Chemical analysis of corn cob-based biochar and its role as water decontaminants

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ABSTRACT
Production of biochar is accomplished by pyrolysis of corncobs at 350 °C (BC-350) and 450 °C (BC-450) under oxygen-limited conditions. The chemical and physical properties were investigated via XRD, FTIR, BET, SEM and EDX analysis. Batch experiments were conducted for the adsorption of Pb2+ ions from aqueous solution onto biochar with regards to pH, contact time, biochar dose and initial Pb2+ concentration. The adsorption efficiency of Pb2+ was increased as increasing pH and biochar dose up to 1.5 g/L. Kinetic and isothermal studies demonstrated that the experimental data were fitted with the pseudo-second-order model, Langmuir and Freundlich isotherms. The study emphasized the preferable pyrolysis temperature which is 450 °C. According to the Dubinin-Kaganer-Radushkevich (DKR) model, the adsorption process of Pb2+ was a chemical and endothermic reaction. Results showed the applicability of corncob based biochar to be used as an efficient and low cost adsorbent for Pb2+ ions removal.

1. Introduction
Water is very important sources for the continuity of life on earth [1]. Water scarcity worldwide due to droughts and contamination are concerns that intensify global worrying [2]. Globally with increasing population size there are increasing demands of water supply but the rapid rates of urbanization and industrialization resulted in the generation of polluted effluent waste [3]. When the levels of contaminants and pollution are rising, they are influenced both human and ecological system at the same time [4]. So looking for other sources for water is very important for the solution of water scarcity in different countries [2].

Wastewater irrigation affects plants and soil due to the presence of heavy metals elements pollution in most of it [5]. Accordingly, it is extremely important to obtain efficient methods to remove heavy metals from polluted water. Some technologies have been used for this purpose such as membrane filtration, adsorption, electrocoagulation, and chemical adsorption [6]. Among these technologies, the adsorption process is the lowest cost and better effective method due to the use of cheap, non-toxic and recyclable materials Pb2+ is one of the highest toxic metals even at low concentrations. When humans poisoned by lead many internal organs will be affected leading to direct or indirect serious health issues [1].

Using Natural adsorbent, some researchers found that clay minerals can effectively adsorb contaminants from aqueous effluents due to their good adsorption and high cation exchange capacity. The adsorption kinetic study revealed that the dye removal process is mainly governed by a pseudo-first-order mechanism. Thus, surfactant-modified clays are an excellent choice as cost-effective and efficient adsorbents for the purification of water from dye contaminants [7].

Some other scientists used the adsorption isotherms to evaluate adsorption data of synthesize poly(acrylic acid) hydrogel embedded with magnetic cobalt (Co) nanoparticles and to investigate their potential in adsorption and catalysis. Results showed that Freundlich isotherm model was followed with $R^2$ value of 0.95. The hydrogel was also used for catalytic reduction in a toxic pollutant, i.e. 4-nitrophenol. Experimental data for 4-nitrophenol reduction followed pseudo-first-order kinetics model [8].

Synthesized Graphene oxide–silver (GO–Ag) nano composite was used as a sorbent for the elimination of some toxic pollutants from the aqueous medium, as an efficient antibacterial agent for the destruction of some harmful microorganisms existent in wastewater. Various experimental parameters affecting the adsorptive behaviour of nanocomposite were evaluated thoroughly [9].

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The amidoximated p(VBC) prepared beads were used as an adsorbent for the removal of organic dyes from aqueous media. The Langmuir, Freundlich and Temkin adsorption isotherms were applied to the adsorption processes. It was found that the prepared beads were capable of removing significant amounts of arsenate and dichromate ions from tap and river (Saricay, Canakkale–Turkey) water [10].

Recently, there is a high percentage of agriculture resources produced globally which are inefficiently used and not recycled [11]. Burning plant-derived biomass has increased for coal production, but it has some side effects on the environment and human health, therefore, modified methods were added for the biomass for production of higher grade fuels [12]. Biochar (BC) is charcoal made from direct thermal decomposition of biomass. It is an eco-friendly solid material obtained from the pyrolysis or gasification of the biomass in an environment free from oxygen [11]. It has low cost, a wide range of availability as well as mechanical and thermal stability, which assist its implementing in many environmental applications in addition to its high affinity for removal of inorganic and organic contaminants better than commercial activated carbon [13].

Food crops generate wastes such as corn cob, utilized to produce biochar [11]. Corncob is a residue, which is being used in several countries including Saudi Arabia. Globally, corn cob is one of the major causes of solid waste. Therefore, conversion of the corn cob to biochar will be of great value for removal of wastewater contamination [14]. Corncobs can be converted into biochar via a slow pyrolysis process. Some researchers have studied the adsorption of uranium, chromium and cationic dyes by modified corncobs-based biochar [15].

The Kingdom of Saudi Arabia (KSA) has a large size of the desert which put it at risk of drought due to low water supply, especially with the high need of water for agricultural, municipal and industrial sectors [16]. A large amount of industrial and agricultural waste are generated every year in the kingdom and disposed of in landfills or dumpsites after partial segregation, this causes environmental pollution and public health problems [17]. Therefore, there is a need for recycling and purification of the wastewater [18].

A lot of corncobs seems to be natural waste resources and the origin of environmental pollution. There is a high ratio between corn grain and corn cob (100:18) which leads to the accumulation of large amounts of useless corn cob globally and in Saudi Arabia in particular [18]. Therefore, this study will focus on the use of biochar produced from corncob cultivated in Assir Region for removal of lead metal from contaminated water solution.

2. Material and methods

2.1. Biochar samples materials

2.1.1. Corncob material

Corncob was collected from a local farm of Abha, Saudi Arabia. Samples were air-dried at room temperature, impurities were removed, and sorted in a similar mass size (21–26 mm diameter, 64–73 mm length) before pyrolysis runs.

2.1.2. Preparation of corncob

The dried corncob samples were crushed, ground, and sieved (particle size less than 0.25 µg). The obtained powders washed thoroughly using deionized water, dried in the oven at 100°C till constant weight, and washed using hydrochloric acid to eliminates impurities and make the corn cob in chloride form. Samples re-washed using deionized water and dried in the oven at 100°C.

2.1.3. Biochar production, characterization and analysis

To produce (BC), Corncob placed in covered porcelain dishes, kept in a muffle furnace at two different temperatures (350°C and 450°C) for 3 h to obtain BC-350 and BC-450.

2.1.3.1. Biochar chemical and physical characterization.

Fourier Transform Infrared Spectroscopy (FTIR) was utilized to distinguish and characterize the sample analysis of biochar in the mid-IR range (400–4000 cm\(^{-1}\)) as published [17]. While X-ray diffraction (XRD) was used to examine the diffraction pattern of the biochar using Cu K\(\alpha\) radiation at 40 kV and 30 mA. The measurements were performed with a scanning speed of 2°/min and scanning range from 10 to 90°C [19].

Scanning Electron Microscopy (SEM) was used to identify the surface characteristics of the biochar as published [19]. Brunauer–Emmett–Teller (BET) analysis technique was applied for measuring the surface area and significant characteristic of porous materials as reported in literature [20].

2.1.4. Biochar analysis

2.1.4.1. Preparation of Pb\(^{2+}\) solution (adsorbate).

Lead stock solution of 1000 mg/L was prepared by dissolving a specific quantity of Pb(NO\(_3\))\(_2\) with deionized water in a 1000 ml volumetric flask. Then, test samples of different concentration 25, 50, 75, 100 and 200 mg/L were prepared by successive dilution of prepared stock solution according to dilution law [21].

2.1.4.2. Experimental procedure and operating parameters.

Batch experiments were used to investigate the optimum conditions for biochar adsorption of
lead using published techniques [22]. The percentage removal of Pb$^{2+}$ and amount adsorbed (mg/g) were computed using equations reported by Suneetha and Ravindhranath [23].

2.1.4.3. Operating parameters and effects. The effect of contact time, dose, and Pb$^{2+}$ concentration on the pH of the different Pb$^{2+}$ solutions was studied and analysed using ICP-MS as mentioned previously published research [24].

2.1.4.4. Kinetic modelling. To make a comparison for the different driven biochar from corn cobs waste at different pyrolysis temperatures (BC-350 and BC-450) kinetic modelling for sorption of metals pollutants were studied using Intra-particle diffusion model [25], pseudo-first-order [26], and pseudo-second-order [27].

2.1.4.5. Adsorption isotherms. For determination of adsorption isotherms, suitable model for the design process, fitting isotherm data accurately into different isotherm models was applied using published techniques [28,29]. The batch experiments results were subjected to Langmuir [30], Freundlich isotherms [31], and Dubinin-Kaganer-Radushkevich model [32] to study the adsorption mechanisms and efficiencies of the adsorbent.

3. Results and discussion

3.1. Biochar characterization and analysis

3.1.1. Chemical and physical characterization

The following results were reported and demonstrated to investigate the adsorption mechanism of Pb$^{2+}$ onto biochar (BC-350 and BC-450) and its chemical properties.

The obtained XRD spectra of BCs (BC-350 and BC-450) crystalline phases patterns (Figure 1) showed the presence of one peak indicating the occurrence of the pristine structure of carbonaceous materials [33]. No difference peaks diffraction were noticed in both samples, they showed the crystalline structure.

FTIR was used to investigate the functional groups of different BCs (BC-350 and BC-450). The results reported (Figure 2) that there are no distinct peaks within the measurement range, indicating no functional groups are found on the surface of BC-350. The BC-450 exhibited a broad peak at 2950–3650 cm$^{-1}$ related to stretching vibration for –CH$_2$ and CH$_3$ in aliphatic hydrocarbon [34], and other peaks assigned to the stretching vibration of functional groups phenolic/carboxylic OH and C = O groups in –COOH.

The peak at 2430 cm$^{-1}$ band assigned to the stretching vibration of CH groups that were related to aliphatic or alicyclic carbons in biochar or related to COO group. The peak at 1610 cm$^{-1}$, represent stretching C–C, indicated that a few relatively stable aromatic compounds were gradually formed. The broad characteristic peak between 1429 cm$^{-1}$ and 1100 cm$^{-1}$ represented saturated OH in-plane bending vibration, C = O stretching, C–H stretching in double-bonded carbon, C–(OH) bond stretching and C–O stretching in hydrocarbons. The peaks at 975 cm$^{-1}$ and 795 cm$^{-1}$ represented the aromatic CH out-of-plane bending [35].

The surface and textural properties of BC-350 and BC-450 material, nitrogen adsorption/ desorption for materials are investigated. Isotherm and pore diameter distribution result was illustrated in Figures 3 and 4. The obtained isotherm results of BC-450 showed IUPAC I isotherm related to microporous materials while BC-350 has not. This means it has type H4 hysteresis corresponds to limited amounts of mesopores, this was proved incompatible of the study published [36].

BC-450 had a larger specific surface area and pores structure distribution than BC-350. For BC-450, the specific surface area, total pores volume, and micropores volume are 407 m$^2$/g, 0.155 cm$^3$/g, 0.108 m$^3$/g, respectively, these results are greater than those of BC-350. The specific surface area, total pores volume, and micropores volume of BC-350 are lower 80, 77.5, and 60 times than those of BC-450, respectively. The pore distribution diameters were 0.35–0.48 and 0.38–1.5 nm for both BC-350 and BC-450, respectively. The average pore diameters were 1.9 and 3.2 nm for BC-350 and BC-450, respectively.

SEM, BET and EDX Analysis of BC-350 and BC-450 (Figure 5 and 6) show the morphology of the biochar and element mapping provide different BC composition. Analysis of BC-350 and EDX mapping and elemental analysis is shown in (Figure 5). The well-defined channel arrays of hollow carbon were prepared from pyrolysis which revealed that the formation of biochar via biomass pyrolysis is highly important [37]. The EDX
and elemental mapping show the occurrence of carbon with 63 mass % and oxygen with 36 mass %. Figure 6 shows SEM, EDX mapping and element analysis of BC-450. It was found that the structures and folds containing different diameter pores, which provided the large specific surface area to enhance the adsorption capacity of metals. BC-450 showed uniformly distributed pores on the biochar surface (Figure 6) as depicted SEM image. Spectrum from the selected sample region confirmed the presence of carbon with 74.63 mass % and oxygen with 25.37 mass %. To verify the uniformity of nano-composites, further analysis was done on elemental mapping (Figure 6). The elemental mapping showed uniformly distributed of the elemental composition of BC.

3.1.2. Biochar analysis

3.1.2.1. $\text{Pb}^{2+}$ removal from water sample. The adsorption processes of lead ions from wastewater using the obtained biochar (BC-350 and BC-450) were recor
Figure 5. SEM analysis of BC-350 and EDX mapping and element analysis: (a) SEM image, (b) C mapping, (c) O mapping, (d) EDX spectrum.

The initial pH influence of Pb^{2+} ions aqueous samples on the removal efficiency of BC-450 showed (Table 1) that increases in removal from 17% to 72% with...
increasing pH from 2.5 to 6.5. However corresponding values for BC-350 (Table 1) are changed from 12% to 43%. Notably, adsorption of Pb$^{2+}$ ions on biochar surface increased with increase in pH of Pb$^{2+}$ ions aqueous samples. The point of zero charge of biochar is 5.7, so the surface of adsorbent will be positively charged at
lower pH due to adsorption of hydrogen ions on the surface of adsorbents, at the same time, Pb$^{2+}$ ions will be positively charged so it is hardly adsorbed at lower pH. Meanwhile, at higher pH value, the surface of biochar is negatively charged, and suitable for uptake the positively charged metals ions, hence removal efficiency is increased. The increased removal efficiency of Pb$^{2+}$ ions with increasing pH value matched well with previous data [38].

The results for the removal of Pb$^{2+}$ ions and adsorptive capacity are illustrated in Table 2. The removal efficiency of Pb$^{2+}$ ions increased from 13% after 10 min of contact to 37% at 60 min of reaction time for BC-350. Meanwhile, the analogue removal efficiency for BC-450 changed from 23.4% to 67%. There is a slight increase in adsorption after 60 min that is recorded for both materials. Hence, the removal efficiency was progressively increased with time and equilibrium is achieved after 60 min. A similar study found that 60 min are needed for Pb$^{2+}$ ions to reach equilibrium using polyoxometalate/titania composite [39].

The adsorptive capacity of biochar at different pyrolysis temperature for Pb$^{2+}$ ions removal is studied to reveal the influence of the temperature. In particular, the adsorption of heavy metals by biochar is known to be influenced by the substitutable ions content, the existence of different functional groups, the distribution of functional groups such as C=C, hydroxyl and carboxyl groups, and the specific surface area [40, 41]. Increasing the pyrolysis temperature until 600°C increases the specific surface area, the number of functional groups, such as C=C, and the exchange ions capacity [38]. For this reason, it was concluded that the Pb$^{2+}$ ions adsorption capacity of biochar is increased when the pyrolysis temperature is increased.

### Table 1. Effect of pH on the removal efficiency of Pb$^{2+}$ using BC-350 and BC-450.

| pH value | Residual concentration (mg/l) | Removal % | Adsorbed (mg/g) |
|----------|-------------------------------|-----------|-----------------|
|          | BC-350 | BC-450 | BC-350 | BC-450 | BC-350 | BC-450 |
| 2.50     | 44.00  | 41.50  | 12.00  | 17.00  | 06.00  | 08.50  |
| 3.50     | 42.50  | 39.00  | 15.00  | 22.00  | 07.50  | 11.00  |
| 4.50     | 37.00  | 28.00  | 26.00  | 44.00  | 13.00  | 22.00  |
| 5.50     | 32.00  | 17.60  | 36.00  | 64.80  | 18.00  | 32.40  |
| 6.50     | 28.50  | 14.00  | 43.00  | 72.00  | 21.50  | 36.00  |

### Table 2. The effect of contact time of adsorption, the removal efficiency of Pb$^{2+}$ ions using BC-350 and BC-450.

| Time (min) | Residual concentration (mg/l) | Removal % | Adsorbed (mg/g) |
|------------|-------------------------------|-----------|-----------------|
|            | BC-350 | BC-450 | BC-350 | BC-450 | BC-350 | BC-450 |
| 0          | 50.00  | 50.00  | 00.00  | 00.00  | 00.00  | 00.00  |
| 10         | 43.50  | 38.30  | 13.00  | 23.40  | 06.50  | 11.70  |
| 20         | 38.40  | 29.20  | 23.20  | 41.60  | 11.60  | 20.80  |
| 30         | 33.30  | 19.90  | 33.40  | 60.20  | 16.70  | 30.10  |
| 45         | 32.00  | 17.60  | 36.00  | 64.80  | 18.00  | 32.40  |
| 60         | 31.50  | 16.70  | 37.00  | 66.60  | 18.50  | 33.30  |
| 75         | 31.20  | 16.10  | 37.60  | 67.80  | 18.80  | 33.90  |
| 90         | 31.05  | 15.80  | 37.90  | 68.40  | 18.95  | 34.20  |
| 120       | 30.90  | 15.60  | 38.20  | 68.80  | 19.10  | 34.40  |

Figure 7. Intra-particle diffusion of Pb(II) within BC-350 and BC-450 adsorbents using 50 mg/L of lead ions and 1 g/L of sorbents dose.

### 3.2. Kinetic modelling

#### 3.2.1. Intra-particle diffusion model

Results of the intra-particle diffusion of Pb$^{2+}$ within BC-350 and BC-450 adsorbents (Figure 7) occurred in two stages. The linear step is related to fast removal Pb$^{2+}$ using both BC-350 and BC-450 adsorbents. The initial fast stage of adsorption process isn’t passing through the zero point which means that the dominant removal efficiency for both BC-350 and BC-450 are by film diffusion for the intra-particle diffusion process. In the second stage, explain the speed of both BC-350 and BC-450 for lead ions removal which means the non-consecutive diffusion for the Pb$^{2+}$ molecules within both of BC-350 and BC-450 as adsorbent [42].

#### 3.2.2. Pseudo-first-order kinetic model

Results of pseudo-first-order kinetic model analysis were shown in Figure 8 and Table 3. In the figure, it is clear that the linear relationship between log ($q_e$ − $q_t$) against time “t” and $k_1$ and $q_e$ can be obtained from the equation of linear relationship which is the slope...
and intercepts, respectively. On the other hand, Table 3 shows the relation’s parameters of kinetic models for Pb\(^{2+}\) ions adsorption on both BC-350 and BC-450 adsorbents which signify that the model of pseudo-first-order not practically estimated of \(q_e\) for Pb\(^{2+}\) ions removal, as the experimental value \(q_e\) for both BC-350 and BC-450 adsorbents (0.179 and 0.322 meq/g) is not near to the calculated outcome (0.237 and 0.426 meq/g), respectively. This is owing to the number of binding sites \((q_e)\) from the intercept at \(t = 0\) strongly affected by the initial fast reaction lead ions removal by both BC-350 and BC-450 adsorbents which are lesser than the equilibrium removal [42].

### 3.2.3. Pseudo-second-order model

Pseudo-Second-Order Model (Table 3) represents the linear relation between \(t/q_t\) and \(t\) Equation. \(k_2\) is the y-intercept 74.46 and 41.546 for both BC-350 and BC-450 adsorbents, respectively, while \(q_e\) is calculated from the slope 0.21 and 0.39 meq/g for both BC-350 and BC-450 adsorbents, respectively. The \(q_e\) is very near to the obtained result from the experiment (0.179 and 0.322 meq/g) for both BC-350 and BC-450 adsorbents, respectively, which proved the agreement with the pseudo-second-order model (Table 3). Also, the obtained correlation coefficients \(R^2\) were 0.98 for both BC-350 and BC-450 sorbents.

The pseudo-second-order model gives a conclusion on the sorption reaction is chemisorption process [43]. The chemisorption reaction occurs through electrons shares or exchanges between the lead ions and both BC-350 and BC-450 adsorbents in through covalent and/or ion exchange reaction.

### 3.3. Adsorption isotherms

#### 3.3.1. Effect of the sorbent dose

The removal efficiency of lead ions by a different dose of biochar ranged 0.25 to 3 g/L of BC-350 and BC-450 was estimated for initial Pb\(^{2+}\) ions concentration of 50 ppm at the optimum pH of 5.5 were recorded (Table 4). The adsorption capacity versus, different dose of BC-350 and BC-450 adsorbents show an increase in removal rate of metal with increasing dose up to 1.5 g/L, after that no remarkable removal rates are noticed. Meanwhile, the adsorption capacity increased until a dose of 1.0 g of biochar materials.

The adsorption rate of Pb\(^{2+}\) ions enhanced with the biochar amount, whilst the more amount of biochar give a higher surface area and more active sites for adsorption. In case of adsorption of metals, over the amount of adsorbent in the solution may lead to slight increase adsorption rate (ca: 8%) this owe to agglomeration that diminishes the adsorption because active sites for adsorption are not completely occupied [44]. From an economic point of view, 1 g/L is chosen as an optimal dose for Pb\(^{2+}\) adsorption.

#### 3.3.2. Effect of initial Pb\(^{2+}\) concentration

Effect of different lead ions concentrations ranged from 25 to 200 mg/L are agitated at 200 rpm with 1 g/L of BC-350 and BC-450, for equilibrium time of 60 min at pH 5.5. The obtained results are shown in Table 5. It is obvious that for Pb\(^{2+}\) ions percentage removal decreased with increasing initial lead ions concentration as an increase

### Table 3. The parameters of the relation of kinetic models for Pb\(^{2+}\) sorption on BC-350 and BC-450.

| Lead ions | \(q_e\) Expe. (meq/g) | \(q_e\) (meq g\(^{-1}\)) | \(k_1\) (min\(^{-1}\)) | \(R^2\) | \(q_e\) (meq g\(^{-1}\)) | \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) | \(R^2\) |
|-----------|-------------------|------------------|-----------------|-------|-------------------|-----------------|-------|
| BC-350    | 0.179             | 0.24             | 0.08            | 0.97  | 0.21              | 0.288           | 0.98  |
| BC-450    | 0.322             | 0.426            | 0.08            | 0.97  | 0.39              | 0.158           | 0.98  |

### Table 4. Effect of adsorbent dose on the removal efficiency of Pb\(^{2+}\) ions using BC-350 and BC-450.

| Dose (g/l) | Residual concentration (mg/l) | Removal % | Adsorbed (mg/g) |
|-----------|------------------------------|-----------|-----------------|
|           | BC-350                       | BC-450    | BC-350          | BC-450  | BC-350          | BC-450  |
| 0.25      | 46.00                        | 42.50     | 8.00            | 15.00   | 8.00            | 30.00   |
| 0.50      | 42.50                        | 37.00     | 15.00           | 26.00   | 7.50            | 26.00   |
| 1.00      | 32.00                        | 17.60     | 36.00           | 64.80   | 18.00           | 32.40   |
| 1.50      | 31.00                        | 14.50     | 38.00           | 71.00   | 12.66           | 23.66   |
| 2.00      | 29.00                        | 14.00     | 42.00           | 72.00   | 10.50           | 18.00   |
| 3.00      | 27.50                        | 13.50     | 45.00           | 73.00   | 7.50            | 12.16   |
Table 5. Effect of initial Pb\(^{2+}\) concentration on their removal efficiency using BC-350 and BC-450.

| Initial conc. (mg/l) | Residual conc. (mg/l) | Removal % | Adsorbed (mg/g) |
|---------------------|-----------------------|-----------|-----------------|
|                     | BC-350 | BC-450 | BC-350 | BC-450 | BC-350 | BC-450 |
| 25                  | 12     | 5.5    | 52     | 78     | 13.0   | 19.5   |
| 50                  | 31     | 16     | 38     | 68     | 19.0   | 34.0   |
| 75                  | 52     | 28     | 31     | 63     | 23.0   | 47.0   |
| 100                 | 76     | 43     | 24     | 57     | 24.0   | 57.0   |
| 200                 | 164    | 136    | 18     | 32     | 36.0   | 64.0   |

Figure 9. Langmuir plot of lead ions sorption over BC-350 and BC-450.

in metal ion concentration resulted in a lower probability of collision with active surface sites of biochar and removal of metal ions decreased [45]. On the other hand, the adsorption capacity of metal ions increased with increasing lead ions concentration.

3.3.3. Langmuir isotherm model

By plotting of \(\frac{C_e}{q_e}\) against \(C_e\) straight line with high correlation coefficient \(R^2\) are obtained indicating adsorption equilibrium obeys Langmuir equation with \(R^2\) values of 0.953 and 0.997 for BC-350 and BC-450, respectively (see Figure 9). Langmuir model assists in the optimization of treatment capacity for system design [46] by calculation of the maximum monolayer capacities \(q_{\text{max}}\) for lead ions removal which is 43 and 71.5 mg/g for BC-350 and BC-450, respectively.

3.3.4. Freundlich isotherm model

Equilibrium results were achieved from the Freundlich isotherm model and the isotherm parameters of both models are collected for comparison (Table 6, Figure 10). Freundlich isotherm model illustrates the heterogeneous adsorption features onto the sorbent surface [47]. Results show that \(R^2 > 0.90\) for the use of the Freundlich isotherm model which proposed the agreement for heterogeneous adsorption features. Thus, the obtained sorption results at equilibrium were fitted to both models with a maximum sorption capacity \(q_{\text{max}}\) of 42.9 and 71.4 mg Pb\(^{2+}\)/g for both BC-350 and BC-450 adsorbents.

If \(0.1 < 1/n < 1.0\), the adsorption process is appropriate on both BC-350 and BC-450 adsorbents. From Table 4 it is clear that \(1/n\) is 0.38 and 0.39 for BC-350 and BC-450, respectively, which concluded BC-350 and BC-450 adsorbents capable to be used for the treatment of lead ions from aqueous solutions even at low concentration [48].

3.3.5. Dubinin–Kaganer–Radushkevich (DKR) model

The Dubinin–Kaganer–Radushkevich slope and constants of the model were shown in Figure 11 and Table 6. The relation between \(\ln q_e\) versus \(\epsilon^2\), thus the slope was found to be \(0.359 \times 10^{-8}\) mol\(^2\)/J\(^2\) and, \(-0.354 \times 10^{-8}\) mol\(^2\)/J\(^2\) for BC-350 and BC-450 adsorbents respectively along with the intercept as a measure to the adsorption capacity \(X_m\) of BC-350 and BC-450 adsorbents. The free energy of both BC-350 and BC-450 adsorbents for adsorption is determined by assuming that the free energy changed when one mole of Pb\(^{2+}\) are transferred to the surface of BC-350 and BC-450 adsorbents from the solution infinity. Consequently, the adsorption energy can be calculated as follows:

\[
E = \frac{1}{\sqrt{2\beta}}
\]

The adsorption free energy \(E\) for Pb\(^{2+}\) removal by both BC-350 and BC-450 adsorbents were found around

Table 6. Parameters of isotherm models for Pb\(^{2+}\) sorption over BC-350 and BC-450.

| Lead ions | Langmuir model | Freundlich model | Dubinin–Kaganer–Radushkevich (DKR) |
|-----------|----------------|------------------|-----------------------------------|
|           | \(K_L\) (L/mg) | \(q_{\text{max}}\) (mg/g) | \(R^2\) | \(K_f\) | \(n\) | \(R^2\) | \(X_m\) (mol\(^2\)/J\(^2\)) | \(\beta\) (mol\(^2\)/J\(^2\)) | Ekl/mol | \(R^2\) |
| BC-350    | 5.10           | 42.90            | 0.956 | 2.03   | 2.66  | 0.98  | 5.04 \times 10^{-4} | -0.359 \times 10^{-8} | 11.80 | 0.98 |
| BC-450    | 18.50          | 71.43            | 0.99  | 40.08  | 2.6   | 0.91  | 1.15 \times 10^{-3} | -0.3545 \times 10^{-8} | 11.91 | 0.94 |
for lead ions removal by both BC-350 and BC-450 sorbents were found around 11.0 kJ/mol and have a positive value which adsorption reaction is endothermic indicating physical or chemical sorption. Conclusively, corn cobs-based biochar is considered as promising water decontamination materials from metals.

Disclosures
No potential conflict of interest was reported by the author(s).

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