Separation of Cd (II) onto Polypyrrole nitrogen porous carbon composite in the continuous column system

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ABSTRACT
Polypyrrole nitrogen porous carbon composite (PP/N-PCC) was prepared from molasses of the sugarcane industry. PP/N-PCC was characterized and used in the cadmium removal from the aqueous feed in a column system. The inlet metal concentration, flow rate, bed depth and pH were studied. Removal percent was reached 71.45% with a sorption capacity of 233.54 mg/g at pH5, 10 ml/min, and 7.5 bed depths. The column system was modelled using Thomas, Adams-Bohart and Yoon-Nelson kinetic models. The higher $R^2 > 0.98$ indicates that the Thomas model appeared to a well-fitting with the experimental outcomes. PP/N-PCC adsorbent appeared well recycled up to 8 cycles indicating the economic feasibility of PP/N-PCC in the separation of Cd (II) ions from liquid wastes.

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1. Introduction
Treating polluted water is one of the imperative tasks in the industrial and human health fields. Also, water scarcity has led to the use of treated water in many areas to reduce dependence on natural water [1]. The competition in industrial development helped increase the production of many pollutants that change the properties of water and prevent its use [2–4]. Heavy elements such as cadmium, iron, manganese and many other harmful elements are considered the main pollutants produced by various industries such as electroplating, battery manufacturing, paint and leather tanning [5–7]. Many countries enact laws and restrictions that limit the disposal of industrial pollutants into municipal sewers before they are treated, which requires the owners of the factory to implement and design treatment units for liquid wastes before they are discharged [8,9]. Cadmium causes a lot of damage to human health and the environment, as it accumulates in the liver, kidneys, and bones as well, and causes a breakdown or imbalance in the functions of these organs, which leads to death [7,10,11]. Many industries have tended to use different treatment processes such as solvent extraction [12], ion exchange [13], membranes [14], and adsorption [15–18] to remove heavy elements from liquid wastes. The adsorption process is considered one of the least expensive and most effective processes in removing pollutants with low concentrations that are difficult or expensive to remove by other treatment processes [3,19,20]. There are many adsorbent materials such as polyphenol silica nanocomposite [21], char/charcoal black carbon [22], magnetic nanomaterial [23], corn cob [24], keratin magnetic froth carbon [25], palm fibre [26], polyvinylpyrroldone magnetic activated carbon [27], Poly(methacrylic-co-acylonitrile) (p(MAc-co-AN)) microgels [28] and amidoximated poly(acylonitrile) particles [29] are used in the removal of heavy metals. In this research, an adsorbent material with high porosity was prepared from the mixture of chitin and molasses resulting from the sugar industry. Chitin was added to increase the nitrogenous properties of the adsorbent which increases the adsorption capacity. Also, the prepared material was modified by covering it with a layer of an organic polymer such as Polypyrrole, which helps to improve and increase the efficiency and economic feasibility of the adsorbent material. Fixed bed sorption dynamics and kinetic modelling are studied after obtaining the optimum continuous parameters of the adsorption process. Also, the reusability of the material was investigated.

2. Materials and methods
2.1. Preparation of chitin porous carbon (C-PC)
Analytical grade chemicals (Sigma-Aldrich) are used in this work. 20 ml of H3PO4 (80%) and 10 ml of chitin solution in acetic acid were added to 75 ml of molasses obtained from the sugarcane industry in a magnetic heating stirrer for 15 min, then, the mixture was heated to 80°C until the viscous resin was formed. The viscous resin was heated at 200°C in an air oven for 3 h to produce chitin porous carbon (C-PC). C-PC was cooled, ground and washed with distilled water and then dried at 85°C.
2.2. Preparation of Polypyrrole nitrogen porous carbon composite (PP/N-PCC)

Carbonization of the prepared C-PC was carried out at 500°C for 2 h in the nitrogen condition in a cylindrical heating system rate of 10°C/min. The produced nitrogen porous carbon (N-PC) was taken out and immersed for 5 min in 1 mol/L KOH solution and then washed with distilled water then dried at 80°C. A mixture of 25 ml of ethanol with 65 ml of 1 mol/L HCl solution was prepared and 10 ml of Pyrrole was dropped in the mixture and stirred for 15 min. N-PC is dipped in the mixture for 15 min with stirring and then drained for 3 min and then dipped in a solution of (NH₄)₂S₂O₈ dissolved in 25 ml of 1 mol/L HCl in an ice-water bath for 5 min to induce the polymerization effect and crosslink the pyrrole matrix attached to N-PC. Then the Polypyrrole nitrogen porous carbon composite (PP/N-PCC) was separated then washed with distilled water and dried at 55°C overnight.

2.3. Column system studies

A sorption system was carried out in the 15 mm internal diameter and 35 cm long glass column at room temperature. The PP/N-PCC sorbent was packed in the column with bed heights (2.5, 5 and 7.5 cm). The inlet flow feed liquid (10, 15 and 20 ml/min) was performed by the peristaltic pump in the up-flow system. Also, the column operating parameters of pH (2–9) and initial Cd (II) concentrations (50, 75 and 100 mg/l) were investigated. At interval time, samples from treated liquid were taken and analysed by Atomic Emission Spectroscopy (TRACE AI1200). The plotting between outlet concentration (C_{outlet})/inlet concentration (C_{inlet}) with the time was used to study breakthrough curves (BTC) of the column sorption system. The following mathematical equations were used in the design of the column operating system [25,30,31]:

\[ V_{(outlet)treated} = Q_t \]  
\[ S_{total} = \frac{Q_t A}{1000} \]  
\[ q_e = \frac{S_{total}}{x} \]  
\[ m_{total} = \frac{Q_t C_{inlet}}{1000} \]  
\[ R(\%) = \frac{S_{total}}{m_{total}} \times 100 \]

where \( Q_t \): inlet flow rate (mL min\(^{-1}\)), \( A \) (cm\(^2\)): Total area under the BTC, \( t_{total} \): Time of total sorption capacity (min), \( x \): mass of bed height.

2.3.1. Modelling of fixed-bed system

At different operating column systems (bed height, initial concentration, and flow rate), Thomas, Adams-Bohart and Yoon-Nelson kinetic models were used to study the fixed-bed system by linear regression analysis [25,32].

2.3.1.1. Thomas model. The linear form of Thomas model [1]:

\[ \ln \left( \frac{C_{inlet}}{C_{outlet}} - 1 \right) = K_{Th} q_e x Q \]  
\[ - K_{Th} C_{inlet} t \]  

2.3.1.2. Adams-Bohart model. The linear form of Adams-Bohart [25,33]:

\[ \ln \left( \frac{C_{outlet}}{C_{inlet}} \right) = k_{AD} C_{inlet} t - k_{AD} N_0 \frac{Z}{Q} \]

2.3.1.3. Yoon and Nelson model. The linear form of Yoon and Nelson model [25,34]:

\[ \ln \left( \frac{C_{outlet}}{C_{inlet} - C_{outlet}} \right) = k_{YN} t - k_{YN} \tau \]

where \( k_{Th} \): Thomas rate constant (L min\(^{-1}\) mg\(^{-1}\)), \( k_{YN} \): Yoon-Nelson constant (L min\(^{-1}\)), \( k_{AD} \): Adam-Bohart constant (L mg\(^{-1}\) min\(^{-1}\)), \( N_0 \): equilibrium concentration (mg L\(^{-1}\)), \( Z \): bed depth height (cm), \( \tau \): the sorption time of 50% breakthrough (min), sorption time \( t \).

2.4. Desorption studies

The desorption system was performed by pumping using 10 mL/min of 2.0 M HCl at room temperature then the PP/N-PCC bed was washed by distilled water until neutral pH. The residue of the solution in the PP/N-PCC bed column was completely removed by dry air pumping for 7 min. Desorption samples were analysed and the desorption system was stopped when the outlet solution has zero cadmium concentration [35].

3. Results and discussion

3.1. Characterization

3.1.1. BET analysis

The structural characteristics of PP/N-PCC in this work were determined and compared with other carbon materials, as displayed in Table 1. The results appeared that the PP/N-PCC has an improved structure property than biochar materials [17,36]; but it is lower than Granular activated carbon [19] (Figure 1).
Table 1. Structural characteristics of PP/N-PCC compared to other carbon materials.

| Adsorbents                  | Surface area (m²/g) | Pore volume (cm³/g) | References |
|-----------------------------|---------------------|---------------------|------------|
| Granular activated carbon   | 312.03              | 0.128               | [19]       |
| Corn straw biochar          | 13.98               | 0.0132              | [17]       |
| Cordgrass biochar           | 15.1                | 0.0241              | [36]       |
| Mill residues biochar       |                     |                     | [36]       |
| PP/N-PCC                    | 66.25               | 0.0541              | Present study |

Figure 1. SEM analysis of PP/N-PCC before (a) and after (b) Cd (II) sorption.

3.1.2. Elemental mapping analysis
Figure 2 displays the elemental mapping (O, C, and N) of PP/N-PCC which indicates the distribution uniform of O, C, and N constituents in the matrix of PP/N-PCC.

3.1.3. FT-IR analysis
Figure 3 shows the FTIR bands of PP/N-PCC matrix before and after Cd (II) uptake. Before Cd (II) uptake, the peaks at 673 is attributed to N–H vibration whereas, the peaks at 885 and 998 cm⁻¹ are assigned to C–H vibration of out-plane and in-plane of the PPy, respectively [37,38]. The peak at 1314 is assigned to C–N stretching of the PPy and 1502 cm⁻¹ is ascribed to the fundamental vibrations of ring-stretching of PPy ring [39,40]. While the observed peaks at 1130 and 1201 cm⁻¹ are assigned to =C–H vibrations of PPy [4,41]. The peak at 3421 is assigned to N–H and O–H stretching vibrations. The FTIR bands of PP/N-PCC after Cd (II) sorption are almost similar to the FTIR spectrum before sorption but with decreasing in the band intensities and also, slight shifts were noticed in the bands at 673, 998, 1201, 1314, 1502 and 3421 cm⁻¹ which are attributed to the interaction with Cd (II) ions. The weaker in the peaks at 673, 1314 and 3421 cm⁻¹ after Cd(I) sorption are assigned to the Cd²⁺ ions binding with the oxygen of the O group and nitrogen of the amino group of the PP/N-PCC surface which is the main dynamic affecting the sorption of Cd (II) ions [42]. According to FT-IR outline before and after Cd (II) sorption onto PP/N-PCC, electrostatic attraction, complexation and ion-exchange between cadmium ions and oxygen of O–H group and nitrogen-containing in the amino group on PP/N-PCC were the principal mechanisms accountable for Cd (II) uptake [41].

3.1.4. XRD analysis
Figure 4 shows the XRD analysis of nitrogen porous carbon (N-PC), pure Pyrrole and PP/N-PCC. In the N-PC patterns, two peaks at 2θ = 22.9° and 43.9° were appeared owing to graphite carbon structure [43]. Whereas in the PP/N-PCC patterns, the peaks at 2θ = 43.9° was omitted and small weak and shift in the peak at 2θ = 22.9° appeared which is the same of XRD patterns of pure PPy.
indicating the full coating of PPy on the N-PC structure to form the PP/N-PCC matrix [39,44]. Also, the XRD pattern of PP/N-PCC after adsorption appeared the presence of cadmium elements in the pattern at 2θ = 45° and 53.3° indicating sorption interaction of Cd (II) onto PP/N-PCC matrix.

3.2. Sorption column dynamics

Influence of pH: the pH has a major impact on the adsorption capacity of the adsorbent material because it changes the type of charges on the adsorption sites and thus controls the adsorption forces. The range of pH (2–9) was utilized to investigate the effect of pH on the BTC and to determine the optimum pH in the operating column system. The pH of inlet feed was controlled by 0.1 M NaOH and 0.1 M HNO3 and the experiments were performed at (10 ml/min inlet flow rate, 7.5 cm bed depth and 100 mg/l Cd (II) concentration). The results in Table 2 display that the R% of Cd (II) was improved from 22.32% to 71.45% with an increase in pH
Table 2. Effect of pH in the BTCs of Cd (II) sorption onto PP/N-PCC at 10 ml/min, 7.5 cm, bed depth and 100 mg/l inlet Cd (II) concentration.

| pH | $t_b$ (min) | $t_{total}$ (min) | $V_b$ (ml) | $V_{outlet}$ (ml) | $q_e$ mg/g | $R$ (%) |
|----|------------|-------------------|-----------|------------------|------------|-------|
| 2  | 25         | 80.0              | 250       | 800              | 33.64      | 22.32 |
| 3  | 38         | 150               | 380       | 1500             | 66.54      | 45.47 |
| 4  | 75         | 210               | 750       | 2100             | 162.42     | 66.10 |
| 5  | 120        | 310               | 1200      | 3100             | 233.54     | 71.45 |
| 6  | 110        | 295               | 1100      | 2800             | 219.21     | 60.14 |
| 7  | 90         | 250               | 900       | 2200             | 182.54     | 43.44 |
| 8  | 65         | 160               | 650       | 1600             | 71.24      | 35.74 |
| 9  | 40         | 95                | 400       | 950              | 22.24      | 17.45 |

Table 3. Effect of inlet flow rate in the BTCs of Cd (II) sorption onto PP/N-PCC at pH 5, 7.5 cm bed depth and 100 mg/l inlet Cd (II) concentration.

| Flow rate (ml/min) | $t_b$ (min) | $t_{total}$ (min) | $V_b$ (ml) | $V_{outlet}$ (ml) | $q_e$ mg/g | $R$ (%) |
|--------------------|-------------|-------------------|-----------|------------------|------------|-------|
| 10                 | 120         | 310               | 1200      | 3100             | 233.54     | 71.45 |
| 15                 | 66.0        | 190               | 660       | 1900             | 110.64     | 41.55 |
| 20                 | 38.0        | 120               | 380       | 1200             | 33.54      | 19.88 |

until reached 5 and then reduced. The decrease in the $R_\%$ at pH < 5 attributed to the competition between H$^+$ and cadmium ions onto sorption sites of PP/N-PCC [45]. Whereas, at pH 5, the formation of insoluble compounds led to reducing the $R_\%$ of Cd (II) ions [46].

Influence of flow rate: the residence time of the interaction of Cd (II) ions with active sites of PP/N-PCC in the bed column system was controlled by the inlet flow rate of the column feed system. Table 3 shows that the increase of inlet flow rate from 10 to 20 ml/min at optimum column parameters decrease the $R_\%$ from 71.45% to 19.88% and the sorption capacity decreased from 233.54 to 33.54 mg/g owing to the reduction of residence sorption time of Cd (II) ions with active sites of PP/N-PCC [47]. Kinetic modelling of experimental outcomes (Table 4) indicates that the increase in the feed flow rate raises $k_{Th}$ and decreases of $q_{Th}$ of the Thomas model. While the $K_{Ad}$ of the Adam-Bohart model increased with an increase in inlet flow rate. Also, $K_{YN}$ of the Yoon and Nelson model increased with an increase in the feed flow rate but the $\tau$ was decreased. The overall outcomes (Figure 5) indicate that both sorption capacity and breakthrough time decreased and the breakthrough curve becomes faster when the inlet flow rate increased as a result of the reduction in the attraction time of Cd (II) ions with PP/N-PCC [26].

Influence of bed depth: Table 5 shows the $R_\%$ of Cd(II) ions enhanced from 35.32% to 71.45% and the breakthrough curve becomes sharper with increasing of bed depths of PP/N-PCC from 2.5 to 7.5 cm at the optimum parameters obtained as a result of the abundance in the sorption sites [48]. Modelling of bed depths results (Table 6) appeared an increase in $q_{Th}$ and decreasing in $k_{Th}$ of Thomas model owing to the increase in the driving force between Cd (II) ions and sorption sites [31]. Whereas decreased in $k_{Ad}$ of the Adam-Bohart model and $K_{YN}$ of Yoon and Nelson model with an increase in the bed depth of PP/N-PCC appeared. The increase in the PP/N-PCC bed depth increase in the effectiveness of the column sorption system (Figure 6).

Influence of initial Cd (II) concentration: Table 7 shows the sorption capacity of PP/N-PCC increased with increase in the inlet metal concentration (50–100 mg/l) whereas $R_\%$ was decreased from 85.23% to 71.45% to at obtained optimum parameters (Table 3) owing to

Table 4. Results of Thomas, Yoon-Nelson and Adams-Bohart models at different operating inlet flow rates (pH5, 7.5 cm bed depth and 100 mg/l inlet Cd (II) concentration).

| Flow rate (ml/min) | $q_T$ (mg/g) | $k_{Th}$ (ml/min.mg) | $R^2$ | $\tau$ (min) | $k_Y$ (1/min) | $R^2$ | $N_0$ | $K_A$ (1/min) | $R^2$ |
|--------------------|--------------|----------------------|-------|--------------|---------------|-------|-------|--------------|-------|
| 10                 | 213.10       | 63.22                | 0.992 | 824.41       | 333.23        | 0.921 | 22.14 | 8.210        | 0.841 |
| 15                 | 98.33        | 77.32                | 0.988 | 645.29       | 421.36        | 0.983 | 19.21 | 10.21        | 0.758 |
| 20                 | 29.64        | 84.21                | 0.995 | 422.65       | 533.21        | 0.985 | 17.22 | 15.24        | 0.823 |

Figure 5. Kinetic modelling of Thomas (a), Yoon–Nelson (b) Adams-Bohart(c) models at different flow rates.
Table 5. Effect of depth in the BTCs of Cd (II) sorption onto PP/N-PCC at pH5, 10 ml/min and 100 mg/l inlet Cd (II) concentration.

| Depth (cm) | t_b (min) | t_total (min) | V_b (ml) | V_outlet (mL) | q_e (mg/g) | R (%)  |
|-----------|-----------|---------------|---------|---------------|-----------|--------|
| 2.5       | 55        | 130           | 550     | 1300          | 77.42     | 35.32  |
| 5.0       | 85        | 265           | 850     | 2650          | 155.51    | 52.44  |
| 7.5       | 120       | 310           | 1200    | 3100          | 233.54    | 71.45  |

Table 6. Results of Thomas, Yoon-Nelson and Adams-Bohart models at different operating bed depths (pH5, 10 ml/min and 100 mg/l inlet Cd (II) concentration).

| Depth (cm) | q_T (mg/g) | k_th (mL/min.mg) | R^2 | k_Y (1/min) | N_0 (min) | K_A (1/min) | R^2 |
|------------|------------|------------------|-----|-------------|-----------|-------------|-----|
| 2.5        | 222.12     | 55.32            | 0.993 | 824.54      | 333.20    | 0.984       | 22.14 |
| 5.0        | 215.32     | 62.32            | 0.999 | 645.16      | 421.33    | 0.951       | 19.20 |
| 7.5        | 213.10     | 81.21            | 0.997 | 422.63      | 533.25    | 0.982       | 17.27 |

The fast saturation of PP/N-PCC sorption sites [32,34,49]. Kinetic modelling of results (Table 8) indicates an increase in the k_th and q_th values of the Thomas model with increasing in the inlet metal concentration (50–100 mg/l) owing to the growth in the Cd (II) ions in the sorption system [34]. However, an increase in k_AD of the Adam-Bohart model and K_YN of Yoon and Nelson model with an increase in the increasing of metal concentration (50–100 mg/l) was seemed (Figure 7).

3.2.1. Kinetic model fitting

The fitting of sorption outcomes of kinetic models is determined by the colouration coefficient (R^2). The outcomes of kinetic modelling indicate that the Thomas model appeared higher R^2 than the Adams-Bohart model and Yoon–Nelson models at different column operating parameters. These outcomes established that the Thomas model is the best fitting model in the design of the column system[50,51].

3.3. Reusability of PP/N-PCC

The outcomes of the sorption-desorption cycle display that 2.0 M HCL desorbs 99.52% of Cd (II) ion from PP/N-PCC. The sorption-desorption system was carried out at pH5, 10 ml/min, 7.5 cm bed depth, 100 mg/l inlet Cd (II) concentration and room temperature. The results appeared a decrease in the adsorptive capability of PP/N-PCC from 71.45% to 35.23% after 8 cycles indicating good reusability of PP/N-PCC in the column system. Table 9 displays the assessment of sorption capacities of PP/N-PCC and other adsorbents in the uptake of Cd(II) from the liquid system and the data shows that PP-N-PCC appeared an acceptable outcome comparing with the listed adsorbents.

Table 7. Effect of inlet Cd (II) concentration in the BTCs of Cd (II) sorption onto PP/N-PCC at pH5, 10 ml/min and 7.5 cm bed depth.

| C_inlet (mg/L) | t_b (min) | t_total (min) | V_b (ml) | V_outlet (mL) | q_e (mg/g) | R (%)  |
|---------------|-----------|---------------|---------|---------------|-----------|--------|
| 50            | 110       | 280           | 1100    | 2800          | 116.23    | 85.23  |
| 75            | 70.0      | 205           | 700     | 2050          | 163.21    | 66.23  |
| 100           | 120       | 310           | 1200    | 3100          | 233.54    | 71.45  |
Figure 7. Kinetic modelling of Thomas (a), Yoon–Nelson (b) Adams-Bohart(c) models at different initial Cd concentration.

Table 8. Results of Thomas, Yoon-Nelson and Adams-Bohart models at different operating inlet Cd (II) concentrations (pH5, 10 ml/min and 7.5 cm bed depth).

| C_{inlet} (mg/L) | q_T (mg/g) | k_{Th} (ml/min.mg) | R^2 | r (min) | k_Y (1/min) | R^2 | N_0 (min) | k_A (1/min) | R^2 |
|------------------|------------|---------------------|-----|---------|------------|-----|-----------|------------|-----|
| 50               | 166.21     | 45.32               | 0.992 | 824.21 | 333.2      | 0.921 | 22.14     | 8.21       | 0.841 |
| 75               | 195.21     | 67.21               | 0.988 | 645.32 | 421.3      | 0.983 | 19.2      | 10.21      | 0.758 |
| 100              | 213.10     | 75.32               | 0.995 | 422.26 | 533.2      | 0.985 | 17.2      | 15.24      | 0.823 |

Table 9. Comparison of Cd (II) adsorption capacity of PP/N-PCC with other adsorbents.

| Adsorbent | pH | Sorption capacity (mg/g) | References |
|-----------|----|--------------------------|------------|
| Poly(methacrylic-co-acrylonitrile) (p(MAc-co-AN)) microgels | 6.0 | 334.5 | [28] |
| Amidoximated poly(acrylonitrile) particles | 6.0 | 87 | [29] |
| Activated Carbon | 5.0 | 30.6 | [15] |
| Crosslinked magnetic Chitosan-phenylthiourea resin | 5.0 | 120 | [52] |
| Chitosan/activated carbon composite | 5.5 | 52.63 | [19] |
| Crosslinked chitosan/polyvinyl alcohol blend beads | 6.0 | 142.9 | [8] |
| C-PC | 5.0 | 123.87 | Present study |
| PP/N-PCC | 5.0 | 233.54 | Present study |

4. Conclusions
The prepared PP/N-PCC appeared better efficient in the removal of Cd (II) ions from aqueous wastes in the column procedure. The inlet metal concentration, flow rate, PP/N-PCC bed depth and pH are important fundamentals in the design of the column sorption system. Lowering flow rate, increasing bed depth, pH5 are the recommended parameters for a good operation of the column system. According to the outcomes of R^2 analysis, the kinetic modelling indicates that the Thomas model is the best fitting model in the design of column system than Adams-Bohart and Yoon–Nelson models. PP/N-PCC adsorbent appeared well recycled by using 2.0 M HCl and its reusability reached 8 cycles indicating the economic feasibility of PP/N-PCC in the separation of Cd (II) ions from liquid wastes.

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