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Paperboard Mill Sludge Derived Nanocellulose as a Biosorbent for Hexavalent Chromium

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ABSTRACT

In the present study, paperboard mill sludge derived nanocellulose as biosorbent for removal of hexavalent chromium from simulated aqueous solution prepared from potassium dichromate. The adsorbents namely, CA-NC and FA-NC were prepared through citric and formic acid hydrolyses of the nanocellulose. The prepared sorbents were utilized for the adsorption of Cr(VI), with parameters such as pH, adsorbent dosage, solute concentration and contact time played pivotal role in the study. The ideal circumstances of these parameters to perform well were notably pH of 2, with adsorbent dose of 1.5 g, solute concentration of 100 $mg \cdot L^{-1}$, with a contact duration of 60 minutes. The adsorption followed pseudo second order reaction and fitted the Langmuir isotherm model indicating chemisorption coupled with monolayer adsorption of adsorbate onto the adsorbent.

Keywords: Cr(VI), adsorption, sludge, nanocellulose, paperboard mill.

INTRODUCTION

The development of the global economy is significantly influenced by industrialization. There is an enormous quantity of organic matter as waste generated during the recycling of paper that is unable to be utilized in the manufacture of new paper. Arguably the worst environmental issue is the massive amount of sludge that paper mills with heavy paper usage produce. Sustainability issues caused by the growing volume of sludge and the remedial measures that follow are extremely critical. Waste remnants derived from primary treatment, biological treatment, and recycling paper streams are produced in the pulp cum paper manufacturing units (Kaur et al., 2020). These paper and its related industries are anticipated to yield 402.790 Mt of paper and board and 184.4 Mt of pulp annually on a global scale (Turner et al., 2022). As a result, nearly 400 million wet tonnes of sludge from pulp and paper mill is produced annually throughout the world.

In general, 35% remnants is generated when the raw material is used for pulp and paper mills, 56% is used for recovery of energy, allowing 44% of the remainder lacking an economical or ecologically feasible solution (Bajpai, 2015). Since the majority of these by-products cannot be processed and repurposed, they are disposed in an environmentally damaging manner, thus posing a danger for soil and water contamination. A large portion of the agricultural waste is left on the field itself and functions as a manure or soil protector. But even with this activity, a lot of wastes are either burned or buried in waste disposal facilities, which again pollutes the earth and the air.

Even though pulp and paper wastes are not as dangerous as that of other industrial wastes, managing the land, the environment, and related issues requires the use compatible management strategies (Bajpai, 2015). Due to the use of various pulps, fillers, coating materials, pigments, and many other impurities, paper residues have a more complex composition than those found in agro-industrial residues. Despite its complex nature, this waste has the potential to be recycled because, even with the impurities, it is mostly comprised of chemical and mechanical pulps and recovered paper (78%), and it contains a high carbon content (Reshmy et al., 2022). Chromium is primarily present in the effluents of tanneries, electroplating, dyeing, metallurgy, etc. The amount of chromium which is declared as maximum contaminant level (MCL) that marks it as hazardous to the environment is 0.05 $mg \cdot L^{-1}$ (Awang et al., 2021). High concentrations of chromium in aquatic systems leads to skin related diseases such as dermatitis, ulcers. On the other hand, chromium on inhalation causes irritation in the pulmonary tract, etc. Apart from this, prolonged exposure to hexavalent chromium leads to malfunctioning of various internal organs – kidneys, liver, gastro intestinal tract, heart, and a potential carcinogenic and mutagenic agent, etc. (Hossini et al., 2022).

Water scarcity is a pressing issue, compelling to find ways and means to treat industrial wastewaters for its reuse in manufacturing, irrigation, etc. (Devi et al., 2011). Predominant methods of treating effluents for the removal of heavy metals is chemical precipitate separation, filtration using membrane set-up, ion exchange methodology, electrodialysis, and adsorption (Awang et al., 2021). It is to be noted that in all the methods mentioned except the adsorption method, there are costs involved with respect to electricity employment, which might add to expenses for treating. Adsorption is defined as transfer of ions along with its mass from heavy metal ions present in the liquid to the adsorbent surface. It is believed to be an apt method for heavy metal removal from industrial effluents (Dev et al., 2022). In general, the adsorbents used in conventional methods of heavy metal removal are organic materials like chitosan, activated carbonaceous substances, carbon nanotubes, sawdust while inorganic materials like zeolites, silica based adsorbents, metallic oxides and clay (Singh et al., 2021).

The current study focuses on using nanocellulose extracted from paperboard mill sludge was employed in the wastewater treatment, with special reference to heavy metal, chromium in particular. Trivalent and hexavalent chromium are observed in tannery effluents which focus on chrome-tanning the hides to prepare leather. Hence, to mimic the tannery wastewater, chromium solutions were prepared in the laboratory.

MATERIALS AND METHODS

Paperboard mill sludge was collected from the primary clarifier of the Effluent Treatment Plant (ETP) of recycled paper based paper mill located at Coimbatore, India. The sludge sample was then treated with 9:1 of 3M citric acid:concentrated hydrochloric acid reactant mixture in order to obtain cellulose through hydrolysis (modified method of (Yu et al., 2016). In another method, formic acid was used to hydrolyze the sludge sample for extraction of cellulose (modified method of (Du et al., 2016). Thus, obtained cellulose samples from these two methods were ball milled using zirconia metal balls for synthesis of nanocellulose. The nanocellulose through citric acid digestion is called citric acid nanocellullose (CA-NC), while the nanocellulose formed from formic acid hydrolysis is called formic acid nanocellulose (FA-NC). Dialdehyde nanocellulose (DAC) was formed through treatment with sodium periodate ($NaIO_4$) and later it was quenched with ethylene glycol. This oxidation process paved way for the surface functionalization of DAC using Girard's T reagent, which resulted the cationic DAC (cDAC) (Sirviö et al., 2014). Several studies have confirmed that cDAC have the potential in the removal of pollutants such as heavy metals, dyes, oils, radionuclides, etc. from wastewaters (Dev et al., 2022).

Preparation of adsorbate solution

Standard Cr(VI) adsorbate solution was initially prepared for 1000 $mg \cdot L^{-1}$ concentration by using and 2.83 g of $K_2Cr_2O_7$ (AR grade) in one litre of deionized water. Working standard aqueous solution was then prepared from this stock solution resulted in a series of adsorbate solutions at different concentrations.

Batch experiments

A preliminary study consisting of batch experiments were done to examine the adsorption

potential of the adsorbents in relation to variables like pH, adsorbent dose, solute concentration, and contact time. Four replications of the batch trials were carried out using a completely randomized design. Statistical analysis was carried out in SPSS for the ANOVA. Optimization study was done for hexavalent chromium adsorption from synthetic solution for the following factors such as solution pH, adsorbent dose, contact time and solute concentration are described below.

Solution pH vs Cr adsorption

Erlenmeyer flasks (250 ml) were filled with 100 ml each of Cr(VI) solution with a 200 mg·L^{-1} concentration, and the pH of the adsorbate was changed from 1 to 9 by using 1N NaOH or 1N HCl. 2 g of the adsorbent (nanocellulose) was added to each flask. For 24 hours, the suspension was kept in a shaker with a rotary motion at 250 rpm and 25 °C. Following that, Whatman no. 42 filtration and centrifugation (8000 rpm for 10 minutes) were applied to the samples. MP-AES (Perkin Elmer-AA400) was used to measure the remaining chromium (Cr) ion concentration.

Adsorbent dose vs Cr adsorption

The influence of nanocellulose dose on Cr adsorption was examined using batch technique because the dosage of the adsorbent plays a significant role in Cr adsorption by creating binding sites for adsorption. Adsorbent was allowed to come into contact with adsorbate (200 mg L^{-1}) of 100 ml with pH adjustment, and the reaction mixture was maintained and analysed as mentioned in the section above.

Solute concentration vs Cr adsorption

In a batch experiment, 100 ml of Cr(VI) solutions of various strengths, from 100 to 1000 mg L^{-1} with modified pH, were added into flasks comprising 2 g of adsorbent. As described in the section above, the reaction mixture was maintained and examined.

Removal efficiency

The preceding equation was used to compute the effectiveness of chromium removal in the adsorption studies:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where: C_0 – denotes the initial concentration of Cr(VI) (mg L^{-1}); C_e – denotes the concentration of Cr(VI) after adsorption process (mg·L^{-1}).

The subsequent equation was used to calculate adsorption capacity:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where: q_t – the adsorbed amount after time t; C_0 – the initial concentration of metal ions (mg ·L^{-1}); C_t – the concentration of metal ions after time t (mg·L^{-1}); V – the volume of the solution (L); and m is the adsorbent weight (g).

Adsorption isotherm for Cr(VI) adsorption

The Langmuir adsorption isotherm model remains valid when the adsorbate forms just one film on the surface of the adsorbent, which is specified by the following equation.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where: q_e – the quantity of Cr adsorbed per gram of adsorbent at equilibrium, C_e – the concentration of chromium at equilibrium (mg·L^{-1}), and K_L – the constant denoting the affinity of active binding regions (L ·mg^{-1}), q_m – the maximal monolayer coverage capacity. The intercept and slope of a plot between C_e/q_e vs. C_e and the values of q_m and K_L were used to determine these values (Langmuir, 1918).

The preceding equation represents the Freundlich isotherm equation, which is frequently used to describe adsorption on heterogeneous surfaces (Dada et al., 2012).

$$q_e = K_F C e^{1/n} \quad (4)$$

where: n – represents the amount of the adsorbent and K_F gives the adsorption capacity constant (mg·g^{-1}). The information about n and K_F is provided by the slope and intercept of the Freundlich plot of log q_e vs. log C_e. The size of 'n' exponential value indicates the benefit of adsorption.

Adsorption kinetics for Cr(VI) adsorption

The pseudo first order equation or Lagergren Rate Equation is represented as:

$$\log(q_e - q_t) = \log q_e - (K_1/2.303) \times t \quad (5)$$

where: q_e and q^t – the amount of chromium adsorbed at equilibrium and time t, respectively (mg·g^{-1}), and $K1$ – the pseudo-first-order adsorption rate constant. T employed to plot a graph against the resultant value of log ($q_e - q_t$). K_1 and q_e from the ensuing linear connection were calculated using the slope and intercept of the plot (Abechi et al., 2011).

The following formula provides the pseudo--second order kinetic formula:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (6)$$

where: K_2 – represents the pseudo second order rate constant (g·ml^{-1}·min^{-1}). From the plot, t/q_t and t provide the details on linear relationship. K_2 and q_e are deciphered from the intercept and slope of the plot, respectively.

RESULTS AND DISCUSSION

An adsorption study was carried out for understanding the adsorption behaviour of hexavalent chromium by two types of adsorbents, namely CA-NC and FA-NC that are governed by different factors such as pH, adsorbent dosage, concentration of chromium and contact time.

Effect of pH on adsorption

In the first set, the effect of pH on Cr(VI) adsorption by nanocelluloses were studied. The pH varied from 1 to 9, their results are provided in Figure 1. The adsorption onto CA-NC and FA-NC were observed to follow similar trend. The highest adsorption of 83.50 per cent in CA-FC and 84.70 per cent in FA-NC at a pH of 2. The least adsorption was detected at a pH of 9 both in CA-NC (36.50 per cent removal) and FA-NC (45.80 per cent removal) (Fig. 1). It was clearly evident that as the pH increased, the adsorption reduced gradually, indicating pH of 2 had an important role to play. Because the pH of the medium controls the speciation of every metal ion present in the solution, the adsorption of metallic ions is strongly linked to pH. As the species of metallic ions change, so do the affinities of the adsorbent surfaces embedded with an array of functional groups. The size, shape, and charge of various species of the same metal ions vary. This could change its affinity for the surface active centres, its encapsulation characteristics, and the diffusion phenomena. Therefore, the primary focus of adsorption chemistry is pH optimisation (Zia et al., 2020). Similar results of higher adsorption of hexavalent chromium were noted by (Xu et al., 2021) using amino functionalized dialdehyde nanocellulose. The adsorption was supported by electric attraction due to lower pH. Criticality of lower pH is the presence of H^+ ions which aide in the sorption of CrO_4^{2-} and $Cr_2O_7^{2-}$ which results in their protonation and result in their adsorption onto the nanocellulose surfaces. As the pH increased the availability of the protons was substantially reduced, which in turn hampered the Cr(VI) adsorption. On the contrary, the hydroxyl ion content was increased at higher pH, which results in repulsion between the electrostatic forces (Fan et al., 2019; Mohamed et al., 2022).

Effect of adsorbent dosage on adsorption

Another experiment was carried out for the effect of adsorbent quantity on the hexavalent chromium elimination from the solution. The adsorption dosage was studied from 0.25 to 2.50 g/100 ml of solution while the pH was kept constant at 2. It was noticed that the highest removal efficiency was seen at an adsorbent dose of 1.50 g for 100 ml with 86.40 per cent adsorption by using CA-NC, correspondingly 88.0 per cent exclusion by involving FA-NC. The lowest adsorption efficacy of 12 per cent in CA-NC and 14 per cent in FA-NC was also evident for an adsorbent dose of 2.5 g per 100 ml. General trend of gradual increment in the adsorption was observed, which declined sharply after reaching a maximum at the dose of 1.5 g per 100 ml (Fig. 2). The amount of nanocellulose as adsorbent is a crucial factor that marks an influence on the adsorption process by impacting the availability adsorption site. Similarly, the available surface area for adsorption could be determined by the concentration of the nanocellulose material, which plays a major role in the adsorption procedure. The surge in removal of Cr(VI) with increasing nanocellulose can be ascribed to the

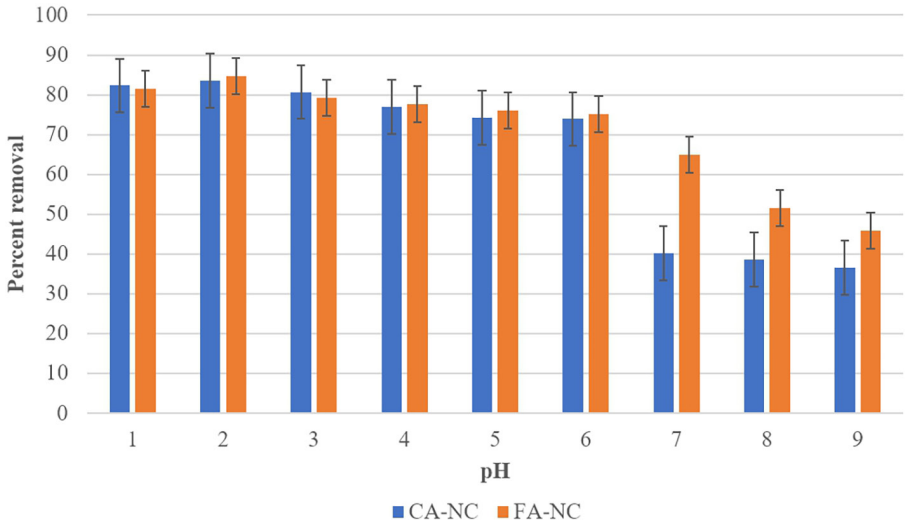

Fig. 1. Effect of pH on percent removal of Cr(VI) by nanocellulose

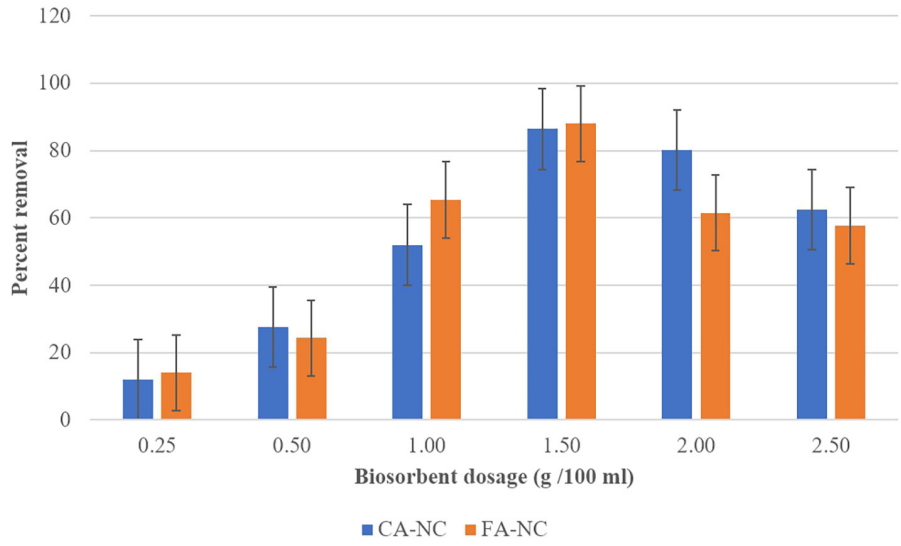

Fig. 2. Effect of sorbent dosage on percent removal of Cr(VI) by nanocellulose

upsurge of negative surface charge accessible for Cr(VI) adsorption. For dosage exceeding the 1.5 g displayed reduced adsorption which explained the saturation of nanocellulose surface with adsorbed metal ions (Abu-Danso et al., 2017; Wabaidur et al., 2020).

Effect of solute concentration on adsorption

Solution concentration was the next parameter tested for understanding concentration of nanocellulose as adsorbate towards hexavalent chromium through adsorption. Accordingly, highest removal per cent was observed at 100 g per 100 ml solute concentration, 87.85 g/100 ml for CA-NC and 99.12 per cent removal was observed in FA-NC. The least adsorption efficacy was noticed at a solute concentration of 2000 g per 100 ml, which was supported by the observations of 47.56 g for every 100 ml in case of CA-NA while the same was 51.85 g per 100 ml for FA-NC which clearly indicated that the ideal concentration of adsorbate to work with was 100–200 g per 100 ml, whilst the concentration of 2000 g per 100 ml was far more than being able to handle (Table 1). Apart from this, the increased dosage resulted in the aggregate formation, which again caused a reduction in the adsorption of adsorbates (Xu et al., 2021). Also, it is reported that as the C_0 increased in the solution, the adsorption efficiency of adsorbent showed an upward indication, after a certain

Table 1. Effect of solute concentration on Cr(VI) adsorption

Solute concentration (mg L^{-1})	Amount sorbed (mg g^{-1}) by CA-NC	Amount sorbed (mg g^{-1}) by FA-NC	% Removal by CA-NC	% Removal by FA-NC
100	4.39	4.96	87.85	99.12
200	8.74	9.69	87.35	96.92
300	12.83	14.06	85.56	93.73
400	17.05	18.31	85.26	91.54
500	21.19	22.61	84.76	90.44
600	25.37	25.94	84.56	86.45
700	29.39	30.54	83.96	87.25
800	33.50	34.98	83.76	87.45
900	37.60	38.95	83.56	86.55
1000	41.48	42.43	82.96	84.86
1100	45.52	46.18	82.76	83.96
1200	47.32	50.44	78.87	84.06
1300	47.38	51.27	72.89	78.87
1400	47.60	51.37	68.01	73.39
1500	47.71	51.38	63.62	68.50
1600	47.46	51.53	59.33	64.42
1700	47.55	51.79	55.94	60.93
1800	47.65	51.87	52.95	57.64
1900	47.36	52.01	49.86	54.74
2000	46.00	51.85	47.56	51.85
Mean	35.16	37.61	74.07	79.13
SEd	0.52	0.57	0.98	1.31
CD(0.05)	1.04	1.15	1.95	2.63

Table 2. Isotherm parameters for Cr(VI) adsorption

Model	Parameter	CA-NC	FA-NC
Langmuir	R^2	0.994	0.995
	K_L (L g^{-1})	20.25	49.86
	Q_{max} (mg g^{-1})	53.19	55.25
	R_L	0.114	0.022
Freundlich	R^2	0.906	0.968
	K_f (mg g^{-1})	1.46	2.12
	N (L mg^{-1})	2.07	2.77

point, there was gradual reduction in the metal removal and makes the adsorption curve to become flat which is evident from the adsorption isotherms such as Langmuir and Freundlich (Akl et al., 2023).

Based on the adsorption studies, the Langmuir in addition to Freundlich isotherm models were fit. The R^2 values for Langmuir isotherm were 0.99 (Table 2). The K_L value denotes the energy involved in adsorption between the adsorbent and absorbate which was Cr(VI) in this case. Higher the value of K_L explained faster reaction which were explained by (Xu et al., 2021). R_L defines the dimensionless constant of Langmuir isotherm. These R_L values for CA-NC and FA-NC were between 0 and 1, which illuminates that these adsorbents are favourable towards adsorption of Cr(VI) onto their surface (Kadirvelu et al., 2001). Based on the observation of the adsorption isotherm models, the R^2 values of Langmuir isotherm were near 1, on the contrary the R^2 values of Freundlich isotherm were less than 0.99 (Fig. 3 and 4).

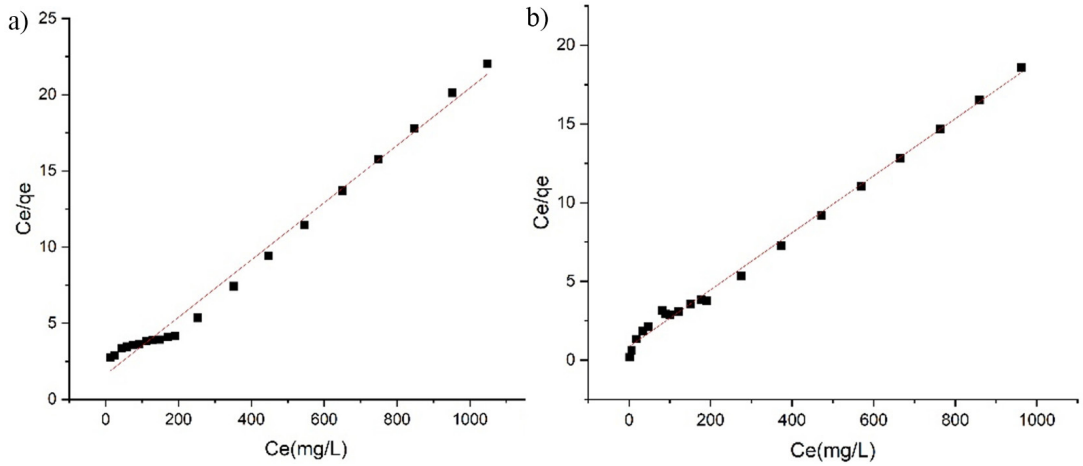

Fig. 3. (a) Langmuir Isotherm for Cr(VI) adsorption by CA-NC;
(b) Langmuir Isotherm for Cr(VI) adsorption by FA-NC

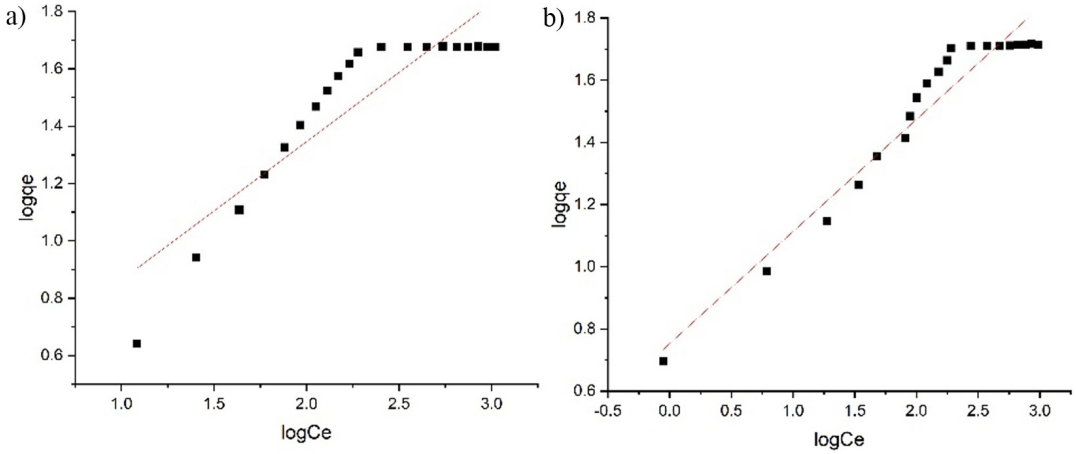

Fig. 4. (a) Freundlich Isotherm for Cr(VI) adsorption by CA-NC;
(b) Freundlich Isotherm for Cr(VI) adsorption by FA-NC

Effect of contact time on adsorption

The final batch experiment dealt with the contact time between the adsorbent and adsorbate over different times from 10 to 80 minutes. A maximum of 90 per cent removal was witnessed in CA-NC and 87.78 per cent in case of FA-NC for a time duration of 60 minutes. On the contrary, the lowest removal per cent of 33.50 and 32.67 per cent was noticed in CA-NC and FA-NC when the contact time was just 10 minutes, respectively (Fig. 5). The efficiency of the metal adsorption was observed to be prominent as the time of contact increased from 10 minutes to 80 minutes. It is attributed to the fact that as the adsorbent dose increased, the adsorbate had an incremented surface for enhancing the metal removal from the solution, but there was substantial reduction in the percent removal of the adsorbate when the duration increased above 60 minutes owing to the saturation of the surface of the adsorbents (Al-Salehin et al., 2019; Wabaidur et al., 2020).

Based on the kinetic studies, the R^2 of pseudo first order was far from 1 for both the sorbents. On the other hand, pseudo second order had R^2 values approaching 1 as compared to the pseudo first order (Fig. 6 and 7). This explains that the pseudo second order had consistent observations, hence can be expected to fit perfectly explaining that the reaction had chemisorption approach for the reaction. Similar observations were made in Cr(VI), Cu(II) and Hg(II) study by (Akl et al., 2023).

Considering the advantages of nanocellulose from paperboard mill sludge, they have

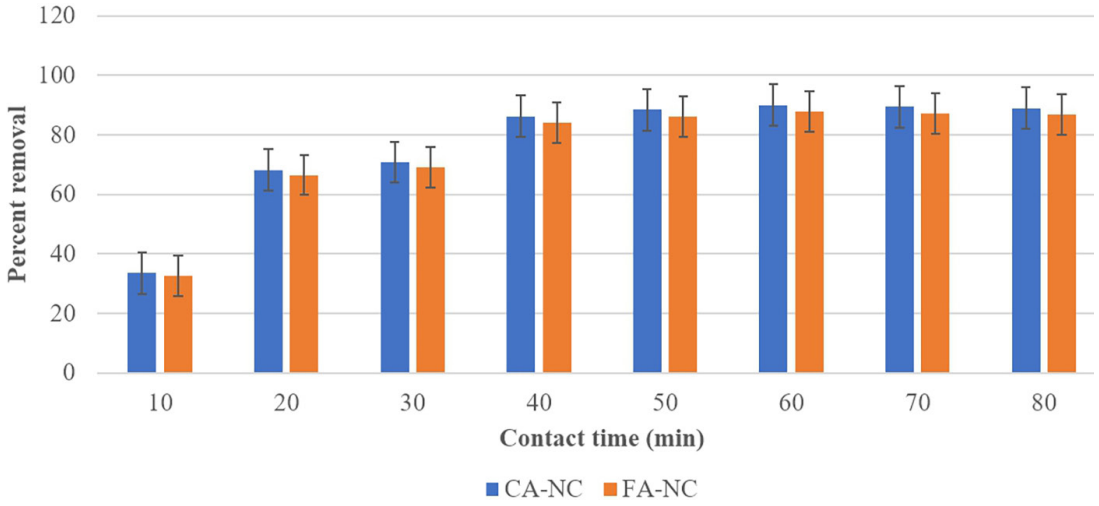

Fig. 5. Effect of contact time on percent removal of Cr(VI) by nanocellulose

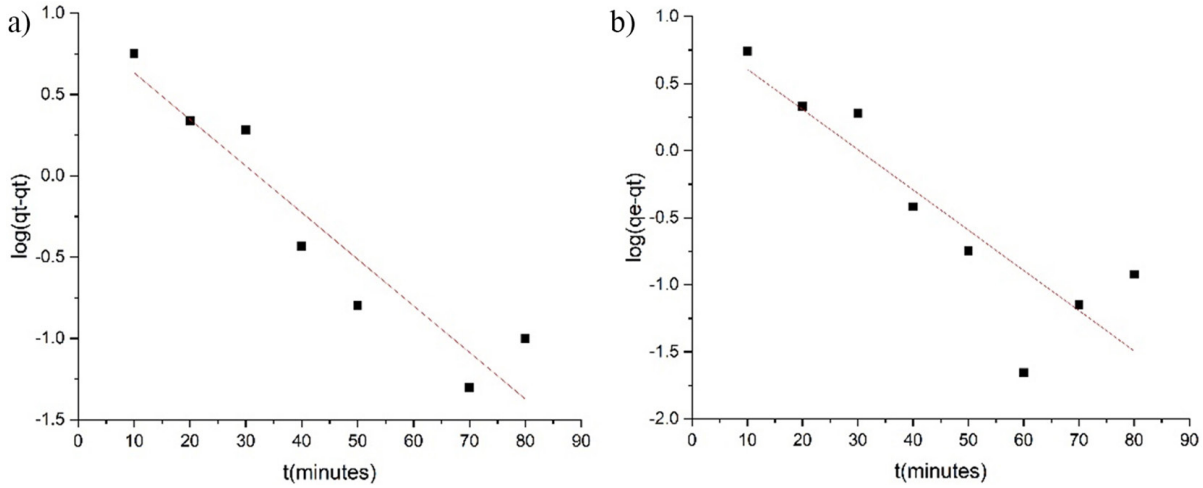

Fig. 6. (a) Pseudo first order reaction for Cr(VI) adsorption by CA-NC;
(b) pseudo first order reaction for Cr(VI) adsorption by FA-NC

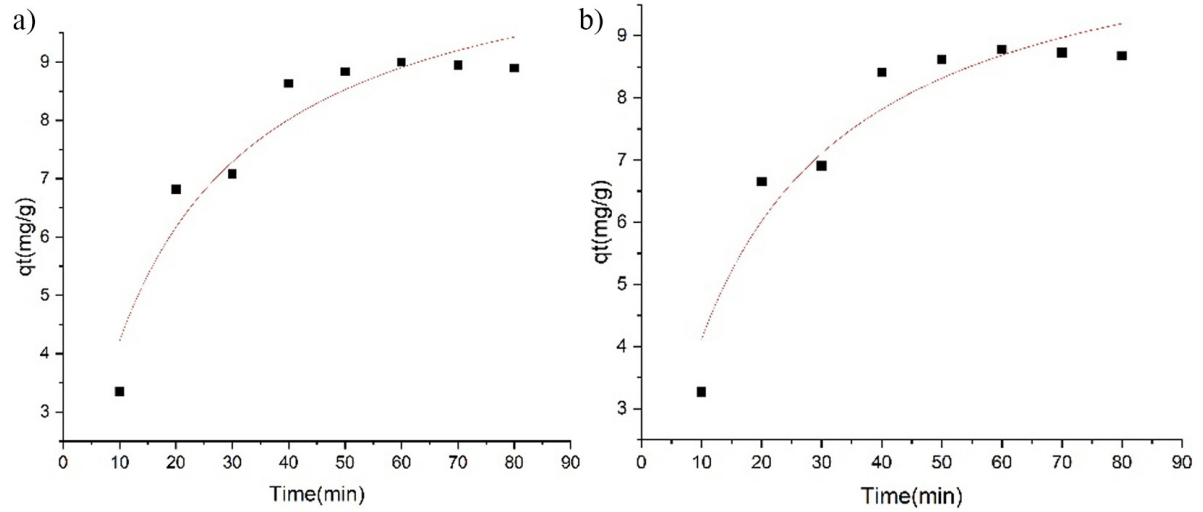

Fig. 7. (a) Pseudo second order reaction for Cr(VI) adsorption by CA-NC;
(b) pseudo second order reaction for Cr(VI) adsorption by FA-NC

been derived using green chemistry (using citric acid (Yu et al., 2016) and formic acid (Du et al., 2016), unlike the use of harsh chemicals such as concentrated sulphuric acid, sodium hydroxide that are used in conventional methods of the cellulose extraction from plant materials). Hence do not pose any adversity towards the environment. Moreover, they can be reused for three to five cycles after desorption. And they are completely biodegradable (Shatkin & Kim, 2017). As such, there are no disadvantages proposed from the synthesized nanocellulose.

CONCLUSION

The present study used two types of nanocelluloses CA-NC and FA-NC for the adsorption of hexavalent chromium from simulated aqueous solution. Although many adsorbents have been used in various studies, nanocellulose from paperboard mill sludge has the cutting edge over other adsorbents as it paves way for the management of the solid waste generated from the paperboard industry in an eco-friendly manner. Some studies have also mentioned that the nanocelluloses can be reused for a minimum of three to five cycles (Torgbo et al., 2021). Effect of different factors such as pH, adsorbent dosage, solute concentration and contact time. Both the adsorbents were noted to perform on par in case of the adsorption. The pH at 2 helped in better adsorption by means of providing protons for adsorption. The adsorbent dose of 1.50 g had better adsorption of metal ions as compared to other dosages. The solute concentration of 100 and 200 $mg \cdot L^{-1}$ were good enough for adsorption. And lastly, the contact duration of 60 minutes resulted in adsorption of metal ions. The adsorption followed monolayer adsorption as supported by the Langmuir adsorption isotherm. As for the adsorption kinetics, pseudo second order suited better than the pseudo first order kinetics explaining the chemisorption mechanism. Thus, nanocellulose derived through citric acid and formic acid hydrolyses of paperboard mill sludge can be used viably for nanocellulose production, further to be used as an adsorbent for water treatment.

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