loss at ~700°C, indicating the occurrence of carbonation during synthesis. The total mass losses of the samples are approximately 87.5, 90, 95 and 95 wt.% for CC1A, CC2A, CC3A and CC4A, respectively. The decomposition temperature of CC2A was 515.19°C while, for CC1A, CC2A and CC4A, they were 486.81, 499.71, 510.19°C, respectively. This proves that CC3A has higher thermal stability (Wu et al., 2011).

The zeta potential of CC2A without adsorbed species is given in Fig. 1d. The pHzpc values were listed in Table 1, and the surface charge of all samples is positive when pH > pHzpc and was negative at a solution pH higher than pHzpc.

Fig. 2 represents the structural and morphological changes in native cellulose, CC2A before and after adsorption. It is clear from the SEM images (Fig. 2a-d) that the nanocomposites are indicating a heterogeneous surface with agglomerated particles, which reveals the existence of the intercalated structure. It can be shown that the morphology of the CC2A nanocomposite presents a highly porous structure compared to the other samples. Also, the EDX spectrum in Appendix A Fig. S1a-d before F⁻ and Sb(V) adsorption confirms the existence of C, O, Al and Ca elemental peaks. The SEM images (Fig. 2e-f) after adsorption of Sb(V) and F⁻ onto CC2A showed different morphology indicating the surface is deteriorated and the total amount of elements also differs according EDX spectrum (Appendix A Fig. S1). The amount of Ca initially decreased which is attributed to the leaching of Ca during adsorption of Sb(V) and F⁻ onto CC3A. Likewise, the amount of C and O also decreased after adsorption which complemented the results of FTIR regarding the formation of outer-sphere complexes influenced by an anion exchange mechanism. Additionally, a significant amount of Sb(V) and F⁻ onto CC2A was observed in the EDX spectrum.

### 2.2. Adsorption performance

#### 2.2.1. Effect of the Ca/Al ratio

The effect of different Ca/Al molar ratio in the synthesis material CC2A was investigated at temperature (25°C) and contact time 1440 min. The concentration 5 and 12 mg/L of Sb(V) and F⁻ ions, respectively were treated with 10 mL 1 g/L of CC2A. It is clear from Appendix A Fig. S2 that the material CC2A with the Ca/Al ratio of 3 showed maximum adsorption for both Sb(V) and F⁻. Further, an increase in ratio results in a decrease of adsorption capacity. The amount of adsorption increased with increasing the Ca/Al ratio, with decreasing in the same time the content of Al ion in the compound, which explains by the fact that the Al ions presented in the brucite like layer produce the anion exchange site. The above results indicate the adsorption of Sb(V) and F⁻ ions at the hydroxyl groups of Ca which was positively charged due to replacements of trivalent ions Al with divalent ones Ca. The obtained results obtained are similar to the previous studies described elsewhere for cellulose-Zn/Al-LDH (Iftekhar et al., 2017b) and Zn-Al base LDH calcined at 200°C (Z3A200) (Iftekhar et al., 2018d). On the other hand, the further addition of Ca/Al leading to the disordering of the anionic clay (LDH) due to the difference of ionic sizes of Ca and Al, which explain the decrease in adsorption. Consequently, the adsorption experiments were carried out with CC2A nanocomposite prepared using a ratio of 3:1 of Ca/Al.

#### 2.2.2. Effect of adsorbent dosage

The effect of the CC2A adsorbent dose on the removal of Sb(V) and F⁻ at natural pH is evaluated, and the results are illustrated in Fig. 3, in which the removal percentage and adsorp-
**Fig. 2** – Scanning electron microscopy (SEM) images of (a) CC1A, (b) CC2A, (c) CC3A, (d) CC4A, and CC3A after (e) F− and (f) Sb(V) adsorption.

**Fig. 3** – Adsorption of Sb(V) and F− on CC3A nanocomposite as a function of (a) dose, (b) pH, (c) reaction time, and (d) initial concentration (C0). $q_e$: adsorption capacity; $R$: removal percentage.
tion capacity of Sb(V) and F\textsuperscript{−} are plotted against adsorbent dose. The experiments were conducted using amounts of adsorbent ranging from 7 to 25 mg in 10 mL sample volume for 1440 min. It can be seen that Sb(V) and F\textsuperscript{−} removal increases for higher dosage while loading capacity gradually decreased for the same. This may be due to the increase in active sites. It is also obvious that the percentage removal of increase from 82.4\% to 96.6\% for Sb(V) and from 80.33\% to 94.71\% for F\textsuperscript{−} while adsorption capacity gradually decreases from 5.88 to 3.22 mg/g for Sb(V) and from 13.77 to 7.57 mg/g for F\textsuperscript{−} as the dose increased from 7 to 15 mg in 10 mL solution. Beyond 15 mg, there was no appreciable increase in removal, mainly related to the saturation of the active adsorption sites.

It should be mentioned that the permissible limit of Sb(V) and F\textsuperscript{−} in drinking water according to WHO of 6 μgL/L and 1.5 mg/L, respectively, was attained at a CC\textsubscript{3}A dose of 10 mL (1.5 g/L), so the mentioned dose was considered an optimal dose for both Sb(V) and F\textsuperscript{−} removal.

2.2.3. Effect of initial pH
The solution pH is an important parameter in the control of the adsorption process. About 15 mg of CC\textsubscript{3}A adsorbent was added to 10 mL of 12 mg/L F\textsuperscript{−} and 5 mg/L Sb(V) solutions and the pH was fixed from 1.8 to 11.54 by keeping all other parameters constant (temperature 25 ± 2°C, shaking speed 250 r/min and contact time 1440 min). The experimental data are presented in Fig. 3b. It is obvious from Fig. 3b, that F\textsuperscript{−} ion removal is not affected in the wide pH range of 1.8-11.54 for CC\textsubscript{3}A. It can be suggested that F\textsuperscript{−} ion adsorption on CC\textsubscript{3}A is not a purely physiosorption phenomenon, and perhaps there is the appreciable contribution of chemisorption and even a chemical process, leading to the partial formation of aluminum-fluoride and calcium fluoride species. Therefore, it can be said that the removal of F\textsuperscript{−} ion with CC\textsubscript{3}A material is not pH-dependent compared to the other adsorbent, i.e. activated alumina (Tripathy et al., 2006).

On the other side, it was known, that the most inorganic forms of antimony species were (Sb(OH))\textsuperscript{5−} in the pH range of 3–11 (Guo et al., 2014). However, in extreme acidic conditions (pH below 2) Sb(V) species were positively charged (Mishra et al., 2016). As can be seen from Fig. 3b, the adsorption of Sb(V) was maximum between pH 3 and 8 (pH\textsubscript{pzc} i.e. zero point charge), mainly due to the electrostatic attraction between the negatively charged (Sb(OH))\textsuperscript{5−} ion and the positively charged of surface material CC\textsubscript{3}A. Further increase in pH (pH\textsubscript{pzc}) results in a decrease in adsorption, explained by the repulsion between the negatively charged antimonate species Sb(OH))\textsuperscript{5−} and negatively charged of surface sites. It should be mentioned that other researchers found the same results as Li et al. (2012) studied the removal of Sb(V) from aqueous solution by iron-based adsorbents. Besides, the decrease in adsorption of Sb(V) ions with pH below 2 mainly due to the repulsion between the positively charged antimonate species and positively charged surface. Therefore, the experiments will be performed at pH = 4.5 (±0.2) for adsorption of Sb(V) and at natural pH (5.87) for adsorption of F\textsuperscript{−} onto CC\textsubscript{3}A nanocomposite.

2.2.4. Effect of reaction time
It is clear from Fig. 3c that the removal of both Sb(V) and F\textsuperscript{−} ion increase with an increase in run time. Removal of 79% Sb(V) is achieved in 10 min operation and increases to 99.8\% at 45 min and afterward, no appreciable increase in removal is observed. On the other hand, the removal of F\textsuperscript{−} was very fast. Almost 88\% was achieved in the first 10 min of process and then increased to 93.07\% at 45 min. At run time 45 min, 93.07\% of F\textsuperscript{−} removal gives a residual F\textsuperscript{−} concentration of 0.80 mg/L (< 1.5 mg/L: maximum contaminant level for F\textsuperscript{−} according to WHO guidelines), while Sb(V) removal does not achieve WHO drinking water guidelines. Hence according to the experimental data, for the removal of 100% Sb(V) (residual concentration ≤ 6 μgL/L), we must select 60 min (time phase) for all other adsorption experiments.

2.2.5. Effect of initial Sb(V) and F− concentration
Fig. 3d illustrate the effect of initial concentration (C\textsubscript{0}) on the removal of Sb(V) and F\textsuperscript{−}. Initial concentration was varied from 5 to 85 mg/L by keeping all other parameters constant. It can be noted that with the increase in initial Sb(V) and F− concentration, adsorption capacity also increases, while the removal of Sb(V) and F− on CC\textsubscript{3}A decreases. This observation is obvious due to the availability of a higher number of Sb(V) and F− ions at a higher concentration gradient. In this case, most of the adsorbent sites were occupied and ions left un-adsorbed in the solution. It can be said that the present material has good prospects for the filtration of high Sb(V) and F− concentration.

2.2.6. Effect of temperature and adsorption thermodynamics
The novel adsorbent was evaluated at different temperatures to assess the feasibility and spontaneity of the adsorption process. It is shown in Appendix A Fig. S4a that increasing temperature from 298 to 318 K for Sb(V) and F\textsuperscript{−} does not affect the removal of both Sb(V) and F\textsuperscript{−} onto CC\textsubscript{3}A, so 298 K was chosen as the optimum temperature in the following experiments.

The thermodynamic parameters such as the standard enthalpy change (\Delta\text{H}\textsuperscript{°}), standard entropy change (\Delta\text{S}\textsuperscript{°}) and standard free energy change (\Delta\text{G}\textsuperscript{°}) can be computed using the following equations (Iftekhar et al., 2018d, 2018c; Srivastava et al., 2018):

\[ \Delta G\textsuperscript{T} = -RT \ln K_{ads} \]  

(3)

\[ K_{ads} = \frac{C_{eq, solid}}{C_e} \]  

(4)

where \( K_{ads} \) (L/g) is thermodynamic equilibrium constant, \( C_{eq, solid} \) (mg/g) is solid-phase concentration of ions at equilibrium, \( C_e \) (mg/L) is equilibrium concentration of Sb(V) and F\textsuperscript{−} in solution, \( R \) (8.314 J/(mol·K)) is universal gas constant and \( T \) (K) is temperature.

The values of enthalpy change (\Delta\text{H}\textsuperscript{°}) and entropy change (\Delta\text{S}\textsuperscript{°}) are obtained from the slope and intercept of the following Eq. (5):

\[ \ln K_{ads} = \frac{\Delta S\textsuperscript{T}}{R} - \frac{\Delta H\textsuperscript{T}}{RT} \]  

(5)

The results are illustrated in Appendix A Fig. S4b, where it can be seen that the plot of \( \ln K_{ads} \) vs 1/T is linear. The experimental data of thermodynamic constants are given in Table 2. It can be found that all \( \Delta G\textsuperscript{°} \) values were negative for Sb(V) and F\textsuperscript{−} over CC\textsubscript{3}A nanocomposite, which indicates the feasibility
and spontaneous nature of the adsorption process. The negative values of $\Delta H^\circ$ for Sb(V) also confirm the exothermic nature of the adsorption, whilst the values of $\Delta H^\circ$ were positive for F$^-$, indicating the endothermic nature of the adsorption. The positive values of $\Delta S^\circ$ for F$^-$ can also be explained by the exchange of ions with more mobile ions present on the exchanger, and this may be due to a rise in entropy during the adsorption process (Sert et al., 2008).

The activation energy ($E_a$) of adsorption at various temperatures can be estimated from the relation of $E_a = \Delta H^\circ + RT$ (En and Escuela, 2012). The average energy of activation was measured at 26.21 kJ/mol for Sb(V) and -25.22 kJ/mol for F$^-$. 

### 2.2.7. Adsorption kinetics

It is apparent from Fig. 3c that about 50% of the adsorbed Sb(V) and F$^-$ ions at equilibrium took place during the first 5 min of the reaction, indicating high initial adsorption rates for the adsorbents. After 30 min, the rate of adsorption slowed down until equilibrium was reached within 60 min.

To identify the dynamic of the Sb(V) and F$^-$ adsorption process, it is necessary to investigate the adsorption kinetics by the linear fitting method using Lagergren's pseudo-first-order (Eq. (6)) (Iftekhar et al., 2018b, 2018c, 2018e) and Ho's pseudo-second-order (Eq. (7)) (Ho and Mckay, 1999; Iftekhar et al., 2018b, 2018c, 2017b).

#### Pseudo-first order equations:

$$ \log (q_t - q_e) = \frac{k_1 t}{2.303} $$  \hspace{1cm} (6)

#### Pseudo-second order equations:

$$ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} $$  \hspace{1cm} (7)

where $t$ (min) is time, $q_e$ and $q_t$ (mg/g) are the adsorption capacity of Sb(V) and F$^-$ onto CC3A at equilibrium and at time $t$, respectively; $k_1$ (min$^{-1}$) and $k_2$ (g/(mg·min)) are rate constants for pseudo-first-order and pseudo-second-order, respectively.

The value of parameters and correlation coefficient $R^2$ of the pseudo-first-order and pseudo-second-order kinetic model are presented in Table 3. As indicated in Table 3, the correlation coefficient $R^2$ was higher with the pseudo-second-order equation for Sb(V) and F$^-$ adsorption on CC3A. Furthermore, the $q_e$ calculated from pseudo-second-order kinetic models are very close to the experimental results. According to these results, it can be said that adsorption of F$^-$ and Sb(V) over CC3A obey the pseudo-second-order kinetic, which confirm the assumption of chemisorption including, the exchange between the adsorbate and adsorbent (Zhu et al., 2015).

In order to understand the kinetic behavior of the adsorption process, the intra-particle diffusion model was used to verify the diffusion mechanism of the adsorption process and it is represented by the following equation (Eq (8)):

$$ q_t = k_1 t^{1/2} + C $$  \hspace{1cm} (8)

where $k_1$ (mg/(g·min$^{1/2}$)) is the intra-particle diffusion constant and C is a constant.

The plot of intra-particle diffusion shows multiple steps which controlled Sb(V) and F$^-$ adsorption on CC3A at different time intervals (Appendix A Fig. SS5c). The first linear step indicates the diffusion adsorption stage, which mean the adsorption of Sb(V) and F$^-$ onto the external surface of CC3A. The second step indicates the intra-particle diffusion of Sb(V) and F$^-$ ions through the pores of CC3A. The final linear step describes the equilibrium adsorption stage. Based on the results in Appendix A Fig. SS5c, we assume that the surface adsorptions, as well as intra-particle diffusion, seem significant in the rate-controlling step.

### 2.2.8. Adsorption isotherms

It was important to ascertain the adsorption performance of CC3A nanocomposite. The equilibrium data by non-linear fit was studied using Langmuir, Freundlich, and Temkin models. The equations are given below:

**Langmuir model** (Gases, 1918):

$$ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} $$  \hspace{1cm} (9)
Freundlich model (Ghosh et al., 2014):

\[ q_e = K_T \left( \frac{C_e}{q_m} \right)^{1/n} \]  

(10)

Temkin model (Barathi et al., 2013):

\[ q_e = B_T \ln(K_T C_e) \]  

(11)

where \( q_m \) (mg/g) is the maximum amount of adsorbate, \( C_e \) (mg/L) is the equilibrium concentration of metal ions in solution, \( K_L \), \( K_T \) and \( K_T \) (L/mg) are the isotherm constant, \( n \) is the heterogeneity factor of adsorption, \( B_T = \frac{R}{\rho T} \) is the factor related to the heat of adsorption, and \( b_T \) (kJ/mol) is the variation of adsorption energy.

Data fitted with the Langmuir, Freundlich and Temkin isotherms models for removal of Sb(V) and F⁻ ions onto CC₃A are represented in Fig. 4a-d and the values are listed in Table 4. Based on the highest correlation coefficient \( (R^2) \) value and lowest Chi-square \( (\chi^2) \) for these isotherms models, it can be concluded that Sb(V) and F⁻ removal with CC₃A achieved the best fit with the Langmuir \( (R^2 = 0.98, 0.99) \) model, so the monolayer adsorption nature of Sb(V) and F⁻ onto CC₃A can be proposed. The maximum adsorption capacity estimated for Sb(V) and F⁻ were found to be 77.72 and 63.11 mg/g, respectively. It can be stated that the present sorbent has good prospects for removing F⁻ and Sb(V) from groundwater. Also, the \( R_L \) (separation factor) values lying in the range 0–1 suggest favorable adsorption for Sb(V) and F⁻. The multisolute Freundlich parameter \( (n) \) for Sb(V) and F⁻ onto CC₃A are greater than unity \( (n > 1) \), indicating a favorable adsorption process. This in agreement with the data proposed before as per the Langmuir model.

![Fig. 4](image-url) Adsorption isotherms of Sb(V) and F⁻ on CC₃A: (a) Langmuir, (b) Freundlich, and (c) Temkin. CC₃A: equilibrium concentrations of Sb(V) and F⁻.

<table>
<thead>
<tr>
<th>Adsorption isotherm model</th>
<th>Parameters</th>
<th>CC₃A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sb(V)</td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td>77.72</td>
</tr>
<tr>
<td></td>
<td>( q_m ) (mg/g)</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>( K_L ) (L/mg)</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>( R_L )</td>
<td>0.56–0.08</td>
</tr>
<tr>
<td></td>
<td>( \chi^2 )</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>( K_T ) (L/mg)</td>
<td>6.38</td>
</tr>
<tr>
<td></td>
<td>( n )</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>( b_T ) (kJ/mol)</td>
<td>0.88</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>( K_T ) (L/mg)</td>
<td>3.39</td>
</tr>
<tr>
<td></td>
<td>( \chi^2 )</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.88</td>
</tr>
<tr>
<td>Temkin</td>
<td></td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>( K_T ) (L/mg)</td>
<td>3.39</td>
</tr>
<tr>
<td></td>
<td>( \chi^2 )</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.88</td>
</tr>
</tbody>
</table>

\( q_m \): maximum adsorption capacity; \( K_L \): Langmuir isotherm constant; \( \chi^2 \): chi-square; \( R_L \): separation factor; \( K_T \): Freundlich constant; \( n \): heterogeneity factor of adsorption; \( b_T \): the variation of adsorption energy; \( K_T \): Temkin constant.
To further understand the adsorption mechanism, the elemental composition of CC$_3$A adsorbent before and after Sb(V) and F$^-$ adsorption was investigated by XPS analysis and the results are presented in Fig. 5b. The peaks correspond to the elements Ca, Al, C and O are clearly shown in the full scan spectrum. The deconvolution of C1s spectra resulted in peaks at 289.38, 287.89, 286.3 and 284.7 eV corresponding to carboxyl (-COOH), carbonyl (C=O), C-O and C=C, respectively (Ahmad et al., 2017; Ganguly et al., 2011). The O1s peaks for CC$_3$A appeared at 530.4, 531.6, and 532.4 eV assigned to surface carboxyl, hydroxyl and carboxyl groups. The binding energy peaks at 532.4 eV is associated with metal-oxygen either as M-OH or M-O (M = Ca, Al) (Zhang et al., 2019). Compared between the spectra before and after Sb(V) and F$^-$ adsorption, the broad peaks of Sb3d and F1s appeared at 544.54 and 682.91 eV, respectively, which confirm the adsorption of Sb(V) and F$^-$ onto the surface of CC$_3$A. The schematic illustration of Sb(V) and F$^-$ anion adsorption on CC$_3$A is displayed in Scheme 1.

### 2.2.10. Comparative assessment of Sb(V) and F$^-$ with other adsorbents

The performance of this novel adsorbent in Sb(V) and F$^-$ removal was evaluated by comparing it with some materials available in the literature (Table 5). According to the adsorption capacity value in Table 5, it can be concluded that the

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**Fig. 5** – (a) FTIR and (b) X-ray photoelectron spectroscopy (XPS), C1s and O1s scan of CC$_3$A (c) before and (d) after Sb(V) and F$^-$ adsorption.
Scheme 1 – Schematic illustration of Sb(V) and F⁻ ions adsorption on CC₃A. The color balls in the structure of CC₃A represents C, H, O, Al, and Ca for gray, white, red, pink, and blue, respectively.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption Capacity (mg/g)</th>
<th>Adsorption conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Zr impregnated cellulose biopolymer adsorbed (Barathi et al., 2013)</td>
<td>–</td>
<td>C₀ 5 mg/L, pH 5.5, dose</td>
</tr>
<tr>
<td>Iron (III)-aluminum(III)-chromium(III) mixed oxide (Biswas et al., 2010)</td>
<td>–</td>
<td>30 mg/50 mL, time 60 min</td>
</tr>
<tr>
<td>Hydrous Ce(IV)+Zr(IV) mixed oxide (Ghosh et al., 2014)</td>
<td>–</td>
<td>C₀ 10 mg/L, pH 5.6, dose</td>
</tr>
<tr>
<td>La(III)-Al(III) loaded scoria adsorbent (Zhang et al., 2014)</td>
<td>–</td>
<td>0.2 g/50 mL, time 90 min</td>
</tr>
<tr>
<td>Iron-based adsorbent (Li et al., 2016)</td>
<td>58.89</td>
<td>C₀ 10 mg/L, pH 5.8, dose</td>
</tr>
<tr>
<td>Iron-Zirconium bimetal oxide (Li et al., 2012)</td>
<td>51</td>
<td>50 mg/50 mL, time 60 min</td>
</tr>
<tr>
<td>Kaolinite (Xi et al., 2010)</td>
<td>0.059</td>
<td>C₀ 4.89 mg/L, pH 7.2, dose</td>
</tr>
<tr>
<td>Hydrated ferric oxides (Miao et al., 2014)</td>
<td>39.9⁺</td>
<td>10⁷ mg/50 mL, time 300 min</td>
</tr>
<tr>
<td>Hydrated ferric oxides supported by calcite sand (IOCCS); Hydrated ferric oxides supported by polymeric anion exchanger (HFO-201).</td>
<td>60.9⁺</td>
<td></td>
</tr>
<tr>
<td>CC₃A (this study)</td>
<td>77.72</td>
<td>C₀ 20 mg/L, pH 5, dose</td>
</tr>
<tr>
<td></td>
<td>63.11</td>
<td>3 mg/100 mL, time 90 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 mg/100 mL, time 90 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₀ 1 mg/L, pH 6, dose</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 mg/20 mL, time 1440 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₀ 5 mg/L, pH 6, dose</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 mg/100 mL, time 1440 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>303 K</td>
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<tr>
<td></td>
<td></td>
<td>303 K</td>
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<tr>
<td></td>
<td></td>
<td>303 K</td>
</tr>
</tbody>
</table>

⁺ Hydrated ferric oxides supported by calcite sand (IOCCS).
⁻ Hydrated ferric oxides supported by polymeric anion exchanger (HFO-201).
present material shows good prospects for the removal of Sb(V) and F⁻.

3. Conclusions

In the present study, a series of Ca:A LDH intercalated cellulose biopolymer (CC₆A) was synthesized by varying the molar ratio of Ca:Al. CC₆A was characterized as a mesoporous material with the formation of a sheet-like structure of LDH. EDX spectra proved the presence of F⁻ and Sb(V) along with the other major peaks such as C, O, Al and Ca, respectively. This product indicated the highest capacity (77.72 and 63.11 mg/g) for removal of antimony (Sb(V)) and F⁻ ions, respectively. Equilibrium was attained in 60 min for Sb(V) and F⁻. The adsorption isotherm was fitted by the Langmuir isotherm, indicating monolayer adsorption. The pseudo-second-order kinetic model provides the best correlation (R² = 0.99, 1) for Sb(V) and F⁻, respectively. The negative values of ΔG° indicate the spontaneity of the adsorption of F⁻ on CC₆A nanocomposite. Furthermore, the positive value of ΔH° indicates that the adsorption of F⁻ was endothermic. The thermodynamic analysis also indicated the exothermic and spontaneous nature of the adsorption process for Sb(V). Batch adsorption experiments of 10 ml samples conducted with 15 mg of CC₆A reduced the Sb(V) and F⁻ levels from 5 to 12 mg/L to well below the maximum allowable limits (0.006 and 1.5 mg/L, respectively). Overall, the various tests conducted in this study reveals that CC₆A can be applied as a promising adsorbent for effective and simultaneous removal of Sb(V) and F⁻ from contaminated water sources.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jes.2020.09.034.

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