Binary adsorption studies of Cr(VI) and Cu(II) ions from synthetic wastewater using carbon from Feonniculum vulgare (fennel seeds)

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Abstract: This study aims to remove Copper (Cu(II)) and Chromium (Cr(VI)) from aqueous solution using activated carbon (AC) from fennel seeds and potassium permanganate (KMnO₄) treated fennel seeds. The activated carbon adsorbents were prepared from fennel seeds at different temperatures (500, 600 and 700°C). These adsorbents were designated as FS-500, FS-600 and FS-700. Each adsorbent was then chemically treated with KMnO₄ solution to develop activated adsorbents, KMFS-500, KMFS-600 and KMFS-700. These six adsorbents were used for the binary adsorption of Cu(II) and Cr(VI) from an aqueous solution. The adsorbents were characterized by FTIR, SEM, UV-Vis and XRD. FTIR confirmed the presence of oxygen functional groups such as hydroxyl (-OH), carboxyl (-COOH) and carbonyl (-C = O) on the surface of the adsorbents. XRD confirmed a decrease in crystallinity as the temperature increased. SEM images showed that the morphology of the adsorbents was porous. KMFS-700 and FS-700 adsorbed more Cu(II) and Cr(VI) ions than KMFS-600, KMFS-500, FS-600 and FS-500. The maximum adsorption capacities for Cu(II) and Cr(VI) by FS-700 were 19.886 and 8.510 mg/g; for FS-600, it was 15.423 and 1.202 mg/g, and for FS-500, it was 16.921 and 1.722 mg/g, respectively. The maximum adsorption capacities for Cu(II) and Cr(VI) by KMFS-700 were 19.786 and 10.572 mg/g; for KMFS-600 it was 15.735, 8.109 mg/g, and for KMFS-500, it was 17.648 and 3.479 mg/g, respectively. All the adsorbents showed a stronger affinity for Cu(II) than Cr(VI). Kinetic studies showed that Cu(II) and Cr(VI) adsorption followed a pseudo-second-order reaction confirming that a chemical process controlled adsorption.

Subjects: Chemical Engineering; Adsorption Science; Clean Technologies; Environmental

Keywords: Carbonization; potassium permanganate; fennel seeds; adsorption; heavy metals

1. Introduction

Pollution of water due to ever growing urbanization and industrialization by toxic metals such as chromium (Cr), cadmium (Cd), mercury (Hg), copper (Cu), lead (Pb), manganese (Mn), arsenic (As) and nickel (Ni) is alarming (Oladojo et al., 2019). These toxic metals are detrimental to living organisms (Ayub et al., 2018; Nimibofa et al., 2017). Water pollutants are usually deposited into water bodies from unprocessed household and industrial waste causing threat to the living and aquatic life. The metal ions of these pollutants are carcinogenic, causing illness in prolonged existence and when their concentration exceeds the threshold limit (Thabede et al., 2020). The metal ions are non-biodegradable, therefore they tend to accumulate the food chain through a process called biomagnification leading to poisoning of the flora and fauna (Wadhawan et al., 2020). Chromium (Cr)}
and copper (Cu) are found amongst the toxic metals. Cr ions are discharged into the environment through a number of industries, such as electroplating, mining, paint pigments, wood preservation, leather tanning, textile printing and dyeing, refractories (chrome and chromemagnetite) and aerospace (Islam et al., 2019; L. Li et al., 2016). Cr ions released into the environment through poor storage, leakage and inappropriate disposal practices related with industrial processes. Chromium exist in six different oxidation states (Cr(0),Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI)) on the surface of the earth (Islam et al., 2019). However, Cr(VI) is among the top 16 pollutants most toxic to humans and animals (Wan et al., 2018). Exposure to humans cause liver diseases, lung cancer, ulcer formation, kidney failure, diarrhoea, nausea, respiratory troubles and skin irritation (Birhanu et al., 2020; Esmaeili & Tamjidi, 2020). WHO (World Health Organisation) suggested that the maximum allowed Cr(VI) concentration be 0.05 mg/L (Islam et al., 2019). On the other hand, Cu(II) usually comes from industries like mining, refineries, metal cleaning, plating baths, pulp, paper and paper board mills and fertilizer industries (Nimibofa et al., 2017). Trace amounts of Cu(II) ions are needed for the functioning of a human well-beings and it plays a vital role in biological activities (Sfakianakis et al., 2015; Shooto, Naidoo et al., 2019). However, excess amount cause failure in brain, liver and heart and health illness like nausea, hemolytic anaemia, headache, dizziness, respiratory difficulties and massive gastrointestinal bleeding (Shooto, Naidoo et al., 2019). The accepted maximum concentration of Cu(II) ion in drinking water is 1.5 mg/L (Mahmud et al., 2015).

Various techniques such as chemical precipitation (Barbooti et al., 2011), electro coagulation (Ali et al., 2012), and ion exchange (Zewail & Yousef, 2015) have been used in the removal of toxic metal from wastewater to provide clean water for the communities (Arroub et al., 2020; Nkutha et al., 2020). Conversely, some of these techniques produces a secondary waste which requires high amount of energies for its removal and therefore, they cannot be utilized in daily basis (Shooto, Naidoo et al., 2019; Kadiri et al., 2021).

Adsorption is the most preferred method because it is inexpensive, easy to perform, does not require hazardous chemicals nor produces sludge (Thabede et al., 2020). Many agricultural materials have been explored for the adsorption heavy metals. These adsorbents include activated carbon (AC) from agricultural materials, such material includes peanut shell and sawdust (X. Liu et al., 2020), waste wood and straw (Januszewicz et al., 2020), nut shells (Ayub et al., 2018), oak shell (Takmil et al., 2020), ziziphus spina-christi leaf (Abshirini et al., 2019) and tamarix leaves (Koohzad et al., 2019). The agricultural material used for adsorption is the main factor that determines the adsorbent properties, especially the ones that are rich in carbon content, less minerals, volatile and available at low cost (Abshirini et al., 2019; Koohzad et al., 2019).

Furthermore, treating the activated carbon with green oxidizing agent such as KMnO₄ increases hydrophilic sites like carboxylic acid, pore capacity, pore size distribution, surface area and introduces MnO₂ (Thabede et al., 2020). In addition, according to research, there are no reports found on activated carbon and KMnO₄ modified fennel seeds as low cost adsorbents for the adsorption of Cu(II) and Cr(VI). Therefore, activated carbon from fennel seeds and KMnO₄ modified fennel seeds have been not studied.

Hence, this study explores the capacity of the activated carbon and KMnO₄ modified fennel seeds as an inexpensive bio-adsorbent for the removal of Cu(II) and Cr(II) from aqueous solution. Also, Parameters such as concentration, contact time, temperature and pH effect will also be investigated. Additionally, the isotherms, kinetics and thermodynamic studies are examined.

2. Materials and methods

2.1. Materials

Pristine fennel seeds (PFS) were purchased from Dischem in Vanderbijlpark, South Africa. Copper nitrate (Cu(NO₃)₂-98 %, potassium dichromate (K₂Cr₂O₇)-99.5 %, potassium permanganate
(KMnO₄)-99 %, hydrochloric acid (HCl)-32 % and potassium nitrate (KNO₃)-99 % all reagents were ACS grade and purchased from Merck, Johannesburg, South Africa LTD.

2.2. Preparation of adsorbents

2.2.1. Untreated pristine fennel seeds adsorbent (PFS) preparation
Pristine fennel seeds were grounded using a blender. The PFS was used to prepare other adsorbents for the adsorption of Cu(II) and Cr(VI) from an aqueous solution.

2.2.2. Carbonization of pristine fennel seeds
The grounded fennel seeds were calcined at different temperatures of 500, 600 and 700 °C using furnace for 2 h. When the time elapsed, the calcined fennel seeds were allowed to cool down to room temperature and then transferred into sample bottles (Nkutha et al., 2021).

2.2.3. Potassium permanganate modified carbon fennel seeds
The carbonized fennel seeds were modified with potassium permanganate (KMnO₄) and the method was taken from (Thabede et al., 2020) with little changes. This was done by adding 10 g of carbonized fennel seeds into 150 mL of 2.5 M KMnO₄. The solution was then stirred for 2 h. After 2 h, the solution was decanted and the remaining solid sample was washed with deionized water 3 times.

2.3. Adsorption preparation methods

2.3.1. Adsorbate solution preparation
A binary metal stock solution containing 100 mg/L of Cu(II) and Cr(VI) was prepared by dissolving 0.2951 g of copper nitrate salt and 0.2828 g of potassium dichromate salt in 1 L of ultra-pure water (Shooto, 2020). The experimental metal solutions of the desired initial concentrations were prepared by diluting the stock solution. This was done using dilution equation:

\[ C_1V_1 = C_2V_2 \]  

(1)

2.3.2. Adsorption procedure using Batch method
The evaluation of FS-500, FS-600, FS-700, KMFS-500, KMFS-600 and KM FS-700 to remove Cu(II) and total chromium (Cr) aqueous solution was conducted using batch method (Shooto, 2020). Parameters like the effect of contact time at different time intervals (5, 10, 15, 20, 30, 45, 60 and 120 min), temperature (25, 30, 40, 60 and 80 °C), initial concentration (20, 40, 60, 80 and 100 mg/L), pH (1, 3, 5, 7 and 8) were studied. This was done by transferring 20 mL of the stock solution into capped bottles containing 0.1 g of an adsorbent. The shaker was used for each parameter to equilibrate the working standard and adsorbent at 200 rpm. When one parameter was investigated, the other parameters were kept constant at 2 h of contact time, temperature of 25, 100 mg/L initial concentration and at pH 5. Thereafter, the bottles were removed and centrifuged for 5 min. after each experiment to separate the adsorbents from the adsorbate. The concentration of Cu(II) & total Cr after adsorption were determined using AAS Shimdzu SAC 700 auto sampler.

2.4. Point zero charge procedure
0.1 g of each adsorbent (FS-500, FS-600, FS-700, KMFS-500, KMFS-600 and KM FS-700) was placed separately in a centrifuge flask. 20 mL of 0.1 M KNO₃ solution was added and the solution was then agitated using a shaker for 24 h. The pH was measured from the range of 1–12 before and after agitation.

2.5. Reusability studies
0.1 g of each adsorbent was placed in 50 mL centrifuge flask. In each flask, 20 mL of Cr/Cu solution was added and shaken for 2 h. After 2 h it was then centrifuged for 5 min, taking this step as initial
or first step and the results were analysed with AAS. In the same centrifuge flask with the used adsorbent, 20 mL of 0.05 M HCl solution was added, the solution was shaken for 60 min using a shaker and centrifuged for 5 min. The HCl solution was then removed. To the same centrifuge flask, 20 mL Cr/Cu solution was then added and shaken for 2 h and centrifuged for 5 min, taking this step as a first cycle. These steps were repeated 3 times.

2.6. Adsorption data management

The adsorption capacity (qe) and % removal of Cr(II) and Cu(II) ions at equilibrium were calculated using the equations below:

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

\[
%A = \frac{(C_0 - C_e)}{C_0} \times 100\%
\]

Where \(C_0\) is the initial concentration, \(C_e\) is the equilibrium Cu/Cr concentration at a specific time, \(V\) is the volume of Cu/Cr solution and \(W\) is the adsorbent dosage in g. Isotherm models Langmuir and Freundlich were estimated using non-linear equations (3–4) subjected to KyPlot software.

\[
q_e = \frac{Q_o bC_e}{1 + bC_e}
\]

Where \(Q_o\) (mg/g) represents the maximum adsorption capacities for Cu(II) and Cr(VI) per unit weight, \(b\) stands for the solute surface interaction energy constant. The Freundlich model was estimated using the following equation:

\[
q_m = k_f C_e^{1/n}
\]

Where \(k_f\) stands for capacity factor constant and \(1/n\) represents linearity factor. Kinetics studies were estimated to better understand the adsorption mechanism using pseudo first order (PFO), pseudo-second order (PSO), and intraparticle diffusion (IPD) models. The kinetic models were estimated using non-linear equations subject to KyPlot software.

\[
q_e = q_t \left(1 - e^{-k_1 t}\right)
\]

Where, \(q_e\) (mg/g) is the amount adsorbed at equilibrium, \(q_t\) (mg/g) is the amount adsorbed at interval \(t\), \(k_1\) (min\(^{-1}\)) stands for the rate constant for the first order, and \(t\) is the time

\[
q_e = \frac{1 + k_2 q_e t}{k_2 q_t^2 t}
\]

Where \(k_2\) (g g\(^{-1}\) min\(^{-1}\)) is the rate constant for the second-order reaction.

\[
q_t = k_1 \left(t^{1/2}\right) + C
\]

Where \(k_1\) (g g\(^{-1}\) min\(^{1/2}\)) is the IPD rate constant and \(C\) stands for the concentration of Cu(II) or Cr(VI) on the adsorbent surface.
Thermodynamic parameters: enthalpy change ($\Delta H^0$), Gibbs free energy ($\Delta G^0$), entropy change ($\Delta S^0$) and $K_c$ were estimated at 288, 298, and 308 K using the following the equations:

\[
\ln K_c = -\frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R} \tag{9}
\]

\[
\Delta G^0 = -RT \ln K_c \tag{10}
\]

\[
K_c = \frac{q_e}{C_e} \tag{11}
\]

The enthalpy change ($\Delta H^0$) and the entropy change were estimated from the plot of $\ln K_c$ vs $1/T$ were ($\Delta H^0$) was the intercept and ($\Delta S^0$) was the slope of the graph.

3. Characterization of adsorbents
The adsorbents were characterized using FTIR, SEM, EDX, XRD and UV-Vis instruments to determine the functional groups, morphology, elemental composition, crystal phase and phase purity of all adsorbents. Nicolet iS50 FTIR spectrometer was used for functional groups determination. SEM images were taken using Joel-JSM-IT 500. EVOLUTION 220 UV-Visible spectrometer was used for phase purity. Maxima XRD-7000 (Shimadzu corporation, Kyoto, Japan) was used to determine the crystallinity of the adsorbents with the scan range was set at 10 to 80 ($2\theta$°) and scan speed was set at 10° min⁻¹.

4. Results and discussion
4.1. Characterization techniques
4.1.1. XRD analysis
The XRD results in Figure 1(a-b) shows the spectra of carbon from fennel seeds (FS-500, FS-600 and FS-700) and carbon treated with KMnO$_4$ (KMFS-600 and KMFS-700) respectively. From graph (a) a diffraction peak at $2\theta = 26^\circ$ was observed and it might be attributed to the presence of activated carbon (Abshirini et al., 2019). Another diffraction peaks were noted at $2\theta = 23, 29,$ and $43^\circ$. According to Koohzad et al. (2019), these peaks could be due to the presence of cellulose and its crystalline structure and (002), (100) and (101) crystalline phase of the graphite structure. It was also noticed that the intensity and crystallinity of the spectra decreased with an increase in calcination temperature. This might be attributed to the breaking down of the lignocellulose materials present in fennel seeds when temperature was increased (Wei et al., 2020). However,
for chemically treated carbon with KMnO₄, the diffraction peaks of the spectra decreased in intensity and KMFS-600 became more crystal compared to KMFS-500 and KMFS-700.

4.1.2. FTIR results

FTIR was used to determine the changes on the surface functional groups of the carbon from fennel seeds and carbon treated with KMnO₄, and the results are shown in Figures 2(a) and (b). The broad peak at 3054.38 cm⁻¹ is attributed to the hydroxyl (−OH) stretching vibration of cellulose. This peak vanishes with an increase in temperature and that is due to the fact that cellulosic hydroxyl groups were disintegrated. However, the broad peak is more pronounced after the carbon was chemically treated with KMnO₄, with decreased intensity as the temperature increased. The intensity was shifted to higher wavenumber of 3164.99 cm⁻¹ and this might be due to the presence of KMnO₄ causing the formation of hydroxyls (G. Liu et al., 2018). The weak peak at 1551 cm⁻¹ is assigned to asymmetric vibration of COO⁻ and this peak disappears with increase in temperature after treatment with KMnO₄. This might be attributed to the fact that the surface of the carbon was oxidized (N. Li et al., 2019). Another peak at 1396.61 cm⁻¹ was observed and it was assigned to -C = C- bonds. The peaks at 1069. 28 cm⁻¹ and 564.71 cm⁻¹ were due to—C-O-C/ C-O present. The peak at 871.51 cm⁻¹ is due to bending oscillation of the -CH group from aromatic hydrogen (Rahman et al., 2020). The presence of the oxygen functional groups on the surface of the adsorbent offers the active sites for the adsorption of Cu(II) and Cr(VI).

4.1.3. SEM and EDX results

SEM micrographs in Figures 3(a-f) were examined to study the surface morphology of carbon from fennel seeds and chemically treated fennel seeds. It was observed that the surface morphology of FS-500 in (Figure 3a) was porous. While surface morphology of adsorbents in Figures 3(b-f) was amorphous because their morphology was damaged by extreme heating. EDX results shows that all adsorbents were mainly made of C, O and K elements with small traces of Ca, Mg, Na, P and Cl. However, the amount of these elements decreased with an increase in temperature and this suggest a release of CO₂ gas as the material was decomposed (Nkutha et al., 2021). Nevertheless, the amount of these elements increased when the materials were treated with KMnO₄, suggesting that all adsorbents were oxidized by KMnO₄.

4.1.4. UV-Vis analysis

Figure 4a shows the spectra for carbon samples from fennels seeds and Figure 4b shows the spectra of chemically treated carbon. In Figure 4a it was observed that the peaks at 218 nm considerably decreased when the temperature was increased from 500°C to 700°C for FS-500, FS-600 and FS-700. This was attributed to the disintegration of lignin, celluloses and hemicelluloses that are present in the material (Shooto, 2020). The absorbance were recorded to be 2.213, 1.650 and 1.052 for FS-500, FS-600 and FS-700, respectively. However, when the carbonized fennel seeds
Figure 3. SEM and EDX results for (a) FS-500, (b) FS-600, (c) FS-700, (d) KMFS-500, (e) KMFS-600 and (f) KMFS-700.

| Element | Mass % | Atom % |
|---------|--------|--------|
| C       | 57.09±0.51 | 67.85±0.61 |
| O       | 31.28±1.01 | 27.91±0.90 |
| K       | 11.63±0.86 | 4.25±0.31 |

**FS-500**, **FS-600** and **FS-700**

| Element | Mass % | Atom % |
|---------|--------|--------|
| C       | 40.53±0.31 | 56.31±0.43 |
| O       | 27.61±0.57 | 28.80±0.59 |
| K       | 17.72±0.60 | 7.56±0.25 |
| Na      | 1.62±0.13  | 1.17±0.09  |
| Mg      | 1.77±0.13  | 1.21±0.09  |
| Ca      | 4.75±0.39  | 1.98±0.16  |
| p       | 1.90±0.17  | 1.02±0.09  |
| Cl      | 4.10±0.23  | 1.93±0.11  |

**KMFS-500**, **KMFS-600** and **KMFS-700**

| Element | Mass % | Atom % |
|---------|--------|--------|
| C       | 31.93±0.44 | 47.30±0.65 |
| O       | 31.49±1.13 | 35.02±1.26 |
| K       | 17.38±1.07 | 7.91±0.49  |
| Na      | 1.93±0.24  | 1.50±0.19  |
| Mg      | 2.11±0.26  | 1.54±0.19  |
| Ca      | 15.16±1.12 | 6.73±0.50  |

| Element | Mass % | Atom % |
|---------|--------|--------|
| C       | 65.00±0.66 | 71.21±0.72 |
| O       | 35.00±1.25 | 28.79±1.03 |

| Element | Mass % | Atom % |
|---------|--------|--------|
| C       | 63.56±0.42 | 70.34±0.47 |
| O       | 34.28±0.78 | 28.48±0.64 |
| Mg      | 2.16±0.19  | 1.18±0.10  |

| Element | Mass % | Atom % |
|---------|--------|--------|
| C       | 54.00±0.40 | 62.27±0.47 |
| O       | 38.21±0.83 | 33.61±0.73 |
| Mg      | 1.67±0.17  | 0.96±0.10  |
| Ca      | 6.12±0.55  | 2.15±0.19  |
were chemically treated, the absorbance became 2.620, 1.388 and 6.00 for KMFS-500, KMFS-600 and KMFS-700, respectively.

4.1.5. Point zero charge
Point zero charged (pH$_{pzc}$) is a very crucial physicochemical parameter that influences the adsorption of Cu(II) and Cr(VI) by determining the state of the surface charge of FS-500, FS-600, FS-700, KMFS-500, KMFS-600 and KMFS-700. The results are shown in Table 1. It was observed that all the adsorbents were very alkaline. This reveals that the functional groups on the surface were protonated and the surface became positively charge since the pH of the solution was less than pH (pzc; Birhanu & Leto, 2020; Shooto, 2020). In addition, the solution had a strong affinity for anions. The maximum adsorption was found at solution pH 8 for Cu(II) and pH 1 for Cr(VI) adsorption. High Cr(VI) adsorption at low pH could be attributed to the fact that it exists as HCrO$_4^-$ and the solution was beneficial for electrostatic attraction between the negatively charged HCrO$_4^-$ and positively charged adsorbent surfaces.

4.2. Adsorption studies

4.2.1. Effect of initial concentration of adsorbate
Cr(VI) and Cu(II) initial concentration was investigated on FS-500, KMFS-500, FS-600, KMFS-600, FS-700 and KMFS-700 and Figure 5 displays the results. An increase in adsorption capacity was observed as the initial concentration increased from 20 to 100 mg/L when all the adsorbent was used. The increase in adsorption capacity at higher initial concentration might be attributed to high number of metal ions present in a solution leading to repulsion between each other (Thabede et al., 2020). This enhances the collision between bulk solution and the surface of the adsorbent, hence high adsorption capacity (Asim et al., 2020; Lee & Choi, 2018; Thabede et al., 2020). The results shows that the KMnO4 modified carbonized fennel seeds enhanced adsorption capacity of both Cr(VI) and Cu(II). This might be due to an increase in active binding sites and high surface area shown by the modified samples (Shooto, 2020). FS-500 and KMFS-500 showed an adsorption capacity at 100 mg/L of 16.921 and 17.648 mg/g for Cu(II) and 1.722 and 3.479 mg/g for Cr(VI), respectively. FS-600 and KMFS-600 displayed adsorption capacity of 15.423 and 15.735 mg/g for Cu(II) and 1.202 and 8.109 mg/g for Cr(VI). FS-700 and KMFS-700 displayed the adsorption capacity of 19.892 and 19.786 for Cu(II) and 8.1510 and 10.572 mg/g for Cr(VI).

| Table 1. Point zero charge pH$_{pzc}$ of the adsorbent |
|---------------------------------|--------|--------|--------|--------|--------|
| Adsorbent | FS-500 | FS-600 | FS-700 | KMFS-500 | KMFS-600 | KMFS-700 |
| pH$_{pzc}$ | 11     | 10.9   | 11.5   | 9.4     | 9.5     | 10       |
4.2.2. Effect of contact time
The rate at which Cr(VI) and Cu(II) ions were removed from solution onto the adsorbents was examined as shown in Figure 6. It was observed that there was a rapid uptake of Cu(II) and Cr(VI) in the initial stages between 5 and 30 min for all the adsorbents. This was attributed to high number of available active sites on the surface of the adsorbents (Inthapanya et al., 2019).

| Model | Parameter | FS-500 | FS-600 | FS-700 |
|-------|-----------|--------|--------|--------|
|       | Cu(II)    | Cr(VI) | Cu(II) | Cr(VI) | Cu(II) | Cr(VI) |
| PFO   | Qe (mg/g) | 18.341 | 2.393  | 15.741 | 2.460  | 19.885 | 8.962  |
|       | B         | 0.404  | 0.023  | 0.714  | 0.089  | 0.639  | 0.523  |
|       | R^2       | 0.928  | 0.991  | 0.917  | 0.915  | 0.999  | 0.955  |
| PSO   | k_f       | 19.186 | 3.117  | 15.958 | 2.774  | 20.036 | 9.189  |
|       | N         | 0.046  | 0.006  | 0.219  | 0.045  | 0.237  | 0.185  |
|       | R^2       | 0.990  | 0.987  | 0.997  | 0.997  | 0.985  | 0.995  |
| IPD   | Qe (mg/g) | 15.855 | 1.039  | 14.999 | 1.084  | 19.487 | 8.257  |
|       | k_i       | 0.384  | 1.063  | 0.123  | 0.164  | 0.052  | 0.111  |
|       | R^2       | 0.907  | 0.956  | 0.953  | 0.930  | 0.917  | 0.949  |
| EPA   | %         | 18.049 | 52.471 | 7.602  | 58.467 | 2.110  | 11.888 |
| ESA   | %         | 81.951 | 47.529 | 92.298 | 41.533 | 97.890 | 88.112 |
| Experimental Qe (mg/g) | 19.347 | 2.186 | 16.233 | 2.610 | 19.907 | 9.371 |
Thereafter, a steady increase was observed until 60 min and the reaction reached equilibrium and this was due to a decrease in the number of active sites present in an adsorbents (Esmaeili & Tamjidi, 2020).

4.2.3. Effect of temperature
The effect of temperature was investigated at 288, 298 and 308 K. It was observed in Figures 7 (a-d), that there was a general increase in adsorption when the temperature of the reaction was increased. This suggested that when temperature was increased it resulted in metal ions gaining more kinetic energy and that facilitated in higher uptake. This also suggested that the adsorption processes were endothermic. The maximum adsorption capacities Cu(II) were 18.782 for FS-500, 18.839 for KMFS-500, 15.752 for FS-600, 19.912 for KMFS-600, 19.892 for FS-700, 19.821 mg/g for KMFS-700, and for Cr(VI) were 1.649 for FS-600, 0.933 for FS-500, 3.479 for KMFS-500, 7.085 for KMFS-600, 9.203 for KMFS-700, 11.043 mg/g for KMFS-700.

Cr(VI) on FS-500, FS-600; (c) Cu(II) on KMFS-500, KMFS-600 and KMFS-700 and Cr(VI) (d) KMFS-500, KMFS-600 and KMFS0700. [Conditions: pH(5), adsorbent dosage (0.1 g), concentration (100 mg/L, solution volume (20 mL), time (2 h) and agitation speed (200 rpm)].

4.2.4. Effect of solution pH
The effect of solution pH is critical since it influences chemical properties of the metal solution, ionic competition and the functional group on the adsorbent surface. Therefore, the solution pH for the uptake of Cu(II) and Cr(VI) was investigated ranging from 1 to 8. The results are shown in Figures 8(a-d). It was observed that there was an increase in adsorption capacity as the solution pH increased from 1 to 8 for Cu(II) ion adsorption on FS-500, FS-600, FS-700, KMFS-500. Whereas, the Cu(II) ion adsorption onto KMFS-600 was at pH 7 and pH 3 on KMFS-600 and KMFS-700. A decrease in uptake as solution pH increased might suggest that Cu(II) ions were precipitated into Cu(OH)₂ which slowed down the contact between the Cu(II) and KMFS-600 and KMFS-700 surface resulting in Cu(OH)₂ precipitation mechanism taking place (Hoslett et al., 2019; Katiyar et al., 2021; Shooto, 2020). The maximum adsorption capacities were 19.336 mg/g on FS-500, 17.931 mg/g on FS-600, 16.214 mg/g on FS-700, 19.917 mg/g on KMFS-500, 19.893 on KMFS-600 and 19.796 on KMFS-700, respectively.

For Cr(VI) adsorption, the results showed a reduction in adsorption capacities as the solution pH was increased. This can be explained by the fact that Cr exist in different oxidation states at different solution pH. At acidic conditions around solution pH 1–6, it exists as HCrO₄⁻ species and at higher pH of 7–8.5, it exist as CrO₄²⁻ and Cr₂O₇²⁻ species (Shooto, 2020). Therefore, the increase at lower solution pH is attributed to the strong affinity between the protonated adsorbent surfaces and HCrO₄⁻ species in the solution (Nkutha et al., 2020). However, at higher solution pH the surfaces of the adsorbents were deprotonated and OH⁻ species dominated. Therefore, this caused a competition between the OH⁻ species on adsorbent with CrO₄²⁻ and Cr₂O₇²⁻ species in solution for the available protons. Thus, leading to repulsion between the two species and hindering the adsorption process (Chen et al., 2017). Additionally, it has been reported that at pH 7–8.5 proportion of Cr(VI) ions were converted to Cr(III). There are several mechanism proposed for the Cr(VI) removal, which are anionic adsorption, anionic and cationic adsorption, adsorption-coupled reduction and reduction and anionic adsorption. Therefore, the predicted mechanism for the adsorption of Cr(VI) on FS-500, KMFS-500, FS-600, KMFS-600, FS-700 and KMFS-700 was reduction of Cr(VI) to less toxic Cr(III) accelerated by the presence atoms with lone pairs on the surface of the adsorbents. Moreover, the Cr(III) became soluble in the solution (Shooto, 2020). The maximum adsorption capacities were at pH 1 and were 2.303 mg/g on FS-500, 1.727 mg/g on FS-600, 8.808 mg/g on FS-700, 15.911 mg/g on KMFS-500, 16.446 mg/g on KMFS-600 and 13.976 on KMFS-700, respectively.
Figure 6. Effect of time for the removal of Cu(II) on (a) FS-500, FS-600 and FS-700; (b) Cr(VI) on FS-500, FS-600; (c) Cu(II) on KMFS-500, KMFS-600 and KMFS-700 and Cr(VI) (d) KMFS-500, KMFS-600 and KMFS-700. [Conditions: pH(5), adsorbent dosage (0.1 g), concentration (100 mg/L, solution volume (20 mL), temperature (298 K) and agitation speed(200 rpm)].

Figure 7. Effect of temperature for the removal of Cu(II) on (a) FS-500, FS-600 and FS-700; (b).

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4.2.4.1. Adsorption kinetics studies. The pseudo first order (PFO), pseudo second order (PSO) and intraparticle diffusion (IPD) models were used to understand the adsorption mechanism(s). From Table 2 and 3 it was observed that correlation coefficient values ($R^2$) for PSO were higher for the adsorption of Cr(VI) and Cu(II) on different adsorbents compared to that of PFO with $R^2$ ranging from 0.972 to 0.999. Therefore, these adsorption data was better described by PSO model and their calculated values agreed with the experimental values. This suggests that the adsorption mechanism involved electrostatic interaction between the metal ion solution and the adsorption sites on different adsorbents (Shooto et al., 2019). This also assumed that the adsorption was chemisorption (Ahmad et al., 2020; Amin, Thabade et al., 2018). However, for the adsorption of Cr(VI) on FS-500 and Cu(II) on FS-700, the $R^2$ value was higher for the PFO compared to PSO with values of 0.991 and 0.999, respectively. Their calculated $q_e$ values had an agreement with the experimental $q_e$ values. This indicated that the adsorption process involved Van de Waals forces (Shooto, Thabade et al., 2019). Intraparticle diffusion model was evaluated to investigate if the adsorption took place on the surface or pores of the adsorbents. It was observed that the adsorption mainly occurred on the surface of the adsorbents. However, it was different for the adsorption of Cr(VI) onto FS-500, KMFS-500 and FS-600 in which the adsorption mainly took place on the pores indicating a physical adsorption mechanism occurred (Nkutha et al., 2021).

The concentration experimental results were best fitted using Langmuir and Freundlich isotherms to understand the adsorption nature of Cu(II) and Cr(VI) onto the adsorbents the results are shown in Table 4. The correlation coefficient values ($R^2$) of Freundlich isotherm were higher

| Parameters | Model | Cu(II) | Cr(VI) | Cu(II) | Cr(VI) | Cu(II) | Cr(VI) |
|------------|-------|--------|--------|--------|--------|--------|--------|
| $q_e$ (mg/g) | PFO   | 17.299 | 4.540  | 19.844 | 6.302  | 19.782 | 10.039 |
| $R^2$       |       | 0.951  | 0.934  | 0.972  | 0.958  | 0.936  | 0.961  |
| $k_r$       | PSO   | 17.543 | 5.293  | 19.882 | 6.493  | 19.825 | 10.249 |
| $R^2$       |       | 0.989  | 0.972  | 0.993  | 0.996  | 0.996  | 0.999  |
| %           | IPD   | 16.610 | 1.471  | 19.738 | 5.733  | 19.658 | 9.406  |
| $k_r$       |       | 0.102  | 0.358  | 0.016  | 0.090  | 0.018  | 0.099  |
| $R^2$       |       | 0.904  | 0.954  | 0.929  | 0.902  | 0.949  | 0.918  |
| %           | EPA   | 5.275  | 70.785 | 0.689  | 12.726 | 0.882  | 9.182  |
| %           | ESA   | 94.725 | 29.215 | 99.311 | 87.274 | 99.118 | 90.818 |
| $q_e$ (mg/g) | Experimental | 17.535 | 5.035  | 19.875 | 6.569  | 19.833 | 10.357 |

Table 3. Adsorption kinetics studies for KMnO4 treated carbonized fennel seeds

| Model | Parameter | Cu(II) | Cr(VI) | Cu(II) | Cr(VI) | Cu(II) | Cr(VI) |
|-------|-----------|--------|--------|--------|--------|--------|--------|
|       | $Q_e$ (mg/g) | 16.78  | 1.664  | 15.02  | 1.001  | 19.56  | 9.882  |
|       | $B$       | 0.004  | 1.845  | 4.168  | 4.505  | 1241   | 1.324  |
|       | $R^2$     | 0.989  | 0.772  | 0.965  | 0.961  | 0.002  | 0.853  |
|       | $k_r$     | 0.175  | 0.879  | 0.018  | 0.002  | 0.188  | 0.807  |
|       | $N$       | 0.997  | 0.234  | 0.683  | 0.710  | 0.988  | 0.380  |
|       | $R^2$     | 0.989  | 0.984  | 0.995  | 0.988  | 0.999  | 0.998  |
| $Q_e$ (mg/g) | Experimental | 16.92  | 1.722  | 15.423 | 1.202  | 19.892 | 10.572 |

Table 4. Adsorption isotherms studies for carbonized fennel seeds
than that of Langmuir for all adsorbents except for the adsorption of Cu(II) onto KMFS-500. Therefore, the Cu(II) adsorption onto KMFS-500 is assumed to occur on precise homogeneous sites inside adsorbent and suggest monolayer adsorption (Yang et al., 2016). However, Freundlich isotherm suggests that the adsorption took place between the metal ion solutions and the heterogeneous surface of adsorbents (Y. Li et al., 2018). The \( n \) value in Freundlich model is less than 1 and that suggests that there is a strong bond between the adsorbate and the adsorbents. But the \( n \) value for Cr(VI) onto KMFS-500 and Cu(II) onto KMFS-600 was greater than 1 and that might suggest that the adsorption was favoured (Lee & Choi, 2018). The \( k_f \) value was less than 1

| Model          | Parameter | KMFS-500 (Cu(II)) | KMFS-500 (Cr(VI)) | KMFS-600 (Cu(II)) | KMFS-600 (Cr(VI)) | KMFS-700 (Cu(II)) | KMFS-700 (Cr(VI)) |
|----------------|-----------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Langmuir       | \( Q_e \) (mg/g) | 17.45             | 3.223             | 15.68             | 8.574             | 19.79             | 9.674             |
|                | \( b \)    | 6.363             | 0.0004            | 0.002             | 5.107             | 1095              | 1331              |
|                | \( R^2 \)  | 0.984             | 0.922             | 0.987             | 0.954             | 0.002             | 0.988             |
| Freundlich     | \( k_f \)  | 0.699             | 0.059             | 0.276             | 0.016             | 0.181             | 0.043             |
|                | \( N \)    | 0.978             | 1.161             | 1.149             | 0.743             | 0.980             | 0.836             |
|                | \( R^2 \)  | 0.940             | 0.985             | 0.988             | 0.976             | 0.999             | 0.997             |
| Experimental   | \( Q_e \) (mg/g) | 17.648            | 3.479             | 15.735            | 8.109             | 19.786            | 10.572            |
for all adsorbents and that indicated the strong affinity between the metal ions and the adsorbents (Foroutan et al., 2021).

4.2.4.2. Adsorption thermodynamic studies. The analysis of thermodynamics parameters such as enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°) were investigated using 288, 298 and

Table 6. Adsorption thermodynamic studies for carbonized fennel seeds

| Model          | FS-500          | FS-600          | FS-700          |
|----------------|-----------------|-----------------|-----------------|
|                | Cu(II)          | Cr(VI)          | Cu(II)          | Cr(VI)          | Cu(II)          | Cr(VI)          |
| ΔH° (KJ/mol)   | -2.466          | -2.099          | -0.456          | -1.942          | -1.912          | -0.383          |
| ΔS° (KJ/molK)  | 0.009           | 0.002           | 0.001           | 0.002           | 0.009           | -0.001          |
| ΔG° 288 K (KJ/mol) | -13.02      | -12.28          | -0.916          | -10.72          | -10.874         | -7.564          |
| 298 K          | -2.303          | -11.93          | -0.874          | -10.39          | -8.129          | -4.569          |
| 308 K          | -2.884          | -11.85          | -0.826          | -10.29          | -9.088          | -4.516          |

Table 7. Comparison with other adsorbents

| Adsorbents                          | Cu(II) Qe(max) (mg/g) | References          |
|-------------------------------------|-----------------------|---------------------|
| Banana biochar                      | 142.86                | Amin et al., 2018   |
| Persimmon leaf bio-waste            | 19.427                | Lee & Choi, 2018    |
| Allium cepa seeds                   | 1.62                  | Sheikh et al., 2021|
| 500 AC-Fennel seeds                 | 16.78                 | Current study       |
| 600 AC-Fennel seeds                 | 15.02                 | Current study       |
| 700 AC-Fennel seeds                 | 19.56                 | Current study       |
| KMnO₄ treated 500 AC-Fennel seeds   | 17.43                 | Current study       |
| KMnO₄ treated 600 AC-Fennel seeds   | 15.68                 | Current study       |
| KMnO₄ treated 700 AC-Fennel seeds   | 19.79                 | Current study       |
| Cr(II) Qe(max) (mg/g)               |                       |                     |
| AC-Cocoa shell                      | 94.340                | Fotsing et al., 2020|
| KMnO₄ treated black cumin seeds     | 17.5                  | Thabede et al., 2020|
| AC-Ziziphus spina-christi leaf      | 13.81                 | Abshirini et al., 2019|
| AC-Leucaena leucocephala seed plot | 26.94                 | Yusuff, 2019        |
| AC-Apple peels                      | 36.01                 | Enniya et al., 2018 |
| 500 AC-Fennel seeds                | 1.664                 | Current study       |
| 600 AC-Fennel seeds                | 1.001                 | Current study       |
| 700 AC-Fennel seeds                | 9.882                 | Current study       |
| KMnO₄ treated 500 AC-Fennel seeds   | 3.223                 | Current study       |
| KMnO₄ treated 600 AC-Fennel seeds   | 8.574                 | Current study       |
| KMnO₄ treated 700 AC-Fennel seeds   | 9.674                 | Current study       |
Figure 9. Reusability studies for (a) Cu(II) and (b) Cr(VI) on carbonized fennel seeds and (c) Cu(II) and (d) Cr(VI) on KMnO₄ treated carbonized fennel seeds. Mechanism for Cr(VI) and Cu(II).

Figure 10. Schematic diagram for the adsorption mechanism of Cr(VI) and Cu(II) on the adsorbents surface.
308 K temperatures as shown in Tables 5 and 6. The calculated $\Delta G^0$ values were negative for the adsorption process of Cu(I) and Cr(VI) on different adsorbents. This indicated that the adsorption process was spontaneous. $\Delta G^0$ also decreased with increase in temperature for the adsorption of Cr(VI) on different adsorbents and Cu(I) on FS-600. This suggested that the increment in temperature favoured the adsorption process. The negative $\Delta H^0$ values confirmed the exothermic reaction of the adsorption process. The positive $\Delta S^0$ values indicated an increase in randomness at the solid-liquid interface (Lee & Choi, 2018).

Comparison studies of KMnO₄, treated AC and AC form fennel seeds with other plant-based adsorbents for the Cu(I) and Cr(II) ion adsorption were conducted and the results are shown in Table 7. According to the results, the maximum adsorption capacities of the mentioned above adsorbents were higher than some of the adsorbents from other studies, especially for Cu(I) removal. Therefore, this suggest that the AC and AC modified fennel seeds can be used as an effective and in-expensive adsorbents for the metal ions removal from aqueous solution.

4.3. Reusability studies

The reusability studies of Cu(I) and Cr(VI) on adsorbents were investigated and the results are shown in Figures 9(a-d). It was observed that high percentage removal for both metal ions was higher at the initial test. This might be due to high number of available active sites on the surface of adsorbents. However, a decrease in removal percentage was observed as the number of cycles increased to 3 for both metal ions and all adsorbents. Nonetheless, the adsorbents showed a good percentage removal until the third cycle.

4.4. Results for after adsorption studies

4.4.1. FTIR results for post adsorption

The FTIR results for adsorbents before and after adsorption are shown in Figure 11. The FS-600 and KMFS-700 before and after adsorption results were chosen to explain the effect of adsorption on function groups present on adsorbents surface. The results revealed that the intensity of transmittance decreased after adsorption for both FS-600 and KMFS-700. Additionally, shifting of peaks after adsorption were observed in both FS-600 and KMFS-700. For FS-600, it was observed that the $-\text{O-H}$ peak was more pronounced and it was found at 3294 cm⁻¹. The $-\text{C} = \text{O}$, $-\text{C} = \text{C}$ and $-\text{C-O-C}$ peaks also shifted to wavenumbers of 1564, 1409 and 1028 cm⁻¹. While for KMFS-700, the $\text{-O-H}$ peak became broad at wavenumber 3324 cm⁻¹ and the $-\text{C} = \text{C}$ and $-\text{C-O-C}$ peaks shifted to 1405 and 1026 cm⁻¹ wavenumbers. The $-\text{C-H}$ peak found around 871 cm⁻¹ wavenumber did not shift but its intensity of transmittance decreased after adsorption in both adsorbents. The decreased intensity, shifting and broadening of peaks suggest that the mentioned above functional group were involved during adsorption. This also might suggested that the adsorption involved physical interaction, hydrogen bond and electrostatic interaction between the adsorbents surface and adsorbate (Shooto, 2020) as proposed by Figure 10.
Figure 12. SEM images and EDX results for (a) FS-500, (b) FS-600, (c) FS-700, (d) KMFS-500, (e) KMFS-600 and (f) KMFS-700 after adsorption.

| Element | Mass %     | Atom %     |
|---------|------------|------------|
| C       | 74.41±0.48 | 79.48±0.51 |
| O       | 25.59±0.78 | 20.52±0.63 |
| Total   | 100        | 100        |

| Element | Mass %     | Atom %     |
|---------|------------|------------|
| C       | 47.43±0.44 | 54.59±0.51 |
| O       | 52.57±1.04 | 45.41±0.90 |
| Total   | 100        | 100        |

| Element | Mass %     | Atom %     |
|---------|------------|------------|
| C       | 56.40±0.73 | 67.08±0.87 |
| O       | 32.38±1.47 | 28.91±1.31 |
| Ca      | 11.23±1.29 | 4.00±0.46  |
| Total   | 100        | 100        |

| Element | Mass %     | Atom %     |
|---------|------------|------------|
| C       | 59.60±0.58 | 66.27±0.65 |
| O       | 40.40±1.19 | 33.73±1.00 |
| Total   | 100        | 100        |

| Element | Mass %     | Atom %     |
|---------|------------|------------|
| C       | 69.20±0.86 | 74.95±0.93 |
| O       | 30.80±1.52 | 25.05±1.24 |
| Total   | 100        | 100        |

| Element | Mass %     | Atom %     |
|---------|------------|------------|
| C       | 48.39±0.79 | 55.54±0.90 |
| O       | 51.61±1.83 | 44.46±1.57 |
| Total   | 100        | 100        |
4.4.2. SEM images and EDX results for post adsorption

SEM imaged and EDX results in Figure 12 for the adsorbents before adsorption were compared to that of post adsorption to check the effect of adsorption on the adsorbents surface. The EDX results revealed that the adsorbents were mainly contained C and O components. However, these components decreased after adsorption and that might be attributed the binding of metal ions and the adsorbents. Small traces of Ca, Mg, Na and K elements were observed on the surface of the adsorbents and they occur naturally in plants. But most importantly, these elements were removed and decreased after adsorption and that might be due to ion-exchange process taking place between these elements and Cr(VI) and Cu(II; Shooto, 2020).

SEM analysis was also carried out for adsorbents after adsorption and they were compared to the SEM images of adsorbents before adsorption in Figure 3. The SEM images after adsorption reveals that more pores and cavities were observed with deposits on the surface of adsorbents. This might be due to the binding of Cr(VI) and Cu(II) ions and adsorbents surface.

5. Conclusion

In this study, the fennel seeds were calcined at 500, 600 and 700°C, successfully. The resulting materials were tested for the binary adsorption of Cu(II) and Cr(VI) from aqueous solution using batch method. Effect of initial concentration of Cr/Cu ions, contact time, temperature and the pH were investigated. The effect of initial concentration showed that there was an increase in adsorption capacity as the initial concentration was increased. In addition, the adsorption of metal ions was more at high initial concentrations. This might be attributed to high number of metal ions to be adsorbed on the surface of the adsorbents. The maximum adsorption capacities of Cu(II) were observed at pH 8 for FS-500, FS-600, FS-700 and KMFS-500. While the adsorption capacity for KMFS-600 was at pH 7 and pH 3 for KMFS-700. Whereas the maximum adsorption capacities for Cr(VI) were at pH 1 for all the adsorbents. This could be attributed to the functional group on the surface being either protonated or deprotonated, depending on the solution pH. The effect of time showed that there was a rapid uptake from 5 min to 45 min and thereafter, the reaction become stable for the adsorbents. The temperature effect revealed that there was an increase in adsorption capacity as the temperature increased from 298 to 308 for all adsorbents and that reveals that the adsorption process is endothermic. The adsorption data better fitted PSO for both Cr (VI) and Cu(II) with R² values ranging from 0.972 to 0.999 onto FS-600, KMFS-500, KMFS-600 and KMFS-700. This reveals there was an electrostatic attraction between the metal ions and the active sites on the adsorbent. However, adsorption of Cu(II) on FS-700 and Cr(VI) on FS-500 fitted PSO and that suggest involvement of Van de Waals forces during adsorption process. Thermodynamic studies confirmed that the reaction was spontaneous and favoured. The reusable studies showed that the adsorbents can be reused many times. The maximum adsorption capacities showed that FS-700 had higher adsorption capacity for both Cr(VI) and Cu(II) at 19.892 and 10.357 mg/g while adsorption capacities for FS-500 were at 16.92 and 1.722 mg/g and for FS-600 at 15.423 and 1.202 mg/g, respectively: FS-700> FS-500> FS-600. It was also noticed that FS-500 had higher adsorption capacity for both metal ions compared to FS-600 and that might be due to Ca, Na, K and Mg elements present in FS-500 surface as shown by EDX results. The maximum adsorption capacity trend was KMFS-700> KMFS-500> KMFS-600 for Cu(II) while for Cr(VI) the trend was KMFS-700> KMFS-600> KMFS-500. The maximum adsorption capacities for Cu(II) were 19.786, 15.423 and 17.648 mg/g while for Cr(VI), it was 10.572, 8.109 and 3.479 mg/g for KMFS-700, KMFS-600 and KMFS-500, respectively. Additionally, all adsorbents had a strong affinity for Cu(II) ions compared to Cr(VI) ions adsorption and that could be attributed to the ion-exchange mechanism between Cu(II) and the Ca, Na, K and Mg elements found on the adsorbents surface.

Nonetheless, all adsorbents had a better adsorption results compared to Allium cepa seeds (Sheikh et al., 2021) for Cu(II) adsorption. But for Cr(VI) adsorption, all adsorbents showed bad
results compared to other authors (Abshirini et al., 2019; Enniya et al., 2018; Fotsing et al., 2020; Thabede et al., 2020; Yusuff, 2019).

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The data supporting the findings of the study may be made available from the corresponding authors on request.

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References
Abshirini, Y., Esmaeili, H., & Foroutan, R. (2019). Enhancement removal of Cr (VI) ion using magnetically modified MgO nanoparticles. Materials Research Express, 6(125513), 1–15. https://doi.org/10.1088/2053-5359/ab5e6e
Ahmad, A., Khan, N., Girij, B. S., Chowdhary, P., & Chaturvedi, P. (2020). Removal of methylene blue dye using rice husk, cow dung and sludge biochar: Characterization, application, and kinetic studies. Bioresource Technology, 306, 1–5. https://doi.org/10.1016/j.biortech.2020.123202
Ali, J., Khan, T. A., & Asim, M. (2012). Removal of arsenate from groundwater by electrocoagulation method. Environmental Science and Pollution Research, 19(5), 1668–1676. https://doi.org/10.1007/s11356-011-0681-3
Amin, M. T., Alazba, A. A., & Shafiq, M. (2018). Removal of copper and lead using banana biochar in batch adsorption systems: isotherms and kinetic studies. Arabian Journal of Science and Engineering, 44(11), 5711–5722. https://doi.org/10.1007/s13369-017-2934-2
Arroub, H., Hissou, R., & Elharfi, A. (2020). Investigation of modified chitosan as potential polyelectrolyte polymer and eco-friendly for the treatment of galvanization wastewater using novel hybrid process. Results in Chemistry, 2(100047), 1–7. https://doi.org/10.1016/j.rechem.2020.100047
Asim, N., Amin, M. H., Samsudin, N. A., Badiei, M., Razali, H., Akhtaruzzaman, M., Amin, N., & Sopian, K. (2020). Development of effective and sustainable adsorbent biomass from an agricultural waste material: Cu(II) removal. Materials Chemistry and Physics, 249, 1–11. https://doi.org/10.1016/j.matchemphys.2020.123128
Ayub, S., Mohammadi, A. A., Yousefi, M., & Changani, F. (2018). Performance evaluation of oro-based adsorbents for the removal of cadmium from wastewater. Desalination and Water Treatment, 142, 293–299. https://doi.org/10.1004/dwt.2019.23455
Barbooti, M., Abid, B. A., & Al-Shuwaikhi, N. M. (2011). Removal of heavy metals using chemicals precipitation. Engineering and Technology Journal, 29(3), 595–612. https://www.researchgate.net/publication/265490687
Birhanu, Y., & Leta, S. (2020). Multivariate optimization of Pb2+ adsorption onto Ethiopian low-cost odaracha soil using response surface methodology. Molecules, 25(21), 6477. https://doi.org/10.3390/molecules25216477
Birhanu, Y., Leta, S., & Adam, G. (2020). Removal of chromium from synthetic wastewater by adsorption onto Ethiopian low-cost Odaracha adsorbent. Applied Water Science, 10(227), 1–11. https://doi.org/10.1007/s13201-020-01310-3
Chen, H., Dou, J., & Xu, H. (2017). Removal of Cr(VI) ions by sewage sludge compost biomass from aqueous solutions: Reduction to Cr(III) and biosorption. Applied Surface Science, 425, 728–735. http://dx.doi.org/10.1016/j.apsusc.2017.07.053
Enniya, L., Rghoui, L., & Jouraia, A. (2018). Adsorption of hexavalent chromium in aqueous solution on activated carbon prepared from apple peels. Sustainable Chemistry and Pharmacy, 7, 9–16. https://doi.org/10.1016/j.scp.2017.11.003
Esmaeili, H., & Tamjidi, S. (2020). Ultrasonic-assisted synthesis of natural clay-Fe3O4/graphene oxide for enhance removal of Cr (VI) from aqueous media. Environmental Science and Pollution Research, 27(25), 31652–31664. https://doi.org/10.1007/s11356-020-09448-y
Es-sohbayn, H., El Hachimi, M. L., Hissou, R., Belfaquir, M., Es-sohbayn, K., Nkhill, S., Loutif, M., & Elyoubi, M. S. (2021). Adsorption of heavy metal (Cadmium) in synthetic wastewater by the natural clay as a potential adsorbent (Tanger-Tetuouan-Al Hoceima – Morocco region) Materials today: Proceedings. 45. 7299–7305. https://doi.org/10.1016/j.matpr.2020.12.1102
Es-sohbayn, H., Hissou, R., El Hachimi, M. L., Alloumi, K., Nkhill, S. M., & Elyoubi, M. S. (2021). Investigation of the adsorption of heavy metals (Cu, Co, Ni and Pb) in treatment synthetic wastewater using natural clay as a potential adsorbent (Sale-Morocco). Materials Today: Proceedings. 45. 7290–7278. https://doi.org/10.1016/j.matpr.2020.12.1100
Foroutan, R., Peighambardous, S. J., Hosseini, S. S., Akbari, A., & Ramavandi, B. (2021). Hydroxyapatite biomaterial production from chicken (femur and beak) and fishbone waste through a chemical less method for Cd2+ removal from shipbuilding wastewater. Journal of Hazardous Materials, 413, 1–13. https://doi.org/10.1016/j.jhazmat.2021.125428
Fotsing, P. N., Woumfo, E. D., Mezghich, S., Mignot, N., Mofaddel, N., Derf, F. L., & Vieillard, J. (2020). Surface modification of biomaterials based on cocoa shell with improved nitrate and Cr(VI) removal. Royal Society of Chemistry, 10, 20009–20019. https://doi.org/10.1039/d0ra03027a
Hoslett, J., Ghazal, H., Ahmad, D., & Jouhara, H. (2019). Removal of copper ions from aqueous solution using low temperature biochar derived from the pyrolysis of municipal solid waste. Science of the Total Environment, 673, 777–789. https://doi.org/10.1016/j.scitotenv.2019.04.085

Inthapanya, W., Xu, X., Han, Z., Zeng, G., Wu, M., & Yang, C. (2019). Adsorptive removal of anionic dye using calcined oyster shells: Isotherms, kinetics, and thermodynamics. Environmental Science and Pollution Research, 26(6), 5948–5954. https://doi.org/10.1007/s11356-018-3980-0

Islam, M. A., Angove, M. J. M., & Morton, D. W. (2019). Recent innovative search chromium (VI) adsorption mechanism. Environmental Nanotechnology, Monitoring & Management, 12, 1–21. https://doi.org/10.1016/j.enmm.2019.100267

Januszewicz, K., Katarzynski, P., Klein, M., Kardas, D., & Luczak, J. (2020). Activated carbon produced by pyrolysis of waste wood and straw for potential wastewater adsorption. Materials, 13(2047), 1–13. https://doi.org/10.3390/ma13052047

Kadiri, L., Ouass, A., Hisso, R., Sofi, Z., Wazzan, N., Essaadioufi, Y., Lebkiri, I., Khattabi, J., & Lebkiri, A. (2021). Adsorption properties of corriander seeds: Spectroscopic kinetic thermodynamic and computational approaches. Journal of Molecular Liquids, 343(116971), 1–12. https://doi.org/10.1016/j.molliq.2021.116971

Katyary, R., Patel, A. K., Nguyen, T.-B., Singhania, R. R., Chen, C.-W., & Dong, C. D. (2021). Adsorption of copper (II) in aqueous solution using biochars derived from Asphodelium nasodum seaweed. Bioresource Technology, 328, 1–7. https://doi.org/10.1016/j.biortech.2021.124829

Koohzad, E., Jafari, D., & Esmaeili, H. (2019). Adsorption of lead and arsenic ions from aqueous solution by activated carbon prepared from tamarix leaves. Chemistry Select, 4, 12356–12367. https://doi.org/10.1002/slct.201903167

Lee, S.-Y., & Choi, H.-J. (2018). Persimmon leaf bio-waste for adsorptive removal of heavy metals from aqueous solution. Journal of Environmental Management, 209, 382–392. https://doi.org/10.1016/j.jenvman.2017.12.080

Li, L., Liu, F., Duan, H., Wang, X., Li, J., Wang, Y., & Luo, C. (2016). The preparation of novel adsorbent materials with high efficient adsorption performance for both chromium and methylene blue. Colloids and Surfaces B: Biointerfaces, 141, 253–259. https://doi.org/10.1016/j.colsurfb.2015.06.023

Liu, G., Lin, S., Pile, L. S., Fang, Z., & Wong, G. G. (2018). Effect of potassium permanganate and pyrolysis temperature on the biochar produced from rice straw and suitability of biochars for heavy metal (Cd & Pb) mobilization in paper sludge. Fresenius Environmental Bulletin, 27(12A), 9008–9018. https://www.fs.usda.gov/nrs/pubs/jml/2018/nrs_2018_liu_g_001.pdf

Liu, X., Xu, X., Dong, X., & Park, J. (2020). Competitive adsorption of heavy metal ions from aqueous solutions onto activated carbon and agricultural waste materials. Pol. J. Environ. Stud., 29(1), 749–761. https://doi.org/10.15244/pjes/104455

Li, N., Yin, M., Tsang, D. C. W., Yang, S., Liu, J., Li, X., Song, G., & Wang, J. (2019). Mechanisms of U(VI) removal by biochar derived from Ficus microcarpa aerial root: A comparison between raw and modified biochar. Science of the Total Environment, 697, 1–9. https://doi.org/10.1016/j.scitotenv.2019.134115

Li, Y., Zhang, Y., Zhang, Y., Wong, G., Li, S., Han, R., & Wu, W. (2018). Reed biochar supported hydroxyapatite nanocomposite: Characterization and reactivity for methylene blue removal from aqueous media. Journal of Molecular Liquids, 263, 53–63. https://doi.org/10.1016/j.molliq.2018.04.132

Mohr, H. N. M. E., Hoa, A. K. O., & Yohaya, R. B. (2015). Removal of heavy metal ions from wastewater aqueous solution by polypyrrole-based adsorbent: A review. Royal Society of Chemistry, 6, 14778–14791. https://doi.org/10.1039/C5RA24358K

Nimbiofa, A., Tobin, E. A., Shoooto, N. D., Donbebe, W., & Dikio, E. D. (2017). Equilibrium, kinetic and thermodynamic studies of the uptake of copper by layered double hydroxide. Hemijska Industria, 17(5), 429–437. https://doi.org/10.2298/HEMIND150608005N

Nkutha, S. C., Naidoo, E. B., & Shoooto, N. D. (2021). Adsorptive studies of toxic metal ions of Cr(VI) and Pb(II) from synthetic wastewater by pristine and calcined coral limestones. South African Journal of Chemical Engineering, 36, 43–57. https://doi.org/10.1016/j.sojce.2021.01.001

Nkutha, S. C., Shoooto, N. D., & Naidoo, E. B. (2020). Adsorption studies of methylene blue and lead ions from a synthetic solution by using mesoporous coral limestones. South African Journal of Chemical Engineering, 34, 153–157. https://doi.org/10.1016/j.sojce.2020.08.003

Oladipo, A. A., Akaha, E. O., & Gozi, M. (2019). High adsorptive potential of calcined magnetic biochar derived from banana peels for Cu(2+), Hg(2+), and Zn(2+) ions removal in single and ternary systems. Environmental Science and Pollution Research, 26(31), 20185–20199. https://doi.org/10.1007/s11356-019-06321-5

Rahman, A., Rahim, A., Mohsimm, H. M., Tharanabalan, M., Rabat, N. E., Saman, N., Mat, H., & Johari, K. (2020). Effective carbonaceous desiccated coconut waste adsorbent for application of heavy metal uptake by adsorption: Equilibrium, kinetic and thermodynamics analysis. Biomass and Bioenergy, 142, 1–12. https://doi.org/10.1016/j.biortech.2020.105805

Sfakianakis, D. G., Renieri, E., Kentouri, M., & Tsatsakis, A. M. (2015). Effect of heavy metals on fish larvace deformities: A review. Environmental Research, 137, 246–255. https://doi.org/10.1016/j.envres.2014.12.014

Sheik, Z., Amin, M., Khan, N., Khan, M. N., Sahi, S. K., Khan, S. B., Hafeez, I., Khan, S. A. B. E. M., & Cheng, C. (2020). Application of Allium Cepa seeds as a novel biosorbent for efficient bio-sorption of heavy metals ions from aqueous solution. Chromosphere, 279(130565), 1–10. https://doi.org/10.1016/j.chromosphere.2021.110545

Shoooto, N. D. (2020). Removal of toxic hexavalent chromium (Cr(VI)) and divalent lead (Pb(II)) ions from aqueous solution by modified rhizomes of Acorus calamus. Surfaces and Interfaces, 20, 1–9. https://doi.org/10.1016/j.surfins.2020.100624

Shoooto, N. D., Naidoo, E. B., & Maubane, M. (2019). Sorption studies of toxic cations on ginger root adsorbent. Journal of Industrial and Engineering Chemistry, 76, 133–140. https://doi.org/10.1016/j.jiec.2019.02.027

Shoooto, N. D., Thabede, M. P., & Naidoo, E. B. (2019). Simultaneous adsorptive study of toxic metal ions in quaternary system from aqueous solution using low cost black cumin seeds (Nigella sativa) adsorbents. South African Journal of Chemical Engineering, 30, 15–27.

Takmil, F., Esmaeili, H., Mousavi, S. M., & Hashemi, S. A. (2020). Nano-magnetically modified activated carbon prepared by oak shell for treatment of
wastewater containing fluoride ion. Advanced Powder Technology, 31(8), 3236–3245. https://doi.org/10.1016/j/apt.2020.06.015

Thabede, M. P., Shuto, N. D., Xaba, T., & Naidoo, E. B. (2020). Adsorption studies of toxic cadmium(II) and chromium(VI) ions from aqueous solution by activated black cumin (Nigella sativa) seeds. Journal of Environmental Chemical Engineering, 8(4), 1–12. https://doi.org/10.1016/j.jece.2020.104045

Wadhawan, S., Jain, A., Nayar, J., & Mehta, S. K. (2020). Role of nanomaterials as adsorbents in heavy metal ion removal from waste water: A review. Journal of Water Process Engineering, 33, 1–17. https://doi.org/10.1016/j.jwpe.2019.101038

Wan, Z., Li, M., Zhang, Q., Fan, Z., & Verpoort, F. (2018). Concurrent reduction-adsorption of chromium using m-phenylenediamine-modified magnetic chitosan: Kinetics, isotherm, and mechanism. Environmental Science and Pollution Research, 25 (18), 17830–17841. https://doi.org/10.1007/s11356-018-1941-2

Wei, L., Zietzschmann, F., Rietveld, L. C., & van Halem, D. (2020). Fluoride removal by Co-Al-CO3 layered double hydroxides at environmentally-relevant concentrations. Chemosphere, 243(125307), 1–8. https://doi.org/10.1016/j.chemosphere.2019.125307

Yang, L., Wei, Z., Zhong, W., Cui, J., & Wei, W. (2016). Modifying hydroxyapatite nanoparticles with humic acid for highly efficient removal of Cu(II) from aqueous solution. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 490, 9–21. https://doi.org/10.1016/j.colsurfa.2015.11.039

Yusuff, A. S. (2019). Adsorption of hexavalent chromium from aqueous solution by Leucaena leucocephala seed pod activated carbon: Equilibrium, kinetic and thermodynamic studies. Arab Journal of Basic and Applied Sciences, 26(1), 89–102. https://doi.org/10.1016/j.ajbas.2018.09.003

Zewail, T. M., & Yousef, N. S. (2015). Kinetic study of heavy metal ions removal by ion exchange in batch conical air spouted bed. Alexandria Engineering Journal, 54 (1), 83–90. https://doi.org/10.1016/j.aej.2014.11.008