Application of black cumin (Nigella sativa L.) seeds for the removal of metal ions and methylene blue from aqueous solutions

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Abstract: This paper reviews the use of black cumin seeds (BCS), also known as Nigella sativa L., as an adsorbent for the sorption of harmful pollutants and methylene blue (MB) dye in aqueous solutions. Information for the adsorption of cobalt-Co(II), nickel-Ni(II), copper-Cu(II), chromium-Cr(VI), lead-Pb(II), cadmium-Cd(II) and methylene blue (MB) from aqueous solutions using black cumin seeds is discussed. The Brunauer–Emmett–Teller (BET) surface area of pristine seeds of 2.7 m²/g increased to 10.1, and 9.3 m²/g for KMnO₄ and H₃PO₄ treated seeds, respectively. Activation of the BCS with 10% and 20% H₂SO₄ increased the surface area to 20.14 and 21.54 m²/g, respectively. Seeds activated with 20% H₂SO₄ showed larger pore width of 7.13 nm compared to 6.81 nm for 10% H₂SO₄. Seeds treated with HCl and NaOH for quaternary adsorption studies showed that the maximum capacity for base treated-BCS was 190.7 mg/g whilst acid treated-BCS showed capacities of 180.1. Pristine seeds, H₃PO₄ and KMnO₄ treated seeds showed that the trend for the removal of Cr(VI) ions was KMnO₄ > H₃PO₄ > pristine with capacities of 16.12, 15.98 and 10.15 mg/g, respectively. Magnetite-sucrose functionalized seeds and pristine seeds had adsorption capacities for Cr(VI) were 15.6 and 13.0 mg/g, respectively. The same adsorbents had maximum sorption capacities of 39.7 and 37.9 mg/g for Pb(II) ions, respectively. The effectiveness of the defatted BCS using acetone and N,N dimethylformamide (DMF) showed that the acetone treated BCS had higher sorption capacities of 99.82 mg/g for MB, 96.89 mg/g for Cd(II), and 87.44 mg/g for Cr(VI) compared to DMF treated seeds.

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PUBLIC INTEREST STATEMENT
Increasing industrialization and urbanization has resulted in the release of toxic metal ions and dyes into the environment. Substances such as arsenic, lead, chromium, copper, cobalt, zinc, nickel and methylene blue are both carcinogenic and poisonous to human beings. This paper reviews the feasibility of black cumin seeds as a potential adsorbent for the removal of toxic metal ions and dyes from aqueous solution. This paper is beneficial for the protection of water quality.
1. Introduction
Dyes and waste products from mining, tanneries, metal plating facilities, and industries that deal with pesticides, batteries, industries, and paper are harmful to the environment and human health (Kausar et al., 2018). For instance, mining activities generate large quantities of wastes laden with both harmful and hazardous metals ions as well as some noble metals such as Pb, Cd, Cr, Ag, As, Hg, Zn, Cu, Ni, Se, Co, Fe, I, Mn, Mo, and Zn, that are released into the environment and pollute the ecosystem (Ebenebe et al., 2017). Since toxic metals are soluble in aquatic environments, they can be absorbed by living organisms (Barakat, 2011). Large concentrations of these toxic metals may accumulate in the human body when enter the food chain. Unlike organic contaminants, toxic metals ions are not biodegradable and are known to be carcinogenic and poisonous (Fu & Wang, 2011). Therefore, contaminated wastewater that contain toxic metal ions must be treated prior to its discharge to the environment. METHYLENE BLUE (MB) is a cationic dye used as an indicator, a textile dye, and in other industries (Hevira et al., 2021; Iwuozor et al., 2021). Owing to its many uses, MB is a common pollutant in the environment and has negative ecotoxicological implications (Ahmadi & Igwegbe, 2020; Igwegbe et al., 2019).

The World Health Organization (WHO) has developed standards for water quality to monitor acceptable levels of chemical toxins in water. The removal of toxic metals ions from wastewater is crucial to protect the environment and the public. Several physical and chemical technological solutions were developed and used to remove high concentrations of toxic metal ions from wastewater. These methods include membrane technology (Li et al., 2017; Zhao et al., 2015), photodegradation (Singh et al., 2018), and other biological processes (Citrarasu et al., 2019). Some of the limitations of these techniques include: high maintenance and operational costs and complicated procedures involved in the treatment and generation of the toxic sludge (Bhatnagar et al., 2015). Adsorption is one of the methods used for the uptake of metal ions. Adsorption is considered a better alternative in water and wastewater treatment due to its ease of operation, simplicity of design, convenience, easily regenerated and adsorption of pollutants at low concentration (Eletta et al., 2020; Ighalo et al., 2021). Adsorption occurs when a gas, liquid or solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate) (Lakherwal, 2014). Adsorption occurs in most biological, natural, physical, and chemical systems. Further, it is widely used in industrial applications such as water purification.

Various types of materials have been used as adsorbents in the wastewater treatment. Most of them are low-cost materials derived from agricultural by-products and industrial waste. Generally, an adsorbent is classified as “low-cost” if it is abundant in nature, needs minimum processing, and is regarded as waste material or a by-product from another process. Conversion of these materials into adsorbents for the removal of toxic ions helps to reduce the cost of waste disposal (Lakherwal, 2014). The adsorption of toxic metal ions from industrial wastewater using agricultural waste and industrial by-products has been widely investigated. Over the years, many adsorbents with different constituents and nature have been used to reduce toxic metal ions in an aqueous solution (Zwain et al., 2014). Among the popularly explored materials, black cumin seeds (BCS), also known as Nigella sativa L., have been used for the adsorption of toxic metal ions. This article reviews different modifications or functionalization’s done on BCS to enhance the adsorption capacity.

2. Nigella sativa L. (black cumin)
*Nigella sativa* L. (Family: Ranunculaceae; also known as Black Cumin) is an annual herb with a wide range of medicinal properties. *Nigella sativa* (Figure 1) grows mainly in countries from the southern and eastern rim of the Mediterranean basin to Iran, Pakistan and India (Ahmad et al., 2013). The seeds contain significant quantities of compounds with bioactivities that are used to treat a wide
range of diseases and skin and respiratory ailments, including gastrointestinal (Farzaneh & Carvalho, 2015). The seeds proximate composition of the seeds include: moisture (3.8–8.65%), oil (24.48-40.35%), protein (20.8–26.7%), ash (3.7–4.86%) and total carbohydrate (24.9–40.0%) (Yimer et al., 2019). The presence of the organic compounds in the black cumin seeds offers various functional groups on the surface of the seeds, which suggests that they may provide attractive sites for charged molecules and ions (Rathi et al., 2020). Black cumin seeds have been used as a sustainable and cheaper material for the adsorption of toxic metal ions in aqueous solutions.

Selection of black cumin seeds as potential absorbent in this work was based on their on their accessibility, eco-friendliness, abundance, low cost, reusability, easy generation, not selective towards pollutants, and their surface having several functional groups (carboxyl, hydroxyl and amide). These features put the black cumin seeds in an advantageous position for the adsorption process. However, few studies on the adsorptive potential of black cumin seeds exist in the literature. To the best of our knowledge, this work is the first study on alkaline-treated BCS for water treatment. It is the first report evaluating the quaternary adsorptive study of toxic metal ions using acid and base treated BCS.

2.1. Pristine Black Cumin Seeds (BCS) as adsorbent material
El-Said et al. (2009) used pristine black cumin seeds for the adsorption of arsenite and arsenate. The study showed that the carbonyl, amine and hydroxyl groups were responsible for the sorption of arsenic ions on the surface of BCS. The positively arsenic ions were trapped by electrostatic attraction of the negatively charged BCS. The adsorption of lead by BCS was studied by Bingol et al. (2012), also reported that hydroxyl, carboxyl and amine groups in the BCS were responsible for adsorption of Pb(II). The adsorption capacity for Pb(II) by BCS was reported also by Addala et al. (2018). The study showed that the carbonyl and hydroxyl groups were in interaction with ions at the interface. The biosorption of toxic Cu(II) ions from aqueous solutions was reported by Ahmad and Hoseeb (2014). The removal of Cu(II) ions was attributed to fast sorption by extra-cellular binding whilst the slower sorption was due to intracellular binding. The study further indicated that the activation energy for the process leads to conformation of chemisorption. BCS was used for the removal of Pb(II) and Cu(II) ions from aqueous solutions by Rahman et al. (2015). The efficiency of BCS for the adsorption of Ni(II), Pb(II), Co(II) and Cu(II) ions from aqueous solutions in a quaternary system was determined by Shooto et al. (2019). The SEM images showed that the surface
morphology of the BCS after adsorption consisted of cavities that trapped and adsorbed the Ni(II), Pb(II), Co(II) and Cu(II) ions.

2.1.1. Characterization of pristine black cumin seeds

2.1.1.1. SEM images. SEM images (Figure 1a,b) were used to evaluate the surface morphology of pristine-BCS material before and after adsorption of Pb(II), Ni(II), Cu(II) and Co(II). Figure 1a shows that the BCS is composed of relatively spherical shaped particles before adsorption. After adsorption, the surface morphology of the pristine-BCS show cavities that are irregular in shape (Figure 1b).

2.1.1.2. FTIR analyses. The FTIR spectrum of BCS shows functional groups present on the surface pristine-BCS, as indicated in Figure 3. The broad peak at 3282 cm⁻¹ on the spectrum was attributed to the hydroxyl (-OH) stretching, and the small peak at 2978 cm⁻¹ was due to (-CH) band. The bands at 2923 and 2853 cm⁻¹ were attributed to (-CH) stretch of (-CH₃) and (-CH₂), respectively. The ketonic group (-C = O) was observed at 1743 cm⁻¹. The two sharp peaks due to (-C = O) and (-NH₂) of amide groups were observed at 1637 and 1541 cm⁻¹, respectively. At 1413 cm⁻¹ the peak due to the carboxylic (-COOH) was observed whilst the band at 1239 cm⁻¹ was assigned to (-CO) group. Most bands showed the presence of large oxygen containing groups on the pristine-BCS surface.
2.1.1.3. XRD pattern. The X-ray diffraction spectra of pristine BCS is shown in Figure 4. The pattern showed broad peaks between (2θ) of 17 and 21° which represented cellulosic content in the adsorbent material. Other peaks at 44° and 75° were assigned to the amorphous nature of the adsorbent.

2.2. Chemical treatment of black cumin seeds

2.2.1. Black cumin seeds acid treatment

Although pristine black cumin seeds can adsorb metal cations and dyes from aqueous solution, few studies exist where chemical activation by acids was carried out on black cumin seeds. The following sections highlight some of the literature that used different acids to activate black cumin seeds chemically.

2.2.1.1. HCl and HNO₃ treated black cumin seeds. Shooto et al. (2019) used acid treatment of BCS for the removal of quaternary Ni(II), Pb(II), Co(II) and Cu(II) ions. The treatment of sorption materials with acid breaks the chemical bonds on the plant material’s surface and organic compounds since metal ions are weakly bonded (Rathi et al., 2020). A schematic representation of BCS treatment with a mixture of 1 M hydrochloric acid (HCl) and nitric acid (HNO₃) in a ratio 1:1 is shown in Figure 5. The adsorption mechanism is shown in Figure 6. The proposed mechanism shows that the adsorption took place through electrostatic interactions. The adsorption capacity of the acid-treated adsorbent was high at 90.41 mg/g for Ni(II), 188.20 mg/g for Pb(II), 80.0 mg/g for Co(II) and 179.20 mg/g for Cu(II) ions. On the other hand, the untreated material showed maximum sorption capacities of 50.0, 135.3, 161.5 and 160.2 mg/g for Ni(II), Pb(II), Co(II) and Cu(II) ions, respectively.

Acid-treated BCS images before and after adsorption of cations are shown in Figure 7(a,b). The images show that before adsorption, the morphology of the adsorbent was irregular. Similarly, as observed in Figure 7b, the shape of the material was irregular after adsorption. However, the adsorbent was porous and composed of cavities that could have been attributed to capturing and adsorbing the metal ions.
Siddiqui et al. (2018) conducted an acid wash on BCS for the adsorption of methylene blue (MB) dye using HCl. Their study revealed that the acid-treated BCS had a higher sorption capacity than the pristine BCS. The enhancement of sorption capacity was attributed to functional groups on the surface of the acid-treated BCS. The proposed mechanism is shown in Figure 8.

2.2.1.2. H₂SO₄ treated black cumin seeds. Modification of BCS with 10% and 20% sulfuric acid (H₂SO₄) for the adsorption of Cd(II) ions and MB was carried out by Thabede et al. (2020a). The acid-treated BCS showed higher sorption capacity than the untreated seeds. The 10% H₂SO₄ favoured the removal of Cd(II) ions, whereas the 20% H₂SO₄ tended to remove MB. The maximum
adsorption capacities for MB were 15.89 mg/g for the 10% H₂SO₄ treated BCS and 16.42 mg/g for the 20% H₂SO₄ treated adsorbent. The adsorption capacity for Cd(II) was 13.66 mg/g for 10% H₂SO₄ treated BCS and 13.25 for the 20% acid-treated BCS. The isotherms for Cd(II) fit the Freundlich model while methylene blue fit the Langmuir model. The 20% acid-treated BCS had a higher capacity than the 10% treated BCS for MB. The adsorbents maximum trend for Cd(II) indicated that the 10% acid-treated BCS>20% acid-treated BCS. The physical properties and surface morphology of the 10% and 20% treated BCS adsorbents are shown in Figure 9(a,b). The 10% treated BCS in Figure 9a showed tiny pores on the surface of the adsorbent, suggesting that the adsorption of Cd(II) and methylene blue dye molecules were probably adsorbed in the pores. Figure 9b shows that the surface of the 20% treated BCS was rough.

Table 1 shows isotherm parameters of 10% and 20% treated BCS, which were estimated at 25 °C to determine the interaction behavior and capacity of the adsorbents. The sorption of MB on both adsorbents fitted the Langmuir isotherm models with r² between 0.994–0.997, whilst Cd(II) fitted the Freundlich isotherm model with r² between 0.995–0.997. The Langmuir isotherm model suggested that adsorption took place on active sites with equal attraction for the adsorbate. It also implied that there was monolayer adsorption occurring on MB surface The Freundlich model suggested that the process involved multi-layer adsorption with interactions between the pollutants and the materials. It further indicated that the surface is heterogeneous.
Figure 9. SEM images of (a) 10% treated BCS and (b) 20% treated BCS adsorbents.

| Isotherms | 10% treated BCS | 20% treated BCS |
|-----------|-----------------|-----------------|
| Langmuir  |                 |                 |
| $Q_e$     | 15.68           | 13.16           |
| $B$       | 0.27            | 0.16            |
| $r^2$     | 0.904           | 0.914           |
| Freundlich|                 |                 |
| $1/n$     | 45.68           | 46.15           |
| $k_f$     | 0.22            | 1.14            |
| $r^2$     | 0.995           | 0.997           |
| Experimental ($q_e$) | 11.31 | 11.36 |

Three kinetic models (pseudo-first order (PFO), pseudo-second order (PSO), and intraparticle diffusion (IPD)) were used to determine the three kinetic parameters. The data for Cd(II) and MB adsorption on 10% and 20% treated BCS is shown in Table 2. A good fit for adsorption for PFO or PSO is determined by the closeness of the correlation coefficient to 1; the values of sorption capacity need to be close to the experimental data. Table 2 showed that the adsorption of MB on all adsorbents best fitted the PFO model with $r^2$ values from 0.996–0.997 whilst Cd(II) values fitted PSO with $r^2$ of 0.991–0.993. The sorption mechanism of PFO suggested that Cd(II) on the adsorbents involved Van der Waal forces. The PSO suggests that the adsorption process for MB was dependent on the availability of adsorption sites.

Thabede et al. (Thabede, et al., 2020b) treated BCS with 10 and 20% H$_2$SO$_4$ for Pb(II) ions and MB sorption. The acid-treated BCS showed an increase in surface area and pore size. The IR spectra showed that functional group such as bisulfate were responsible for improving the adsorption capacity of the positively charged pollutants. The 10% treated adsorbent’s maximum adsorption capacities were 17.85 and 13.0 mg/g for Pb(II) and MB, respectively. The sorption capacities of the 20% treated adsorbent for Pb(II) was 17.75 and 16.68 mg/g for MB.

The Langmuir and Freundlich isotherms were used to determine the equilibrium data and interaction behaviour of 10% and 20% treated BCS for the sorption of Pb (II) ions and MB (Table 3). The Tables show that the data fitted the Freundlich isotherm whereby ($r^2$) values were close to 1 for both adsorbents. The model suggested that the process involved multi-layer adsorption. It also implied that the surface of the adsorbents was heterogeneous. On the contrary, the Langmuir isotherm model could not explain the adsorption process.
The kinetic data in Table 4 of Pb(II) ions and MB removal on 10% and 20% treated BCS was assessed using the PFO, PSO, and IPD models. The results showed that the adsorption of Pb(II) ions and MB best fitted the PFO model with \( r^2 \) values of 0.99. The calculated sorption capacities were closer to the experimental values for PSO for both types of BCS. The IPD kinetic models included the EPA (estimate pore adsorption) and ESA (estimate surface adsorption), which determines whether adsorption takes place on the pores or surface. Table 4 shows that the sorption for Pb(II) ions took place in the pores (EPA) with percentages of 94.28 and 78.43 on the 10% and 20% treated BCS, respectively. The remainder was due to surface adsorption. The adsorption of MB occurred at the

| Models  | 10% treated BCS | 20% treated BCS |
|---------|-----------------|-----------------|
|         | Cd(II) | MB | Cd(II) | MB |
| PFO     | 14.05  | 14.72 | 12.16  | 17.66 |
|         | 4.19   | 0.073 | 4.23   | 4.13  |
|         | 0.877  | 0.997 | 0.838  | 0.996 |
| PSO     | 8.44   | 8.14  | 6.08   | 4.08  |
|         | 0.020  | 0.085 | 0.022  | 0.030 |
|         | 0.991  | 0.895 | 0.993  | 0.874 |
| IPD     | 3.515  | 4.556 | 7.54   | 5.39  |
|         | 7.716  | 1.79  | 1.89   | 1.35  |
|         | 0.909  | 0.769 | 0.976  | 0.759 |
| EPA*    | 72.47  | 71.69 | 66.55  | 69.21 |
| ESA*    | 27.52  | 28.31 | 33.45  | 30.79 |
| Experimental (\( q_e \)) | 13.23 | 15.24 | 12.57 | 16.42 |

*EPA—Estimated pore adsorption of IPD and *ESA—Estimated surface adsorption of IPD.

| Isotherms | 10% treated BCS | 20% treated BCS |
|-----------|-----------------|-----------------|
|           | Pb(II) | MB | Pb(II) | MB |
| Langmuir  | 15.70  | 18.56 | 12.37  | 26.32 |
|           | 0.77   | 1.09  | 0.56   | 1.09  |
|           | 0.90   | 0.90  | 0.90   | 0.90  |
| Freundlich| 11.70  | 34.72 | 22.37  | 15.31 |
|           | 0.100  | 0.106 | 0.813  | 2.401 |
|           | 0.99   | 0.99  | 0.99   | 0.99  |
| Experimental (\( q_e \)) | 17.75 | 12.68 | 17.54 | 16.56 |
pores for both adsorbents with EPA at 70.82 and 95.74 on the 10%, and 20% treated BCS, respectively.

2.2.1.3. $H_3PO_4$ treated black cumin seeds. Treatment of agricultural materials with mild or strong oxidizing agents such as $H_2SO_4$, phosphoric acid ($H_3PO_4$) and potassium permanganate ($K$MnO$_4$) increases the carboxylic (-COOH) and carbonyl (=CO) functional groups on the surface of materials leading to improved adsorption capacity (Gupta & Saleh, 2013; Lesoona et al., 2019; Yao et al., 2016). Thabede et al. (2020c) used $H_3PO_4$ and $K$MnO$_4$ as activating agents for the adsorption of Cr (VI) and Cd(II) ions from aqueous solutions. The IR spectra showed that oxygen groups (-COOH, = CO and -OH) were on the surface of the BCS and the treatment of the seeds enhanced the BET surface area and improved the surface texture concerning porosity. SEM images of the phosphoric acid and potassium permanganate treated BCS are shown in Figure 10(a,b). Both images showed that the surfaces were rough with cavities and pores. These characteristics were anticipated to improve the adsorption processes of Cd(II) and Cd(VI) ions. The maximum sorption capacities for Cr(VI) ions and Cd(II) were 17.70 mg/g, and 19.79 mg/g on the potassium permanganate treated BCS, respectively. The phosphoric acid-treated BCS’s sorption capacities were 15.98 mg/g for Cr(VI) and 19.09 mg/g for Cd(II) ions.

Nonlinear kinetic models (PFO, PSO and IPD) were used to obtain sorption rate data for Cr(VI) and Cd(II) ions onto $H_3PO_4$ and $K$MnO$_4$ treated BCS to determine the mechanisms involved for adsorption. PFO and PSO models were used to check the model fit (Table 5). The PSO ($r^2$) values for Cr(VI) and Cd(II) on $K$MnO$_4$ treated BCS were 0.9974 and 0.9987, respectively; values for $H_3PO_4$ treated BCS were 0.9912 and 0.9973, respectively. The good fit for the PSO model suggested that electrostatic interactions and porosity influenced the sorption of Cr(VI) and Cd(II). The IPD kinetic model estimates whether sorption occurs through the surface (ESA) or pores (EPA). The Cr(VI) and Cd(II) ions uptake onto $K$MnO$_4$ and $H_3PO_4$ treated BCS were similar for both the ESA and EPA.

To better understand the interaction and concentration effect between the Cr(VI) and Cd(II) ions and the $K$MnO$_4$ and $H_3PO_4$ treated BCS, the results were subjected to the nonlinear Langmuir and Freundlich isotherm models (Table 6). The isotherm data of Cr(VI) ions on $K$MnO$_4$ and $H_3PO_4$ treated BCS had high ($r^2$) values of 0.9956 and 0.9987, respectively, for the Langmuir model. This suggested that the Langmuir better describes the adsorption of Cr(VI) than the Freundlich isotherm. The implication is that Cr(VI) ion uptake on the $K$MnO$_4$ and $H_3PO_4$ treated BCS surfaces
Figure 10. SEM images of (a) phosphoric acid (b) potassium permanganate treated BCS.

Table 5. Kinetics $\text{H}_3\text{PO}_4$ and $\text{KMnO}_4$ treated BCS and their parameters for the adsorption of Cr(VI) and Cd(II) ions

| Models | KMnO$_4$ treated BCS | $\text{H}_3\text{PO}_4$ treated BCS |
|--------|----------------------|-----------------------------------|
|        | Cr(VI) | Cd(II) | Cr(VI) | Cd(II) |
| PFO    | $q_e$   | 10.79  | 43.07  | 17.53  | 15.10  |
|        | $K_1$   | 3.78   | 4.07   | 3.71   | 3.51   |
|        | $r^2$   | 0.9526 | 0.9556 | 0.9167 | 0.9591 |
| PSO    | $q_e$   | 15.59  | 17.20  | 16.18  | 17.04  |
|        | $K_2$   | 1.016  | 0.0294 | 0.0683 | 0.5875 |
|        | $r^2$   | 0.9974 | 0.9987 | 0.9912 | 0.9973 |
| IPD    | $C$     | 6.29   | 8.49   | 8.08   | 9.24   |
|        | $K_i$   | 0.9874 | 0.547  | 2.27   | 0.5401 |
|        | $r^2$   | 0.9814 | 0.9989 | 0.9853 | 0.9835 |
| EPA*   | %       | 50.67  | 55.99  | 52.36  | 52.62  |
| ESA**  | %       | 49.33  | 44.01  | 47.64  | 47.38  |
| Experimental ($q_e$) | 15.59 | 19.40 | 16.23 | 19.21 |
occurred on active sites with equal affinity in monolayer adsorption. The isotherm data of Cd(II) ions on the KMnO₄ treated BCS had a high ($r^2$) value for Langmuir whilst Cd(II) ions sorption onto H₃PO₄ treated BCS fitted the Freundlich model, indicating that the sorption process involved multi-layer formation.

A comparative study of different acid-treated BCS with other parameters is shown in Table 7 and shows that BCS has absorptive potential with good uptake of MB and some toxic ions.

2.2.2. Black cumin seeds treated with a base
Black cumin seeds treated with sodium hydroxide (NaOH) showed that pretreatment with hydroxides of sodium made effective adsorbents (Kim et al., 2016).

2.2.2.1. NaOH treated black cumin seeds. Black cumin seeds treated with 1 M sodium hydroxide (NaOH) for the simultaneous adsorption of Ni(II), Pb(II), Co(II) and Cu(II) ions from aqueous solutions showed that the base treated seeds had a higher sorption capacity than the pristine BCS. Figure 11 shows the preparation of the base treated-BCS using 1 M NaOH.

The adsorption capacities were 95.59, 185.12, 90.23 and 190.73 mg/g for Ni(II), Pb(II), Co(II) and Cu(II) ions, respectively. The SEM images of the surface morphology of the adsorbents before and after adsorption are shown in Figure 12(a,b). Before base treatment—say something about the SEM image. After the alkaline treatment spherical-like shaped particles were formed (Figure 12(b)). The SEM image of the seeds after adsorption showed that the surface was very porous and could have facilitated the adsorption of cations. However, the spherical morphology was not observed after adsorption.

2.3. Carbon from black cumin seeds
Activated carbon derived from biomass can adsorb toxic metal ions and dyes due to chemical interactions of polar functional groups, such as carboxylic, hydroxyl and amino groups (Aghababaei et al., 2017). Carbon containing materials can improve the surface area and the degree of porosity, which ultimately leads to high adsorption capacity. The use of low-cost alternative adsorbents such as BCS has advantages such as inexpensiveness, affordability, locally available (Pyrzynska, 2019) and are also considered as green adsorbents (Kyzas & Kostoglou, 2014).

Carbon derived from BCS was carried out at 200°C for the adsorption of MB and Cd(III) ions by Thabede et al. (2020a). Their results showed that the active sites adsorbed MB and that there was an equal attraction for the adsorbate, suggesting that monolayer adsorption took place on the dye surface. The removal of Cd(II) ions suggested that multi-layer adsorption process was involved and that the surface was heterogeneous. The surface morphology of carbonized adsorbents was investigated using SEM. Figure 13a shows that the carbonized black cumin seeds had an irregular
Table 7. Adsorption of metal ions and MB dye using acid-treated black cumin seeds

| Acid Pollutant | $q_e$ (mg/g) | pH | Dosage (g) | Initial concentration (mg/L) | Contact time (min) | Temperature ($^\circ$C) | Reference |
|----------------|--------------|----|------------|-----------------------------|-------------------|-------------------------|-----------|
| HCl            | 73.53        | 5.0| 1          | 60                          | 120.0             | 27                      | Siddiqui et al. (2018) |
| HCl and HNO$_3$| 90.41        | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Shooto et al. (2019)  |
| Pb(II)         | 188.20       | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede, et al. (2020a) |
| Co(II)         | 80.0         | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020a) |
| Cu(II)         | 179.20       | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020a) |
| 10% H$_2$SO$_4$| 15.89        | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020a) |
| Cd(II)         | 13.66        | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020a) |
| 20% H$_2$SO$_4$| 16.42        | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020a) |
| Cd(II)         | 13.23        | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020a) |
| 10% H$_2$SO$_4$| 13.0         | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020a) |
| Pb(II)         | 17.85        | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020a) |
| 20% H$_2$SO$_4$| 16.68        | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020a) |
| Pb(II)         | 17.75        | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020a) |
| H$_2$PO$_4$, Cr(VI) | 17.70 | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020c) |
| Cd(II)         | 19.79        | 5.0| 0.1        | 100.0                       | 120.0             | 25.0                    | Thabede et al. (2020c) |
surface morphology with rough irregular surfaces and cavities and disintegrated surface morphologies. These cavities, perhaps, enhanced the adsorption of Cd(II) ions and MB.

Another study by Thabede et al. (Thabede, et al., 2020b) carbonized BCS at 300°C for the sorption of lead-Pb(II) ions and MB from aqueous solutions. The adsorption processes of Pb(II) ions and MB was fast and took place within the first 15 min. Gibb’s free energy indicated that the adsorption of
Pb(II) ions and MB were physical in nature and spontaneous. SEM of the surface morphology of the carbonized black cumin seeds showed that surface morphology was irregular and rough with cavities (Figure 14). These cavities were projected to enhance the adsorption of MB and Pb (II). The maximum adsorption capacities were 17.75 mg/g for Mb and 17.95 mg/g for Pb(II). The preparation scheme of carbonized BCS is shown in Figure 15; the suggested mechanism of Pb(II) and MB adsorption on the carbonized adsorbents is shown in Figure 16(a,b).

The illustration of the preparation of acetone and DMF treated BCS is shown in Figure 17. The sorption study of chromium-Cr(VI) ions, Cd(II) ions and MB was conducted by Thabede et al. (2021) using the carbonized BCS which was prepared at 600°C. The seeds were first modified with solvents using acetone and dimethylformamide (DMF).

The acetone treated adsorbent Figure 18a shows dense textural structure and spherical morphology that is porous, rough and composed of cavities. A dense textural structure with an irregular surface is seen in Figure 18b after treatment with DMF and carbonization. The different surface textures could be attributed to the extraction of oil from the biomass leading to harsh effects of...
cell wall breakage and producing such a surface topology (Fontoura et al., 2017). These attributes are considered to increase the adsorption of Cd(VI), Cd(II) ions and MB. The adsorption capacity for Cr(VI) ranged from 65.38–87.44 mg/g, Cd(II) ranged between 73.91–96.89 mg/g, and MB was between 93.90–99.82 mg/g. Carbon from BCS has been shown to be a promising low-cost adsorbent that can adsorb both positive and negative ions due to their carbonaceous nature. These results show that BCS can be turned into a useful material for water purification.

2.4. Black cumin seeds functionalized by nanoparticles
Nanoparticles have attracted the attention of many researchers worldwide because of their outstanding properties such as; mechanical strength, high surface area, and abundant active sites increasing the adsorption of biomaterials. Nanoparticles can be easily attached to the surface of biomaterials. Through interaction with functional groups such as amino (-NH₂) and carboxylic
(-COOH) on the surface of the biomaterials, they can form stable composites. One of the significant challenges of using biomaterials in water treatment is separating the material from the solution. Additional steps such as centrifugation and filtration are required limiting large-scale application of the process. To overcome this challenge researchers have modified the surface of the biomaterial with magnetic nanoparticles. The magnetic biomaterial composites can be separated from the solution by applying a magnetic field. Furthermore, the magnetic biomaterial composites have better attributes such as higher specific surface area and surface functionality than the starting material. Several research groups have modified the surface of black cumin seeds (BCS) with magnetic nanoparticles.

2.4.1. Black cumin seeds-nanoparticles composites
Siddiqui and Chaudhry (2018) produced BCS functionalized by manganese magnetite nanocomposite-MnFe$_2$O$_4$ for the adsorption of MB. The uptake of MB was 10.07 mg/g. In another study, Siddiqi et al. (2019a) used Nigella sativa seed-based nanocomposite-MnO$_2$/BCS for the removal of MB and reported uptake of 9.97 mg/g. The nanocomposite preparation and proposed adsorption mechanism are illustrated in (Figures 19 and 20), respectively. It was shown that the adsorption was controlled by hydrogen bonding and electrostatic interaction. Thabede et al. (2021) also
modified the BCS with magnetite-sucrose nanoparticles to remove Cr(VI) and Pb(II) and reported adsorption of 13.0 and 37.9 mg/g, respectively.

2.4.2. Black cumin seeds-nanohybrid composites
The adsorption potency of *Nigella sativa* seed-based nano-hybrid composite-Fe$_2$O$_3$-SnO$_2$/BC for removing MB from water was 23.84 mg/g (Siddiqui et al., 2019a). The hybrid material Fe$_2$O$_3$-ZrO$_2$/BC for the adsorption of metal ions and dyes from wastewater showed an adsorption capacity of 1.01 and 38.10 mg/g for As(III) and MB, respectively (Siddiqui & Chaudhry, 2019). The adsorption rate for MB was better with this composite.

2.4.3. Black cumin seeds-graphene oxide-nanocomposite
The magnetic BCS-graphene oxide-based nanocomposite (BC-GO@Fe$_3$O$_4$) was used for the removal of As(III) and MB from aqueous solutions (Tara et al., 2020a). The adsorbent removed 1.0 and
| Adsorbent                  | Pollutant | \( q_e \) | pH | Dosage (g) | Concentration (mg/L) | Contact time (min) | Temperature (°C) | Reference                      |
|---------------------------|-----------|-----------|----|------------|-----------------------|-------------------|-----------------|--------------------------------|
| BCS-MnFe\(_2\)O\(_4\)    | MB        | 10.07     | 10 | 3          | 10                    | 120               | 27              | Siddiqui and Chaudhry (2018)  |
| \( \text{MnO}_2/\text{BCS} \) | MB        | 9.97      | 7  | 1          | 10                    | 120               | 27              | Siddiqui. et al. (2019a)      |
| \( \text{Fe}_2\text{O}_3-\text{SnO}_2/\text{BC} \) | MB        | 23.84     | 7  | 2          | 10                    | 120               | 27              | Siddiqui. et al. (2019a)      |
| \( \text{Fe}_2\text{O}_3-\text{ZrO}_2/\text{BC} \) | As(II)/MB | 1.01      | 73 | 2          | 101                   | 120               | 27              | Siddiqui. and Chaudhry, (2019) |
| BC-GO@Fe\(_3\)O\(_4\)    | As(II)/MB | 1.00      | 7  | 110        | 110                   | 150               | 27              | Tara et al. (2020a)           |
| rGO-MnO\(_2/\text{BC}    | As(II)    | 14.7      | 7  | 1          | 110                   | 75                | 27              | Tara et al. (2020b)           |
| \( \text{Magnetite-sucrose-BCS} \) | Cr(VI)    | 13.0      | 5  | 0.1        | 100                   | 120               | 25              | Thabede et al. (2021)         |
|                           | Pb(II)    | 37.9      | 5  | 10         |                       |                   |                  |                                |
10 mg/g of As(III) and MB, respectively. A follow-up study by Tara et al. (2020b) developed a new material with a reduced graphene oxide-manganese oxide-black cumin based hybrid composite (rGO-MnO$_2$/BC) and applied it for the adsorption of As(III) and MB. The absorption capacity for As(III) and MB increased to 14.7 and 232.5 mg/g, respectively. The combination of rGO, BCS and MnO$_2$ increased the surface area and the active sites on the material's surface and increased adsorption. The adsorption parameters and conditions are highlighted in Table 8. The table shows the modification of BCS by nanoparticles for the sorption of different toxic ions and MB investigated by different researchers. The results show that the BCS nano composite are capable of adsorbing toxic ions and MB.

3. Conclusion
Over the years, environmental legislation regarding water quality has become more restricting. Different treatment technologies such as membrane, chemical precipitation, adsorption, filtration, electrodialysis and photocatalysis have removed toxic metal ions from contaminated wastewater. Adsorption is regarded as one of the most effective non-conventional methods to treat contaminated wastewater. The acid (HCl) and base (NaOH) treated BCS adsorbents for adsorption of Ni(II), Cu(II), Pb(II), and Co(II) ions showed that adsorption was dependent on system parameters including contact time, temperature, initial concentration of the metal ions and pH of the solution. The maximum capacity adsorption trend was base-BCS>acid-BCS>pristine-BCS. Of the isotherm models tested, the Langmuir model had the best fit. Kinetic studies using pseudo first order (PSO) and pseudo second order (PSO) showed a good fit with the PFO. suggesting that the adsorption mechanism involved electrostatic attractions and Van der Waal forces. The modification of BCS with 10% and 20% sulfuric acid (H$_2$SO$_4$) for the adsorption of Cd(II) ions and MB indicated that the maximum uptake for MB was 15.89 mg/g and 16.42 mg/g for the 10% and 20% H$_2$SO$_4$ treated adsorbent, respectively. The adsorption of Cd(II) for similar treated BCS was 13.66 and 13.25 mg/g. The acid-treated BCS showed high sorption capacity than the pristine-BCS. The overall adsorption capacities showed that 10% H$_2$SO$_4$-BCS favoured the removal of Cd(II) ions, whereas the 20% H$_2$SO$_4$-BCS favoured the removal of MB. The activation of BCS with KMnO$_4$ for the sorption of Cr(VI) showed maximum adsorption at pH 1, whereas BCS treated with H$_3$PO$_4$ absorbed Cd(II) ions maximally at pH 9. KMnO$_4$ seeds were slightly better adsorbents of Cd(II) at 19.15 mg/g than H$_3$PO$_4$, treated seeds at 19.09 mg/g. Lower capacities for adsorption of Cr(VI) (16.12 mg/g) occurred with KMnO$_4$ and H$_3$PO$_4$ (15.98 mg/g) treated seeds. The sorption of Cr(VI) and Cd(II) ions on pristine-BCS were lower than the chemically (KMnO$_4$ and H$_3$PO$_4$) treated BCS.

The functional groups on the surface of pristine-BCS treated with KMnO$_4$ and H$_3$PO$_4$ were either protonated/deprotonated depending on the pH. This may explain the enhanced electrostatic attraction between Cr(VI)/Cd(II) ions and the functional groups on the adsorbents.

The sorption rates of the KMnO$_4$-BCS and H$_3$PO$_4$-BCS for Cr(VI) were rapid from less than 5 min and increased in the first 30 min. The sorption rate for Cr(VI) ions onto pristine-BCS increased sharply from 5 until 60 min, then stabilized and attained equilibrium after 60 min. The sorption rates for Cd(II) ions were fast at 5 min. Adsorption capacities of all adsorbents increased as the concentration of the ions increased. Carbon-based BCS was developed at 200°C for the adsorption of MB and Cd(II) ions. The adsorption of MB occurred at the active sites. There was an equal attraction for the adsorbate suggesting that monolayer adsorption took place. The sorption of Cd(II) ions suggested a multilayer adsorption process and that the surface was heterogeneous. The surface morphology of the adsorbents was irregular with rough irregular surfaces and cavities. The carbonization of BCS at 300°C for the sorption of Pb(II) ions and MB showed that the adsorption process was rapid. The surface morphology was irregular with cavities which perhaps improved the adsorption of MB and Pb(II) ions. The sorption capacities were 17.75 and 17.95 mg/g for MB and Pb(II) ions, respectively. The carbonization of BCS at 600 °C showed spherical morphology that was rough and porous with cavities. The maximum sorption capacities were 87.44, 96.89 and 99.82 mg/g for Cr(VI), Cd(II) and MB, respectively. In summary, Black cumin seeds can be used as adsorbents for MB and toxic ions. Chemical activation of black cumin seeds with different organic and inorganic solvents showed and enhanced
adsorption. Carbonization of the BCS at different temperatures is also feasible. Modification of the seeds showed several surface functional groups on the adsorbents suggesting that adsorption may be due to electrostatic attraction. Composites are good adsorbents for the removal of toxic ions from aqueous solutions. Black cumin seeds have shown excellent adsorption capacities for metal ions and methylene blue dye. It can therefore be concluded that black cumin seeds are promising adsorbents.

Funding
This work was supported by the National Research Foundation [TTK190403426819].

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

Citation information
Cite this article as: Application of black cumin (Nigella sativa L.) seeds for the removal of metal ions and methylene blue from aqueous solutions, Patience Mapule Thabede & Ntaote David Shooto, Cogent Engineering (2022), 9: 2013419.

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