# Removal of Heavy Metal Ions Using Cellulose Nanocrystals and Succinic Anhydride-modified Cellulose Nanocrystals Prepared from Bleached Soda Bagasse Pulp

Sabah Ashrafi Birgani,[a] Mohammad Talaeipour,[a,]* AmirHooman Hemmasi,[a]
Behzad Bazyar,[a] and Kambiz Larijani [b]

Cellulose nanocrystals (CNC) and succinic anhydride-modified CNC from bleached soda bagasse pulp under different parameters were used to remove $Cd^{+2}$ and $Pb^{+2}$ heavy metal ions from aqueous solution. The aim was to modify the chemical structure of cellulose nanocrystal using succinic anhydride and to investigate the effect of CNC and succinic anhydride-modified CNC on the adsorption capacity of heavy metal ions. The adsorption parameters included pH (3, 5, 6, and 8), contact time (30, 60, and 90 min), and initial metal ion concentration (40, 120, 200, and 280 ppm). It was found at all pHs that the adsorption capacity of the succinic anhydride-modified CNC adsorbent was much higher than that of the default CNC adsorbent, and this difference was greater at higher pHs. The results showed that the maximum metal ion adsorption was obtained at pH 6 for $Pb^{+2}$ and $Cd^{+2}$ ions. Both types of CNC had a higher adsorption capacity for lead ions than cadmium ions. To investigate the kinetic models of adsorption, the pseudo-first-order and pseudo-second-order kinetics model were used. Adsorption on unmodified adsorbent gave a better fit to the Langmuir model than the Freundlich model for both $Pb^{+2}$ and $Cd^{+2}$ metals. In addition, the adsorption mechanism was changed by modifying the adsorbent, and then it had better fit to the Freundlich adsorption model. Adsorption of cadmium and lead metals by adsorbents fit better to the pseudo-first-order kinetics model.

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*Contact information: a: Department of Wood and Paper Science and Technology, Faculty of Natural Resources and Environment, Science and Research Branch, Islamic Azad University, P. O, Box 14515/775, Tehran, Iran; b: Department of Chemistry Science and Research Branch, Islamic Azad University, Tehran, Iran; P. O, Box 14515/775; *Corresponding author: m.talaeipoor@srbiau.ac.ir*

## INTRODUCTION

Water pollution caused by heavy metals resulting from urban activities and industry is an essential global issue due to its accumulation, low biodegradability, and high toxicity in the food chain (Afroze and Sen 2018). Pollutants are produced especially from agricultural sources, chemical industries, and oil leaks. They are in the form of organic chemicals (such as detergents and dyes), oil, battery manufacturing, metallurgical, municipal waste generation, pesticide and fertilizers applications, heavy metal ions, and inorganic chemicals (Kurniawan *et al.* 2006; Wang and Chen 2009; Fu and Wang 2011; da Silva *et al.* 2016; Han *et al.* 2016; Shen *et al.* 2017; Pugazhendhi *et al.* 2018). Heavy metal pollution poses the most serious harm due to its undegradability (Shen *et al.* 2017). If these metals pollute water sources, they are highly toxic to the environment, animals, and humans (O'Connell *et al.* 2008; Yu *et al.* 2013; Wei *et al.* 2019; Tariba *et al.* 2020). The metal ions are non-degradable and stable in the environment. The pollutants of heavy metal ions including zinc, copper, nickel, mercury, cadmium, lead, and chromium are often associated with pollution, leading to ecological imbalance (O'Connell *et al*. 2008; Fu and Wang 2011; Cao *et al.* 2010; Li *et al*. 2014; Tóth *et al*. 2016; Benvenuti *et al*. 2017; Cardoso *et al*. 2017). These metals can lead to damage to the nervous system, bone and brain damage, neurological disorders, and even cancer (Khan and Khatoon 2017).

A wide range of chemical and physical processes are used to remove heavy metals from industrial effluents, including biological treatment, ion exchange and reverse osmosis, electrodialysis, chemical reduction, electrochemical treatment, sedimentation, membrane separation, filtration, flocculation, and coagulation (Dursun *et al*. 2005; Garg *et al*. 2007; Huang *et al*. 2009; Li *et al*. 2012; Elsherif *et al*. 2013a,b; 2014a,b,c; Elsherif and Yaghi 2017a,b). Most of these conventional methods are inefficient or have economic limitations, as they require high costs (Gautam *et al*. 2014; Adeleye *et al*. 2016; Zekić *et al*. 2018). However, adsorption is a suitable alternative method with high potential for removing heavy metals from water; it is relatively simple, low cost and highly efficient, (Rodrigues *et al*. 2012; Do Nascimento *et al*. 2019; Jafari and Yaghmaei 2019; London - Zuluaga *et al*. 2019; Massoud *et al*. 2019; Moreira *et al*. 2019; Peng *et al*. 2019; Yin *et al*. 2019; Chikuruwob *et al.* 2020).

Nanoscale adsorbents are considered to be an effective method for heavy metals removal from polluted wastewaters due to their porous structure and adsorption potential (Yin *et al.* 2017; Mercy *et al.* 2018). However, most adsorbents such as nano silicates, graphene oxide, and activated carbon are non-renewable, non-degradable, and costly (Chavan *et al*. 2015; Lamymendes *et al.* 2018). Thus, the use of renewable, sustainable materials has become increasingly important for producing various high-value products with low environmental impact (Oksman and Bismarck 2014; Pandey *et al*. 2015; Suman *et al*. 2015; Thakur 2015a, b; Kargarzadeh *et al*. 2018). Such materials can be considered instead of non-renewable materials (Jie *et al*. 2019).

There are different contexts for discovering the various capabilities of the attractive cellulose polymer (Mokhena and John 2020; Moohan *et al.* 2020; Trache *et al.* 2020). Nanocellulose has the advantages of hydrogen bonding capacity, low coefficient of thermal expansion, surface-area-to-volume ratio, high tensile strength, high Young's modulus, environmental compatibility, renewability, and non-toxicity (Foster *et al*. 2018; Salimi *et al*. 2019). Despite these advantages, the unmodified cellulose has limitations such as low removal capability and low dimensional stability (Rudie *et al*. 2006; Kara *et al*. 2021), variable physical stability, chemical incompatibility, as well as low density (Naz *et al*. 2019; Vineeth *et al*. 2019), which results in relatively low reactivity in the adsorption or flocculation process (Nikiforova and Kozlov 2011). These problems can be partially alleviated by adding extra cations or anions to the surface of the nanocelluloses to improve its performance (Rol *et al*. 2019; Zhou *et al.* 2020; Kara *et al.* 2021). Therefore, new functional groups on cellulose surfaces can increase their surface polarity and hydrophobicity. These new groups could increase the uptake of polar adsorbents and the selection of cellulose for target pollutants.

The functional characteristics of the cellulose surface can be changed during the preparation phase or the production of nanocellulose (Wei *et al*. 2017). These changes can lead to the achievement of desirable properties, which in turn increase the effectiveness of cellulose for a particular application (Liang *et al*. 2020; Tao *et al*. 2020). Although the production of nanocellulose from various natural sources has been studied extensively, the use of CNC prepared from bleached soda bagasse pulp for adsorb heavy metals has not been investigated. Bagasse is a by-product of the sugarcane factories. Bagasse contains 40 to 50% cellulose in its composition, much of which is in the crystalline structure (Wulandari *et al.* 2016). Due to its characteristics such as availability, low lignin content, and low cost, it is a promising raw material for the extraction and production of nanocellulose.

In this study, the proposed mechanism is to increase the adsorption of metal ions by modifying nanocrystals with succinic anhydride. Therefore, the main aim of the present study was to prepare cellulose nanocrystal from bleached bagasse pulp and then modify the produced cellulose nanocrystal by increasing the functional groups using succinic anhydride. The adsorption performance of cellulose nanocrystals and cellulose nanocrystal modified with succinic anhydride for metal ion adsorption was investigated. Because in previous studies the removal of heavy metals $Pb^{2+}$ and $Cd^{2+}$ was considered (Bhagat *et al*. 2020; Jawed *et al*. 2020), these metals were selected for this study.

## EXPERIMENTAL

### Materials and Methods

Bleached soda bagasse pulp was obtained from the Pars paper company. Acetic acid, sulfuric acid, potassium hydroxide, and sodium hydroxide were purchased from Merck Co. (Darmstadt, Germany). To produce CNC, the bleached soda bagasse pulp was subjected to alkaline hydrolysis and acid hydrolysis, followed by solvent removal, washing, purification, filtration, centrifugation, dialysis, sonication, and freeze-drying. Details are provided below.

### Alkaline Hydrolysis (Production of Alpha Cellulose)

For producing alpha cellulose and removing pigments, 20 g of the bleached soda bagasse pulp was mixed with 8% caustic in a ratio of 20:1 (based on oven-dry pulp) using constant mixing at 30 °C for 90 min. The pulp was drained, then washed with 100 mL of 2% potassium hydroxide, 200 mL of hot distilled water, 200 mL of acetic acid, and 2000 mL of cold distilled water in sequence.

### Preparation of Cellulose Nanocrystals

Nanocellulose was extracted from alpha cellulose by 54% sulfuric acid and was hydrolyzed in a 13:1 ratio. Cellulose hydrolysis was performed for 90 min at 50 °C. The reaction was stopped by adding 250 mL distilled water to the solution, and then the suspension was centrifuged (6500 rpm for 30 min) and dialyzed (for one week) to reach pH 5. The neutral suspension of CNC was exposed to ultrasonic vibrations for 10 min to produce homogeneous dispersed CNC, which was then freeze-dried.

### Preparation of Succinic Anhydride-Modified Cellulose Nanocrystals

A total of 3 g of the freeze-dried cellulose nanocrystals was mixed with 15 g of succinic anhydride and then reacted at 120 °C for 12 h, subject to pyridine reflux (30 mL). To isolate the unreacted succinic anhydride, the sample was washed several times using distilled water, ethanol, and acetone at different times by vacuum pump and centrifuge. The output product was dried under vacuum at 60 °C.

## Analysis Methods

To study the structure and size of cellulose nanocrystals, a scanning electron microscope (SEM; model TESCAN VEGAII, Brno, Czech Republic) with a voltage of 15 KW and transmission electron microscope (TEM; Zeiss - EM10C - 100 KV, Jena, Germany) with a voltage of 100 KW was used. To identify the functional groups of cellulose nanocrystals and succinic anhydride-modified cellulose nanocrystal, Fourier transform infrared spectroscopy (FT-IR) was performed using a Perkin Elmer RXI spectrometer (Waltham, MA, USA) in the wavelength range of 400 to 4000 cm$^{-1}$.

## Metal Solutions Preparation

The metal salts used in this work were $Pb(NO_3)_2$ and $Cd(NO_3)_2$ from Merck Co. (Darmstadt, Germany). Metal ions were used to prepare 1000 mg/L storage solutions using distilled water. Experimental solutions of metal ions were prepared from stock solution using appropriate subsequent dilutions. The concentration range of metal ions prepared from the standard solution ranged between 40 and 280 ppm. To investigate the effect of pH, a buffer was prepared at different pH. For this purpose, 1.483 mL of acetic acid, 1.657 mL of phosphoric acid, and 1.2366 g of boric acid were mixed and brought up to a final volume of 500 mL with distilled water. By adding NaOH drop by drop, the solutions were prepared with pH of 3, 5, 6, and 8. Before mixing the adsorbent, the pH of each solution was adjusted with 0.1 M NaOH or 0.1 M hydrochloride acid.

## Absorption of Heavy Metals Ions

To evaluate the adsorption of cadmium and lead by the adsorbent, the effect of pH, the initial amount of heavy metal, and the processing time were evaluated. For this purpose, 0.1 g of adsorbent was added to 100 mL of a solution containing heavy metal and stirred for different times (30, 60, and 90 min) as well as different pH (3, 5, 6, and 8). After a specified time, the solution was separated from the adsorbent by centrifugation (15,000 rpm, 10 minutes), and the metal concentration was measured by the ICP-OES test. Adsorbent adsorption capacity (mg / g) was obtained using Eq. 1:

$$q_e = \frac{(C_0 - C_e)}{V} \times M \tag{1}$$

The adsorption efficiency was calculated as shown in Eq. 2,

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

where $q_e$ is the metal uptake capacity (mg/g), $C_0$ is the initial concentration, $C_e$ is the final concentration, $V$ is the volume of the metal solution (L), $M$ is the dry mass of adsorbent (g), and $R$ is adsorption efficiency.

# RESULTS AND DISCUSSION

Images obtained by TEM are shown in Fig. 1. The average length of the CNC particles ranged between 192 and 384 nm, and the average diameter ranged between 17 and 56 nm. Also, the particles were fibrillar in shape. CNC particles accumulated in some places, while dispersing in others.

The FTIR spectra of CNC and succinic anhydride-modified CNC are shown in Fig. 2. In both diagrams, there was a broad band in the range of 3200 to 3500 cm$^{-1}$, which is due to stretching vibration of O-H from OH groups of cellulose molecules (Khalil *et al.* 2001; Xu *et al.* 2005; Sain *et al.* 2006; Viera *et al.* 2007; Mandal and Chakrabarty 2011; Li *et al.* 2012; Lu and Hsieh 2012; Hokkanen *et al.* 2013; Rosli *et al.* 2013; Maiti *et al.* 2013; Kumar *et al.* 2014; Maryana *et al.* 2014; Li *et al.* 2014; Almasian *et al.* 2016; Saelee *et al.* 2016; Wulandari *et al.* 2016; Lam *et al.* 2017). The peak from 1649 to 1641 cm$^{-1}$ was also related to the O-H vibration of the adsorbed water (Ramo *et al.* 2000; Alemdar and Sain 2008; Mandal and Chakrabarty 2011; Li *et al.* 2012; Hokkanen *et al.* 2013; Almasian *et al.* 2016; Wulandari *et al.* 2016). Moreover, one peak at 894 cm$^{-1}$ is related to the glycosidic CH deformation with a ring vibration contribution and O–H bending, which are known characteristics of b-glycoside linkages between the anhydro glucose units in cellulose. The peak intensity decreased to 894 cm$^{-1}$, which indicates that the glycosidic bond was broken and more OH groups were released (Fuge Niu *et al.* 2017).

The peak observed at 894 cm$^{-1}$ in the bleached soda bagasse pulp sample is related to $\beta$-glycoside bonds in cellulose (Nelson and O'Connor 1964; Alemdar and Sain 2008; Mandal and Chakrabarty 2011; Wulandari *et al.* 2016). With increasing hydrolysis time, peak intensity was decreased at 894 cm$^{-1}$, indicating that the glycosidic bond was broken and more OH groups were released (Niua *et al.* 2017). The band at 1730 cm$^{-1}$ was attributed to C=O tensile vibrations for ester and acetyl linkages in hemicellulose or lignin (Nelson and O'Connor 1964; Alemdar and Sain 2008; Mandal and Chakrabarty 2011; Li *et al.* 2014; Wulandari *et al.* 2016; Lam *et al.* 2017). The peaks from 1505 to 1511 and 1602 to 1604 cm$^{-1}$ are attributed to C=C stretching vibration in lignin (Kumar *et al.* 2014), and the band at 1245 cm$^{-1}$ is related to C-O stretching vibration of aryl group in lignin (Mandal and Chakrabarty 2011; Rosli *et al.* 2013; Saelee *et al.* 2016).

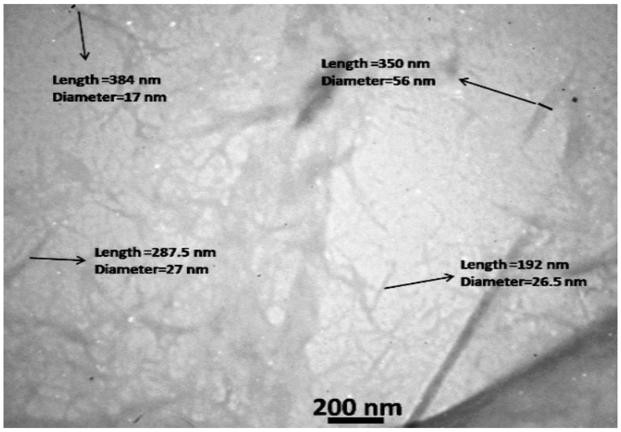


**Fig. 1.** TEM image of cellulose nanocrystals

None of these groups were found in the FTIR spectrum of the studied cellulose. These observations confirmed the successful elimination of lignin in the bleached fibers. Comparison of cellulose nanocrystals with succinic anhydride-modified cellulose nanocrystal showed two new peaks in 1734 and 1574 cm$^{-1}$ in succinic anhydride-modified cellulose nanocrystal, indicating the presence of two carbonyl groups. The band at 1734 cm$^{-1}$ is assigned to the carbonyl groups in -COOH or –COOR. The band at 1574 cm$^{-1}$ is defined as the asymmetric stretching of carboxylic anions; the presence of these peaks confirmed that cellulose nanocrystals was modified successfully (Chen *et al.* 2013). As expected, the absence of bands at 1850 and 1780 cm$^{-1}$ confirmed that the product was free of non-reacted succinic anhydride (Liu *et al.* 2010).

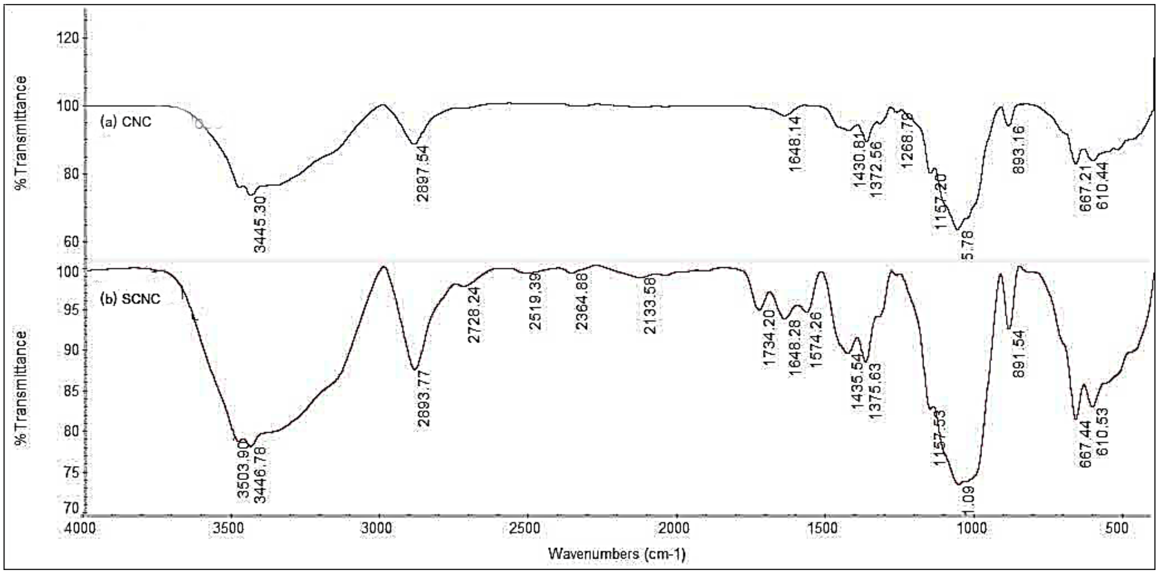


**Fig. 2.** FTIR image of cellulose nanocrystals (CNC)(a) and succinic anhydride-modified cellulose nanocrystals (SCNC) (b)

## Investigating the effect of Varying pH on the Adsorption of Metal Ions

The pH of the metal solutions is one of the most important variables in adsorption. The pH affects the ionization status of the functional groups in the adsorbent. The pH values for the study were varied in the range of 3 to 8. Changes in pH and adsorption capacity for lead and cadmium ions using succinic anhydride-modified cellulose nanocrystal and cellulose nanocrystal adsorbents are shown in Fig. 3.

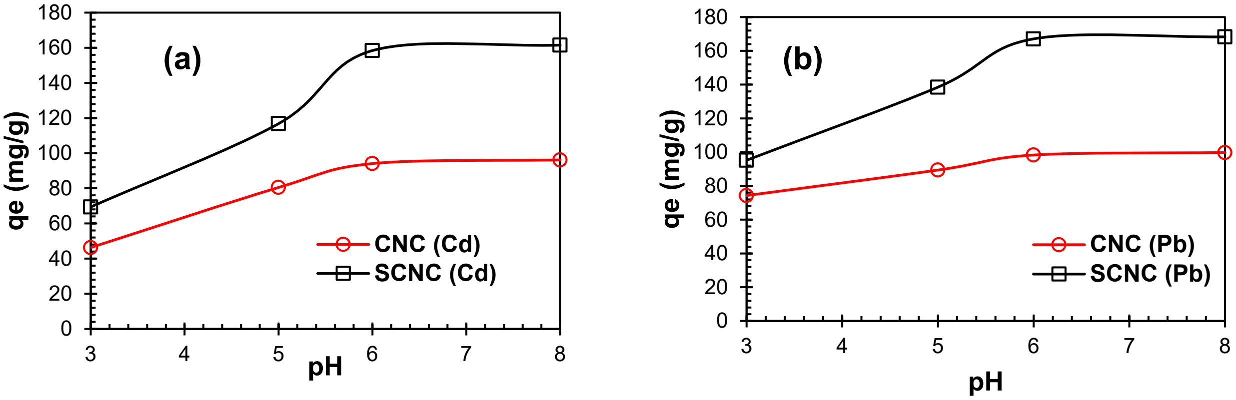


**Fig. 3.** Changes in the adsorption capacity of cellulose nanocrystal and succinic anhydride-modified cellulose nanocrystal adsorbents for (a) cadmium and (b) lead ions

For both succinic anhydride-modified cellulose nanocrystal and cellulose nanocrystal adsorbents, the adsorption capacity of the adsorbent increased with increasing pH of the solution. This was due to the competition between metal ions and $H^+$ ions in acidic solution. In fact, the adsorption of $H^+$ ions on the adsorbent surface caused the adsorption sites to be filled by this ion, and so the adsorption capacity for metal ions was reduced. However, deprotonation of the adsorbent at higher pH caused a more negative surface charge of the adsorbent and improved the conditions for electrostatic adsorption of metal cations (Javidparvar *et al.* 2016). These results also show that at all pHs the adsorption capacity of the succinic anhydride-modified cellulose nanocrystal adsorbent was much higher than that of the cellulose nanocrystal adsorbent, and this difference was greater at higher pHs. It was also observed that both succinic anhydride-modified cellulose nanocrystal and cellulose nanocrystal had a higher adsorption capacity for $Pb^{+2}$ ions than $Cd^{+2}$ ions, which was also observed in the article by Zhang *et al.* (2017). This difference can be due to the effectiveness of the electronegativity of each metal in forming a chemical bond with the absorber. In other words, the electronegativity of lead (2.33) is much higher than that of cadmium (1.69), so lead has a higher absorption efficiency than cadmium.

## Investigating the Effect of Metal Ion Concentration

The influence of initial metal concentration on adsorption is ordinarily investigated to find out the dependence of the initial metal ions concentration in the aqueous phase, adsorption efficiency, and the metal adsorption capacity of the adsorbent. The uptakes of metal ions are dependent on initial concentration. As shown in Table 1, the adsorption capacity increased with increasing initial concentration. CNC modified with succinic anhydride had higher adsorption capacity than cellulose nanocrystal. Also, the adsorption capacity for lead ions was higher than that of cadmium. While, with increasing initial concentration of lead and cadmium increases, the adsorption efficiency for both adsorbents decreased.

As the initial concentration of lead and cadmium increased, the number of ions competing to react with the surface ligands increased, resulting in saturated active adsorbent sites. In addition, increasing the initial concentration of metal ions increased the number of collisions between metal ions and adsorbents, which in turn accelerated the adsorption process.

**Table 1.** Laboratory Results on Adsorbent Adsorption Capacity ($q_e$) and Adsorption Efficiency (%)

| Initial Metal Ions Concentration | Adsorbent | $q_e$ | | Adsorption Efficiency (%) | |
|---|---|---|---|---|---|
| | | Pb | Cd | Pb | Cd |
| 40 ppm | CNC* | 27.25 | 24.4 | 68.12 | 61 |
| | SCNC** | 33.6 | 31.3 | 84 | 78.25 |
| 120 ppm | CNC | 67.5 | 60.4 | 56.25 | 50.33 |
| | SCNC | 90.3 | 82.1 | 75.25 | 68.41 |
| 200 ppm | CNC | 94.1 | 78.3 | 47.05 | 39.15 |
| | SCNC | 145.4 | 130.1 | 72.7 | 65.05 |
| 280 ppm | CNC | 108.5 | 92.4 | 38.75 | 33 |
| | SCNC | 184.2 | 157.1 | 65.78 | 56.10 |

*CNC: cellulose nanocrystal SCNC**: succinic anhydride-modified cellulose nanocrystal

## Investigation on Adsorption Isotherms

Adsorption isotherm models have been used to investigate the effect of initial concentration and to study the mechanism of adsorption of metal ions on the adsorbent surface. For this purpose, two models, Langmuir and Freundlich, which have been used widely in this field, were used. The linear relationship of the Langmuir and Freundlich models is presented in Eqs. 3 and 4, respectively.

$$C_e/q_e = 1/q_mK_l + C_e/q_m \tag{3}$$

$$\ln(q_e) = 1/n \times \ln(C_e) + \ln(K_f) \tag{4}$$

where $C_e$ is the equilibrium concentration (mg $L^{-1}$), $q_e$ is the quantity adsorbed at equilibrium (mg $g^{-1}$), $q_m$ is the maximum adsorption capacity (mg $g^{-1}$), $K_l$ is the Langmuir adsorption constant (L $mg^{-1}$), $K_f$ is the Freundlich constants for binding energy, and $n$ is the adsorption intensity. The diagrams for these two models are shown in Figs. 4 and 5. The results of this modeling are reported in Table 2.

**Table 2.** Laboratory Results on Langmuir and Freundlich Adsorption Models

| Metal | Adsorbent | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|---|
| | | $q_m$ | $K_l$ | $R^2$ | $n$ | $K_f$ | $R^2$ |
| $Pb^{+2}$ | CNC | 144.92 | 0.017 | 0.99 | 1.83 | 7.15 | 0.98 |
| | SCNC | 285.71 | 0.018 | 0.97 | 1.55 | 10.27 | 0.99 |
| $Cd^{+2}$ | CNC | 121.95 | 0.015 | 0.99 | 1.85 | 5.87 | 0.98 |
| | SCNC | 238.09 | 0.016 | 0.98 | 1.59 | 8.23 | 0.99 |

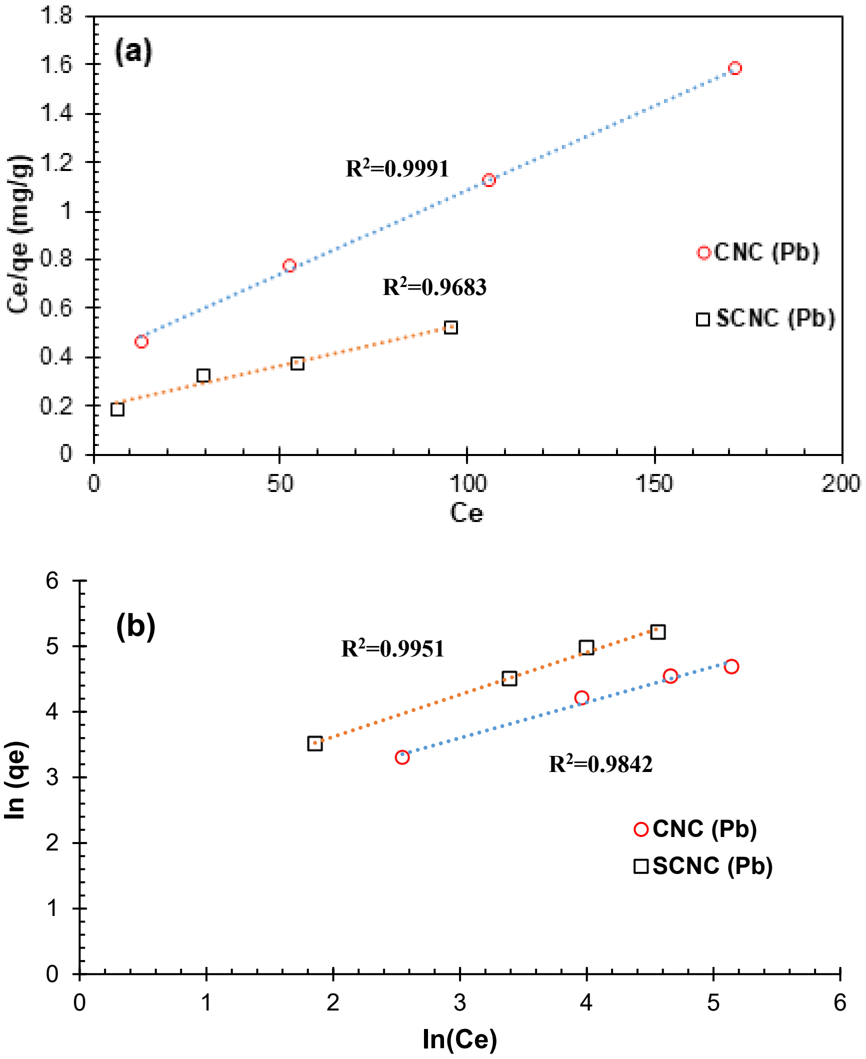


**Fig. 4.** Graphs related to the adaptation of the results of measuring the concentration of lead in the presence of succinic anhydride-modified cellulose nanocrystal and cellulose nanocrystal adsorbent on the adsorption models (a) Langmuir and (b) Freundlich

$R^2$=0.9842

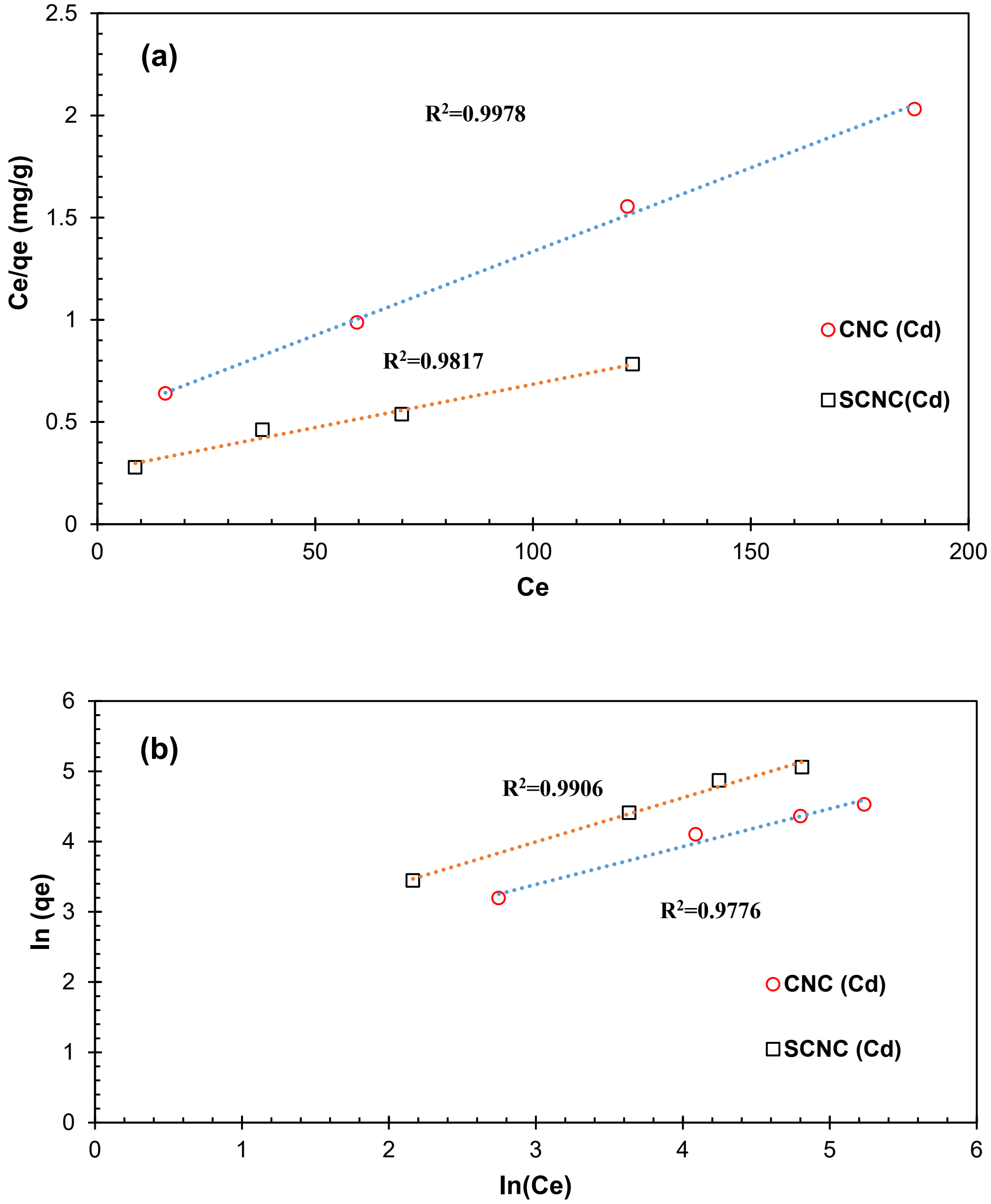


**Fig. 5.** Graphs related to the adaptation of the results of measuring the concentration of cadmium metal in the presence of succinic anhydride-modified cellulose nanocrystal and cellulose nanocrystal adsorbent on the adsorption models (a) Langmuir and (b) Freundlich

According to the values reported in Table 2, the Langmuir model was more suitable for describing the adsorption on the default CNC adsorbent for both the $Pb^{+2}$ and $Cd^{+2}$ metal ions. This adaptation suggests that the Langmuir adsorption in which all adsorption sites have the same affinity for metal ion adsorption is valid here. These results are consistent with the results of Azeez *et al.* (2021). The adsorption mechanism changed with the SCNC. Equilibrium data corresponding to SCNC fit better with the Freundlich adsorption model.

By comparing the maximum adsorption capacity, it is clear that this parameter was higher in the samples in which the SCNC adsorbent was used than in the samples that contained the default CNC adsorbent. This result indicates that the capacity increased significantly after the modification of the CNC adsorbent.

Another parameter that can be extracted from thermodynamic models of adsorption is the amount of free adsorption energy obtained from Eq. 5,

$$\Delta G^{\circ}_{ads} = RT\ln(K_l \times 55.5) \qquad (5)$$

where $\Delta G^{\circ}_{\text{ads}}$ is the Gibbs standard free energy related to adsorption, $R$ is the universal gas constant, $T$ is the absolute temperature, and $K_{\text{l}}$ is the Langmuir equilibrium constant. The amount of free energy of Gibbs for adsorption of lead on CNC and SCNC were -144.1 and -2.47 kJ/mol, respectively. For adsorption of cadmium on CNC and SCNC, this value was -454.2 and -294.3, respectively. Negative Gibbs free energy values mean that the ion adsorption process on the adsorbent surface is spontaneous (Saravanan and Ravikumar 2015). Because these absolute values of this parameter were less than 20 kJ / mol, it can be concluded that the type of adsorption of metal ions on the adsorbent surface, whether in the SCNC state or CNC, is the physical adsorption type as electrostatic adsorption (Salinas-solano *et al.* 2018).

## Investigation of Adsorption Kinetic Models

To investigate the effect of time on the adsorption of metal ions on the adsorbent surface, the pseudo-first-order and pseudo-second-order kinetic models were used, as presented in Eqs. 6 and 7, respectively,

$$\ln(q_e - q_t) = \ln q_e + k_1 t \qquad (6)$$

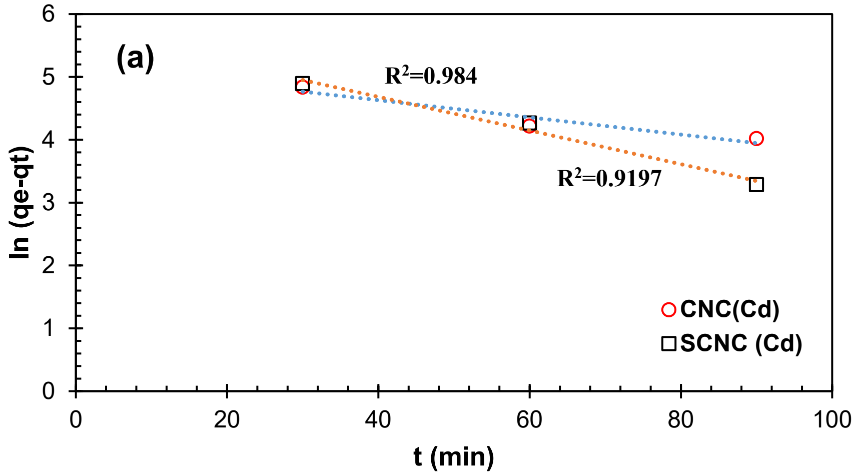
$$q_t = k_2 t \times (q_e^2 / (1 + k_2 t q_e)) \qquad (7)$$

where $q_{\text{t}}$ is the adsorption capacity (mg/g) at time $t$ (min), $q_{\text{e}}$ is the equilibrium adsorption capacity (mg/g), and $K_1$ and $K_2$ are the pseudo-first-order equilibrium rate constant and pseudo-second-order equilibrium rate constant (min$^{-1}$), respectively. The diagrams for these two models are shown in Figs. 6 and 7. The results are reported in Table 3.

**Table 3.** Kinetic Parameters of Pseudo-First-Order Kinetics Model and Pseudo-Second-Order Kinetics Model for $Pb^{2+}$, $Cd^{2+}$

| Metal | Adsorbent | Pseudo-First-Order Kinetics Model | | | Pseudo-Second-Order Kinetics Model | |
|---|---|---|---|---|---|---|
| | | $q_e$ | $K_1$ | $R^2$ | $K_2$ | $R^2$ |
| $Cd^{+2}$ | CNC | 158.1 | 0.014 | 0.92 | 0.00004 | 0.04 |
| | SCNC | 180.8 | 0.027 | 0.98 | 0.00005 | 0. 30 |
| $Pb^{+2}$ | CNC | 177.6 | 0.022 | 0.99 | 0.00005 | 0.04 |
| | SCNC | 189.3 | 0.029 | 0.99 | 0.00006 | 0.73 |

As shown in Table 2, adsorption on adsorbents is more suitable for both lead metal and cadmium metal on the pseudo-first-order kinetics model. When adsorption follows a pseudo-first-order kinetics model, the adsorption process is strongly dependent on the number of adsorption sites present on the adsorbent (Ravishankar *et al.* 2016).



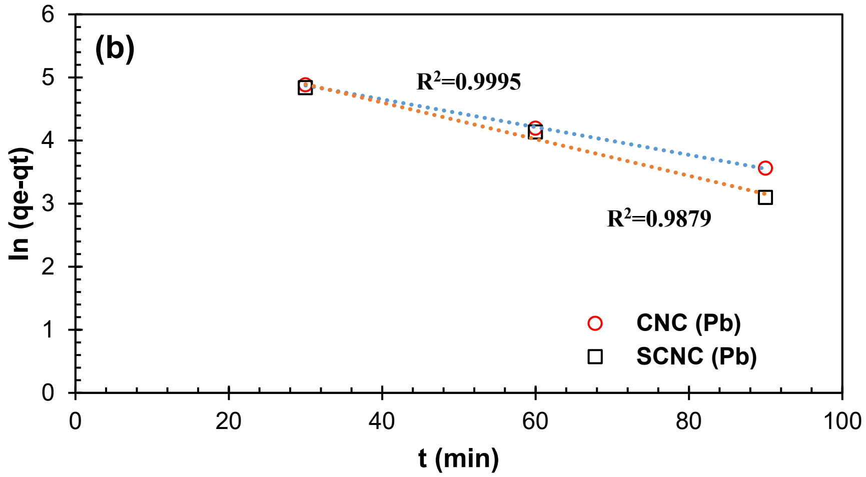


**Fig. 6.** Plots of pseudo-first-order kinetic models for the adsorption of cadmium (a) and lead (b) onto succinic anhydride-modified cellulose nanocrystal and cellulose nanocrystal adsorbents

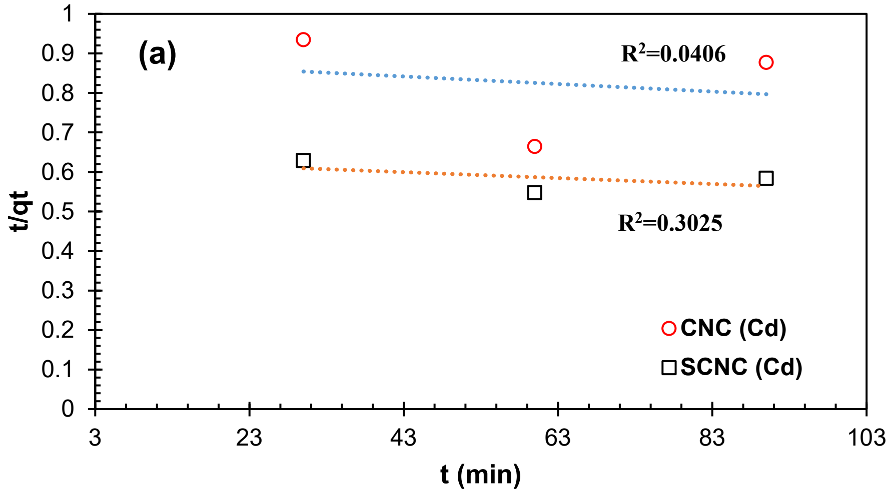


**Fig. 7a.** Plots of pseudo- second -order kinetic models for the adsorption of cadmium (a) and lead (b) onto succinic anhydride-modified cellulose nanocrystal and cellulose nanocrystal adsorbents

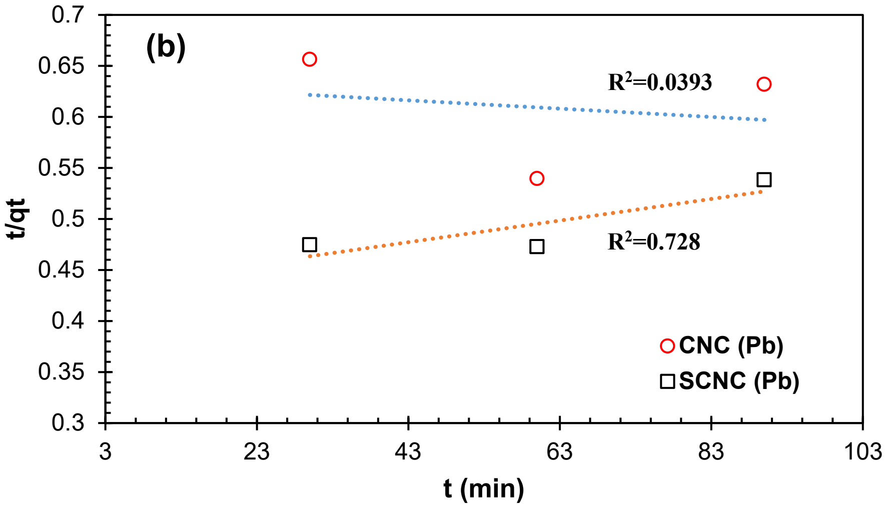


**Fig. 7b.** Plots of pseudo- second -order kinetic models for the adsorption of cadmium (a) and lead (b) onto succinic anhydride-modified cellulose nanocrystal and cellulose nanocrystal adsorbents

## CONCLUSIONS

1. The presence of 1734 cm$^{-1}$ and 1574 cm$^{-1}$ peaks in the succinic anhydride-modified cellulose nanocrystal (SCNC) confirms that the cellulose nanocrystal had been successfully modified with succinic anhydride.
2. The adsorption capacity of the adsorbent increased to pH 6 and then remained constant. Also, more lead ions were adsorbed than cadmium ions.
3. The adsorption mechanism of cellulose nanocrystal adsorbent was more compatible with the Langmuir model. The adsorption mechanism of the succinic anhydride-modified cellulose nanocrystal as more compatible with the Freundlich adsorption model. Also, the adsorption kinetics were more consistent with the pseudo-first-order kinetics model.
4. The type of adsorption of metal ions on the adsorbent surface, whether in the succinic anhydride-modified cellulose nanocrystal or the cellulose nanocrystal, was physical absorption (electrostatic adsorption).

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