

Article

Competitive Adsorption of Quaternary Metal Ions, Ni^{2+} , Mn^{2+} , Cr^{6+} , and Cd^{2+} , on Acid-Treated Activated Carbon

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Abstract: This paper examined the competitive removal of metal ions from quaternary aqueous solutions containing Ni^{2+} , Mn^{2+} , Cr^{6+} , and Cd^{2+} using adsorption on both acid-modified and unmodified activated carbon. Activated carbon (AC) was oxidized with nitric acid, both in granular (AGC) and powder (APC) forms, and tested for the competitive adsorption of Ni^{2+} , Mn^{2+} , Cr^{6+} , and Cd^{2+} from an aqueous solution. Surface oxidation led to a reduction in BET surface area and HK pore width and an increase in the intensities of hydroxyl and carboxyl functional groups for both AGC and APC compared to unmodified activated carbon, AC, as indicated with BET and FTIR analyses. The adsorption capacity of all four metal ions on AC was in the order $\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cr}^{6+} > \text{Mn}^{2+}$, while it was altered for the two oxidized AGC and APC carbons to be $\text{Cr}^{6+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+}$. Acid treatment resulted in high selectivity for Cr^{6+} over all other available ions with a 100% removal efficiency, while it decreased for Ni^{2+} , Cd^{2+} , and Mn^{2+} compared to AC. This improvement in Cr^{6+} adsorption is due to its higher ionic potential and smaller size, which results in a faster diffusion and stronger adsorption to the acidic groups located at the pore edges. Therefore, it will repel and hinder other ions from accessing the activated carbon pores. Modeling of the adsorption isotherms with DKR was better than both Freundlich and Langmuir for the competitive ions. DKR showed strong attraction for both Ni^{2+} and Cd^{2+} by ion exchange on the AC surface, as indicated by their apparent adsorption energy (E) values. Cr^{6+} adsorption was found to be by physical adsorption on AC and by ion exchange on both AGC and APC. Mn^{2+} ions had a very weak attraction to all types of tested activated carbons in the presence of other ions.

Keywords: competitive metal ions; nickel; manganese; chromium; cadmium; oxidized activated carbon



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1. Introduction

Exponential contamination of groundwater and surface resources with heavy metals from mining activity, industrial and municipal waste, and landfill leachates remains a serious threat all over the world due to their high toxicity at very low concentrations [1,2]. Heavy metals are not biodegradable and cannot be removed from ecosystems by natural processes. They are persistent and accumulate in the tissues of animals and fish and therefore have a route into the human body, causing severe and irreversible disorders in the neurological and physiological systems of the body [1–5]. Cadmium ions, Cd^{2+} , in water and food cause kidney failure, bone damage, osteoporosis, and a higher cancer risk [6,7]. Chromium in its hexavalent form, Cr^{6+} , is reported to be a priority carcinogenic toxic metal. It is responsible for lung cancer, organ failure, and dermatitis [8,9]. Nickel, Ni^{2+} , is also classified as a human carcinogen [10]. Ni^{2+} is known to affect the liver, colon, and kidneys. It also causes irreversible damage to the enzymatic, nervous, and cardiovascular systems [11]. Manganese, Mn^{2+} , is essential for normal body growth. However, continuous

and overdose exposure to Mn^{2+} can cause Parkinson-like diseases and affect the nervous system [12,13].

Analysis of data reported and collected over the last five decades, from the 1970s to 2017, in all continents for heavy metal concentrations in surface water showed that the contamination progressed from single-metal contamination to multi-metal pollution over time. Moreover, Cd, Cr, and Ni concentrations increased globally by 25-, 140-, and 60-fold, respectively. Mn concentration was also reported to be five times higher than the threshold limits by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA). Surface water in North America had the lowest heavy metal concentration of all continents and did not exceed the WHO and EPA limits, indicating effective implementation of regulations and standards on heavy metal emissions from different potential pollution sources. Europe met the threshold limits for all metals except Ni and Mn. The developing countries in Africa, Asia, and South America exceeded the limits for all reported heavy metals [14].

Pollution of water with heavy metals may result from different sources. Cd^{2+} , Cr^{6+} , Mn^{2+} , and Ni^{2+} are introduced to water resources and the environment mainly from spent household and rechargeable batteries, electroplating [15,16], the tannery industry [17–20], fertilizers, petrochemicals, and refinery wastewater [21–25]. Additionally, the deterioration in storage and transportation systems introduces Mn^{2+} , which causes water coloration [26,27]. These metals are also present in a concentrated form in municipal landfill leachates [28–30].

Several techniques and methods have been tested for the effective removal of heavy metals from water, including chemical precipitation, coagulation–flocculation, biological treatments, membrane separation, reverse osmosis, nanofiltration, electrodialysis, ion exchange, and adsorption. The reported efficiency for the removal of heavy metals using some of these technologies is as high as 99%. However, these values are valid only under ideal conditions of heavy ion concentration, pH, and the absence of any other ion competitor or other organic or inorganic contaminants. Therefore, it is expected that their actual efficiency will significantly decrease under real industrial operating conditions. Another challenge for these methods is that they could generate secondary pollutants or that they are economically unfeasible. The presence of different heavy metal ionic forms and specificity will also alter the performance of most established technologies. Factors affecting the selection of water treatment technology for heavy metal removal involve simple implementation, low investment, low power consumption and processing pressures, and, preferably, the use of green environmental material. A comparison of the cost of technologies based on these factors showed that reverse osmosis, nanofiltration, and electrodialysis have the highest cost per volume of treated water, while adsorption has the lowest [31].

Many materials were evaluated for their potential as adsorbents to remove heavy metals for the liquid phase including polymers, geopolymers, clays, zeolites, activated carbon in different forms and origins, and biomaterials [18,23,31–37]. Among these, activated carbon is the most famous and well-documented adsorbent used for both organic and inorganic pollutants because of its high available surface area, microporous structure, and the possibility to tailor its surface with different functional groups. Several types of surface tailoring and modification of activated carbon were reported including hydrogen peroxide and nitric acid oxidation, sulfuration, and nitrogenation treatment, as well as anchoring coordination ligands [38]. For the current work, surface modification of activated carbon with HNO_3 was selected among these surface tailoring methods.

The majority of adsorption studies report the adsorption of a single metal ion from the solution. However, this does not reflect the real cases where ions are usually available as a complex mixture and they have to compete for the available surface adsorption sites. Studies on the competitive adsorption of various heavy metals on activated carbon concluded that the presence of other metal ions in the aqueous solution will alter the adsorption behavior of the ions from that of a single ion [39–41]. A limited number of studies attempted to investigate the effect of carbon surface modification on multi-metal ion

adsorption [2,37]. A system of binary ion mixtures, Ni^{2+} - Pb^{2+} and Zn^{2+} - Ni^{2+} , on oxidized activated carbon fibers was reported to have a drastic decrease in the adsorption of Ni^{2+} upon the presence of Pb^{2+} or Zn^{2+} but not the opposite [40].

The current work attempts to bridge part of the gap by evaluating the competitive adsorption of multiple ions under the influence of surface modification. The purpose of this work is to explore the impact of activated carbon surface oxidation on the adsorption of Ni^{2+} , Mn^{2+} , Cr^{6+} , and Cd^{2+} from an aqueous solution. To the best of our knowledge, this work has not yet been performed on more than two ions. The unmodified activated carbon was used for comparison. The selection of these metal ions was based on a previous study on municipal solid waste leachate, where they were found in very high concentrations [30]. Langmuir, Freundlich, and the Dubinin–Kaganer–Radushkevich (DKR) adsorption models were used, and the resulting adsorption parameters were calculated to explain the competitive behavior of the tested metal ions.

2. Materials and Methods

2.1. Adsorbents

Activated carbon was used both in granular and powder form. All carbon was boiled in deionized water and then dried in an oven at 110 °C for a minimum period of 24 h. Further surface modification was performed by boiling part of them with 4M HNO_3 solution for 1 h while applying the total condensation. After cooling, the solution of the acid-treated granular activated carbon (AGC) and acid-treated powder activated carbon (APC) was decanted, and the solids were washed several times with deionized water until a neutral, constant pH was reached.

2.2. Characterization of Adsorbents

The surface area and pore size distribution of the different adsorbents were measured using nitrogen sorption porosimetry on a Quantachrome Instrument (Model Autosorb-1, Boynton Beach, FL, USA). The infrared spectra were recorded with a Thermo Nicolet Nexus 670 FT-IR spectrometer (Madison, WI, USA). Signal noise was reduced by averaging 32 scans (resolution of 4 cm^{-1}) of the single beam spectra.

2.3. Adsorption Isotherms

Stock solutions of heavy metals of 100 mg/L concentration ($\text{Ni}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Cr}(\text{VI})$) and 50 mg/L $\text{Cd}(\text{II})$ were prepared separately by dissolving appropriate quantities of nickel (II) nitrate hexahydrate, cadmium nitrate in nitric acid at a concentration of 0.5 mol/L (Fluka, Buchs, Switzerland), manganese (II) sulfate monohydrate and chromium (VI) oxide (Merck, Darmstadt, Germany). $\text{Cd}(\text{II})$ was tested in a smaller concentration than the other ions since its concentration in real wastewater samples and municipal solid waste leachates is usually less than other metal ions [30]. The ASTM standard bottle point method (ASTM D3860-89a) was used to generate the ion adsorption isotherms. Measurements took place at 25 °C using a simulated solution of the main heavy metals found in the landfill leachates. The composition of the simulated solution was 100 mg Ni^{2+} /L, 100 mg Cr^{6+} /L, 100 mg Mn^{2+} /L, and 50 mg Cd^{2+} /L. The pH of the solution was adjusted to 6. A measure of 10 mL of the simulated solution was added to 15 mL bottles that had pre-weighed amounts (25, 50, 100, 500, and 1000 mg) of the adsorbents. All samples were agitated for 3 continuous days in a temperature-controlled water bath to assure equilibrium achievement. The solid adsorbents were separated from the liquid using centrifugation followed by filtration through 0.45 μm syringe filters. The heavy metal concentrations in the filtrate were measured using the inductive coupled plasma technique (ICP, Perkin-Elmer, Optima 2000 DV, Norwalk, CT, USA). Blank samples were used with every isotherm to compensate for any loss or adsorption on the walls of the tube.

Equilibrium adsorptive quantities of the metal ions on the adsorbent surfaces were calculated using the following relation:

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

where q_e is the amount of metal ion adsorbed per unit mass of adsorbent (mg/g), V is the volume of the solution (L), M is the mass of the adsorbent (g), and C_0 and C_e are the starting vs. the equilibrium concentration of the ion in the aqueous solution, respectively (mg/L).

The percent removal of the metal ion by the adsorbent was calculated using the following mass balance relation:

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

3. Results and Discussion

3.1. Properties of the Adsorbents

The performance of activated carbon in removing heavy metals from water depends to a great extent on three factors: (1) surface properties, including the pore size distribution, surface area, and available surface functional groups (oxygen complex groups); (2) the aqueous solution conditions such as pH and the presence of competitive ions; and (3) the properties of the heavy metal ions including charge density (charge-to-radius ratio), electronegativity, and ionic radius [2].

The surface area properties calculated from N_2 sorption porosimetry data are shown in Table 1. The highest surface area for the tested adsorbents is observed for the powdered activated carbon treated with acid (APC) (892 m^2/g). Surface oxidation with nitric acid caused a 7% reduction in the surface area of AGC (591 m^2/g) compared to untreated activated carbon (AC) (635 m^2/g). The powder sample (APC) has a higher surface area (892 m^2/g) due to a smaller particle size. All measured samples have a microporous structure with pore sizes less than 2 nm based on the Horvath–Kawazoe (HK) model, which is used to determine the pore size distribution in microporous adsorbents such as activated carbon and zeolites. Acid treatment also led to a slight reduction in the pore width for AGC (1.388 nm) compared to AC (1.398 nm), which is attributed to the acidic sites being bonded to the edges of the graphitic basal plane [42]. Similar behavior of the surface area and pore width reduction upon acid treatment was also reported by other researchers [36].

Table 1. Surface area properties of adsorbents.

Adsorbent	BET Surface Area	HK Cumulative Pore Volume	HK Pore Width
	(m^2/g)	(cm^3/g)	(nm)
AC	635	2.99×10^{-1}	1.398
AGC	591	2.79×10^{-1}	1.388
APC	892	4.22×10^{-1}	1.388

The FTIR spectra of AC, AGC, and APC were assessed to identify the functional groups added to the carbon surface upon acid modification, as shown in Figure 1. Increased absorption intensities for the hydroxyl group (O–H, H-bonded), broad stretching vibration at around 3440 cm^{-1} , C–O stretching absorption at 1042 cm^{-1} , and C=O conjugated carbonyl groups at 1630 cm^{-1} are strong indicators of the acid groups loading on the activated carbon surface. Other weak bands for C–H stretching at 2920 cm^{-1} and 2855 cm^{-1} are also observed. Previous work showed that oxygenation of activated carbon with 4M HNO_3 significantly increased the concentration of acidic surface oxygen complexes on the

surface (carboxylic and carbonyl groups), reduced the total number of basic groups on the activated carbon surface, and caused the surface to be more hydrophilic [2,43,44].

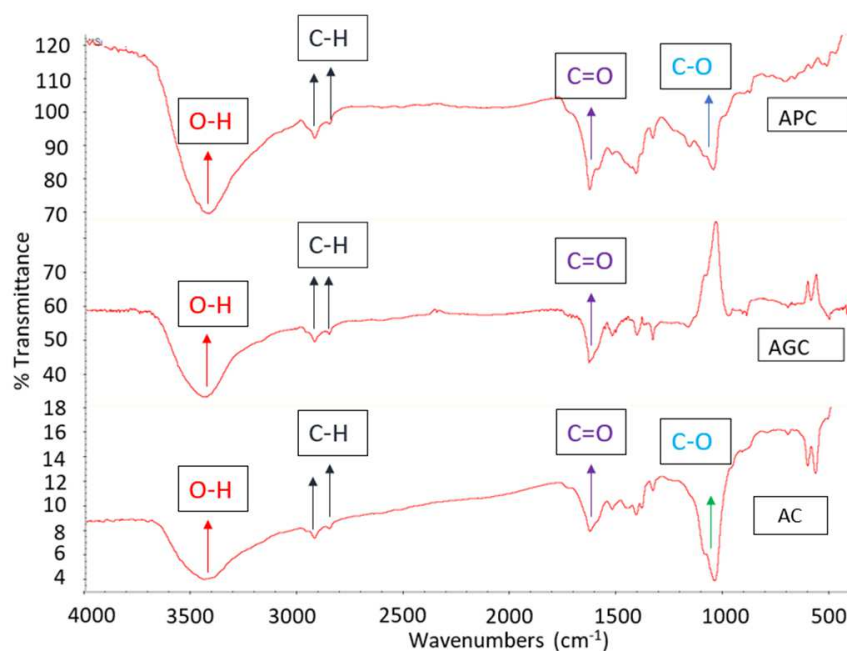
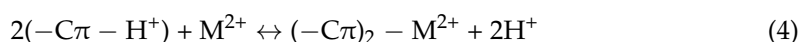


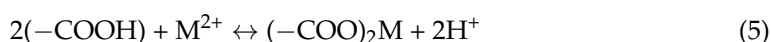
Figure 1. FTIR spectra of AC, AGC, and APC.

3.2. Competitive Adsorption of Heavy Metals

Adsorption remains the most investigated and applied method that has proved to provide high removal efficiency and be cost-effective. Separation with adsorption has several advantages such as the high selectivity for metal ions available in trace amounts, cost effectiveness since it can use abundant adsorbents, and the quality of being environmentally friendly [38]. In general, the mechanism of heavy metal ion adsorption on the surface of activated carbon is by electrostatic attraction to the surface, surface complexation, and ion exchange [2,45]. For the unmodified carbon surface, it was suggested that heavy metal ions adsorb through interactions with the π electrons of the carbon basal planes following the reactions [2,46]:



The presence of metal ions in water will result in the release of protons according to reaction (4). These protons neutralize the OH^- ions released from the addition of activated carbon to water in reaction (3). Therefore, an insignificant change in the solution pH will take place during adsorption [2]. In the presence of acidic groups on the surface of activated carbon, the mechanism becomes surface complexation or ion exchange depending on the solution pH value. If the solution has low pH, the weakly acidic functional groups are more likely to be protonated and will undergo ion-exchange reactions with the metal ions, as described in reaction (5).



At higher pH, the acidic groups will be nonprotonated, and the metal ions will bind to them by surface complexation, which will result in the release of less than one proton by each metal ion adsorbed [2].

Adsorption isotherms for all four metal ions, Ni^{2+} , Cr^{6+} , Mn^{2+} , and Cd^{2+} , are shown in Figure 2. The isotherms are not uniform curves, most likely because of the competition between ions on the available adsorption sites in addition to the repulsion and interaction

between the present ions. Similar behavior for competitive adsorption of heavy metal ions was reported by Covelo et al. [47].

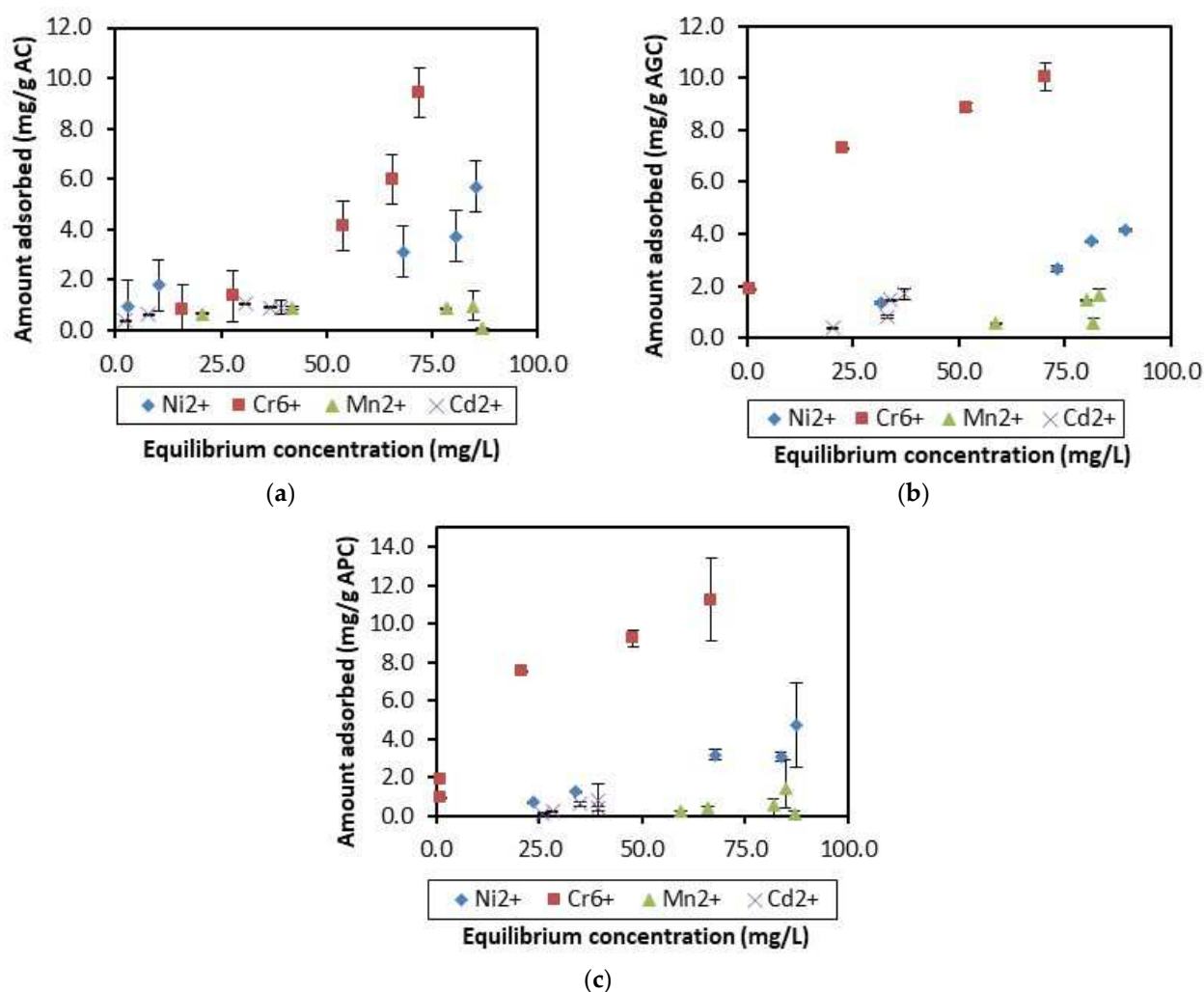


Figure 2. Adsorption isotherms of metal ions on different adsorbents: (a) AC, (b) AGC, and (c) APC.

To understand the behavior of heavy metal ions in competitive adsorption, it is important to compare their ionic characteristics and properties such as ionic radius ($\text{Cd}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+} > \text{Cr}^{6+}$), ionic potential or charge-to-radius ratio ($\text{Cr}^{6+} > \text{Ni}^{2+} > \text{Mn}^{2+} > \text{Cd}^{2+}$), and electronegativity ($\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cr}^{6+} > \text{Mn}^{2+}$) [47–49], as shown in Table 2.

The selectivity of each adsorbent for heavy metals under simulated conditions is shown in Figure 3 for the 500 mg adsorbent isotherms. The results indicate that acid treatment of both granular carbon and powder carbon (AGC and APC, respectively) changed the order of metal selectivity compared to the basic granular carbon (AC). For the basic untreated AC, the order of ion selectivity was $\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cr}^{6+} > \text{Mn}^{2+}$ for the high amounts of adsorbents (1000 and 500 mg AC), while for low amounts of adsorbents (100, 50, and 25 mg), the AC had a similar order to both AGC and APC as $\text{Cr}^{6+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+}$, as shown in Figure 2.

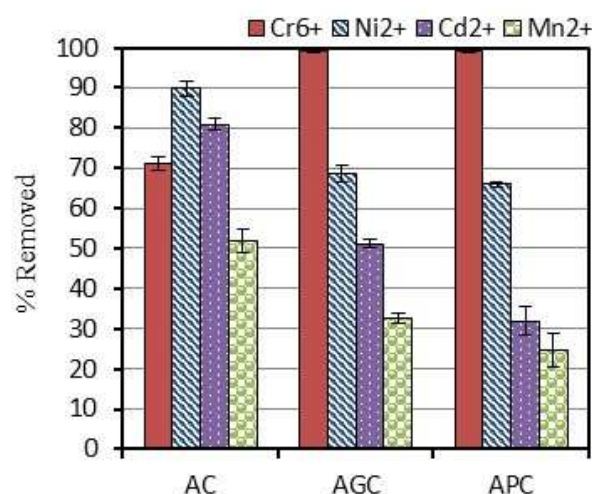


Figure 3. Percent removal of metal ions on different adsorbents (500 mg).

Acid treatment of granular carbon (AGC) increased the Cr⁶⁺ removal efficiency over the untreated AC by 30% while it decreased for Ni²⁺, Mn²⁺, and Cd²⁺ by 23%, 36%, and 37%, respectively. This can be explained by the much higher ionic potential and the small size of Cr⁶⁺ compared to other ions. This will lead to a stronger attraction of Cr⁶⁺ to the acidic surface groups and faster diffusion to the pores of activated carbon. The highly positive Cr⁶⁺ ions will adsorb on the acidic functional sites located at the edges of the pores and will repel other weaker heavy metal ions and reduce their accessibility to activated carbon pores. An investigation of Cr⁶⁺ removal at low pH, as a single ion, upon surface oxidation of activated carbon with HNO₃ reported that Cr⁶⁺ uptake was enhanced with the presence of acidic functional groups and that Cr⁶⁺ was first reduced to Cr³⁺ followed by Cr³⁺ adsorption [50,51].

Table 2. Ion characteristics of the tested heavy metals.

Element	Ionic Radius (Å) [52]	Hydrated Ionic Radius (Å) [53]	Ionic Potential (z/r) (Å ⁻¹)	Pauling Electronegativity Values [54]
Cr ⁶⁺	0.44	4.61 * for Cr ³⁺	13.64 (calculated)	1.66
Ni ²⁺	0.69	4.04	2.90 (calculated)	1.91
Mn ²⁺	0.83	4.38	2.41 (calculated)	1.55
Cd ²⁺	0.95	4.26	2.11 [49]	1.69

The difference between Ni²⁺ and Cd²⁺ removal efficiency increased with activated carbon acid treatment, indicating a higher affinity for Ni²⁺ also over Cd²⁺ and Mn²⁺. This observed behavior of Ni²⁺ over Cd²⁺ is opposite to what was reported by Cao et al., 2019 [35] for their removal by activated carbon derived from *Eichhornia crassipes*. Therefore, the origin of activated carbon also affects the competitive adsorption of heavy metal ions from an aqueous solution.

The removal of Mn²⁺ by all three adsorbents was very poor compared to the other heavy metal ions. Tran and co-workers [36] reported that the adsorption of Mn²⁺ alone by granular activated carbon modified with nitric acid was reported to enhance the capacity to seven times greater than that of unmodified activated carbon. Conversely, in our study, which involved co-existing heavy metal ions, the Mn²⁺ capacity decreased with acid modification, as shown in Figure 3. This is due to the reduced access to the pores of activated carbon and the repulsive forces with other metal ions adsorbed to the acid groups located at the edges of these pores. The adsorption capacity of Mn²⁺ for AC was 1.0 mg/g, which is comparable to that reported by Tran and co-workers (1.29 mg/g) [36].

3.3. Modeling Competitive Metal Ions Adsorption Isotherms

Adsorption isotherm models provide an adequate understanding and interpretation of the adsorption mechanisms and pathways of the adsorbate on different adsorbents at equilibrium conditions. This modeling is critical to develop the relations that accurately describe the results, which will enable the design of an effective and efficient adsorption system. The constants of isotherms reflect the adsorbent capacity and its surface properties as well as the adsorption strength and state [55]. Theoretical investigation of heavy metal adsorption by activated carbon using physical modeling concluded that Ni^{2+} and Cd^{2+} ions are mainly bonded to the carboxylic acidic functional group on the activated carbon surface and that the adsorption capacity is directly proportional to the metal ion electronegativity [56]. In this work, competitive adsorption of Ni^{2+} , Cd^{2+} , Cr^{6+} , and Mn^{2+} on activated carbon (AC) and acid-treated activated carbon (AGC and APC) were modeled using Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich (DKR) isotherms. Analysis and interpretation of the parameters and the assumptions of these models will help in providing a reliable understanding of the adsorption mechanisms of heavy metal ions on a microscopic level under a competitive environment and their interaction with different surface conditions. Data fitting was based on the least-squares regression values (R^2), and the isotherm parameters are summarized in Table 3.

Table 3. Langmuir, Freundlich, and DKR isotherm parameters for the adsorption of tested heavy metals.

Ions	Langmuir				Freundlich			DKR			
	q_{max} (mg/g)	b (L/mg)	R_L	R^2	k_f	n	R^2	X_m (mg/g)	β (mol/kJ) ²	E (kJ/mol)	R^2
AC											
Cr^{6+}	Negative slope	-	-	0.9331	0.01	0.63	0.9675	759.77	0.0175	5.35	0.959
Ni^{2+}	3.98	0.088	0.102	0.9793	0.68	2.63	0.9846	13.22	0.0043	10.78	0.9213
Cd^{2+}	1.04	0.270	0.082	0.9804	0.32	3.19	0.9296	2.90	0.0028	13.36	0.9422
Mn^{2+}	1.05	0.099	0.104	0.9805	0.35	4.55	0.7929	1.85	0.0026	13.87	0.81
AGC											
Cr^{6+}	10.47	0.160	0.061	0.9849	2.24	2.79	0.9963	23.52	0.0032	12.50	0.9992
Ni^{2+}	Negative slope	-	-	0.019	0.04	0.98	0.9495	80.85	0.0118	6.51	0.9452
Cd^{2+}	Negative slope	-	-	0.7352	0.00	0.47	0.8671	5723.39	0.0209	4.89	0.8647
Mn^{2+}	Negative slope	-	-	0.0473	0.00	0.49	0.3216	7.30×10^2	0.0249	4.48	0.3216
APC											
Cr^{6+}	12.092	0.105	0.0904	0.9769	2.02	2.45	0.995	30.01	0.0037	11.62	0.9974
Ni^{2+}	Negative slope	-	-	0.4969	0.02	0.80	0.9652	166.56	0.0143	5.91	0.9666
Cd^{2+}	Negative slope	-	-	0.6087	0.00	0.32	0.7558	1.20×10^5	0.0311	4.01	0.7587
Mn^{2+}	Negative slope	-	-	0.712	0.00	0.28	0.7539	14.1	0.013	6.20	0.0465

3.3.1. Langmuir Model

The Langmuir isotherm is a theoretical model where a monolayer adsorption of molecules to a homogenous solid surface is assumed and in which no interaction takes place between the adsorbed molecules [57]. It is described by the linear form as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \quad (6)$$

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

where q_e and C_e are the equilibrium adsorption capacity (mg/g) and equilibrium metal concentration in the solution (mg/L), respectively. q_{max} is the maximum adsorption capacity (mg/g). b is related to the adsorption rate (L/mg); the higher the b value, the stronger the surface affinity for the metal ion adsorption. R_L , described in Equation (7), is a dimensionless separation factor, which is used to predict whether the adsorption is favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$) [57].

Langmuir fitting for the tested heavy metal ions, Cr^{6+} , Ni^{2+} , Cd^{2+} , and Mn^{2+} , under competitive conditions on the AC, AGC, and APC samples is shown in Table 3. The R_L values showed that the adsorption for Ni^{2+} , Cd^{2+} , and Mn^{2+} is favorable ($R_L < 1$) for untreated AC. However, Cr^{6+} adsorption on AC was poorly fit to this isotherm (negative slope). In contrast, acid treatment of the carbon surface, AGC and APC, resulted in altering the fitting of the Langmuir model to fit only Cr^{6+} . On these samples, Cr^{6+} had the highest removal efficiency and favorable adsorption among the tested metal ions ($R_L < 1$) while Ni^{2+} , Cd^{2+} , and Mn^{2+} had poor fitting data according to Table 3. This means that the Langmuir model does not fit the competitive adsorption of heavy metal ions on an acid-treated activated carbon surface because of their incompliance with the model assumptions. This indicates that there is an interaction between adsorbed molecules and that with acid treatment, the energies of adsorption sites become unequal. The Langmuir isotherm was also reported to be a good fit for the competitive adsorption of both Cd^{2+} and Mn^{2+} by *Borago officinalis* biomass [34], which is in agreement with the adsorption results on the AC sample in this work.

3.3.2. Freundlich Model

The Freundlich empirical model assumes a heterogeneous surface of the adsorbent where the first layer of molecules is adsorbed followed by molecular condensation due to a strong adsorbate–adsorbate interaction [57]. The isotherm is described by the equation:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (8)$$

where q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium metal concentration in the solution (mg/L), k_f is Freundlich constant ($\text{mg}^{1-(1/n)} \text{L}^{(1/n)} / \text{g}$) related to the maximum adsorption capacity, and n is a dimensionless Freundlich constant related to the adsorbent surface heterogeneity. A closer value of $\left(\frac{1}{n}\right)$ to zero or a higher value of n indicate that the adsorbent surface is more heterogeneous [57]. Data fitting parameters for the adsorption of metal ions on AC, AGC, and APC using the Freundlich model are shown in Table 3.

The Freundlich isotherm did not fit either Cd^{2+} and Mn^{2+} , while it fitted both Cr^{6+} and Ni^{2+} for all activated carbons, with higher R^2 values for Cr^{6+} adsorption on AGC and APC. This is due to the higher affinity and favorable adsorption of Cr^{6+} to the bonded acid groups on AGC and APC surfaces, as indicated by their numerical values of n 2.79 and 2.45, respectively (higher than unity). The high values of n for Cr^{6+} isotherms on AGC and APC also indicate the increased surface heterogeneity with acid treatment.

3.3.3. The Dubinin–Kaganer–Radushkevich (DKR) Model

The DKR model is useful for describing gaseous adsorption on microporous activated carbon, mainly by the pore-filling mechanism [58,59]. It was used for modeling single heavy metal ion adsorption from aqueous solution by different adsorbents [33,60]. The DKR model is represented by the following equations:

$$\ln C_{ads} = \ln X_m - \beta \varepsilon^2 \quad (9)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (10)$$

$$E = \frac{1}{(2\beta)^{\frac{1}{2}}} \quad (11)$$

where C_{ads} is the number of ions adsorbed per unit weight of adsorbent (mol/g), β (mol²/J²) is the activity coefficient related to the mean sorption energy per mole of the adsorbate, and X_m (mol/g) is the saturation limit (theoretical monolayer sorption capacity) and may represent the sorbent's total specific micropore volume [61]. ϵ represents the Polanyi potential, where T is the absolute temperature (K), R is the universal gas constant (8.314 J/mol K), and C_e is the equilibrium concentration of a metal ion in the aqueous solution (mol/L). In Equation (11), E (J/mol) is the apparent adsorption energy per mole of the adsorbate when it is transferred from the bulk of the solution to the adsorbent surface [33,62].

The DKR model is used to specify the type of adsorption, physical or chemical, based on the magnitude of E ; $E < 8$ kJ/mol indicates that the adsorption is physical; $8 < E < 16$ kJ/mol indicates that the adsorption is by chemical ion exchange; and $E > 16$ indicates chemical adsorption, which is stronger than ion exchange [32,61–64]. Unlike the Langmuir model, the DKR isotherm does not assume that the adsorbent surface is homogeneous or that it has a constant sorption potential for different molecules [57].

DKR fitting for the tested metal ions is shown in Table 3. The model fitted Ni²⁺ and Cd²⁺ for AC with good R² values. The apparent adsorption energy, $8 < E < 16$ kJ/mol, indicated ion-exchange adsorption for Ni²⁺ and Cd²⁺ on AC, while for Cr⁶⁺, the energy value $E = 5.35$ ($E < 8$) kJ/mol showed physical adsorption to the AC surface. Finally, the DKR isotherm had a very poor fitting for Mn²⁺ on AC. These results are consistent with the order of percent removal by AC: Ni²⁺ > Cd²⁺ > Cr⁶⁺ > Mn²⁺, shown in Figure 3.

Acid treatment of the carbon surface (AGC and APC) resulted in the excellent fitting of the DKR isotherm for Cr⁶⁺ with an R² greater than 0.99, and the type of adsorption was by ion exchange on both types; $E = 12.5$ and 11.6 for AGC and APC, respectively. The model also fitted Ni²⁺ isotherms on AGC and APC but to a lesser extent than Cr⁶⁺ (less R²). Ni²⁺ on both AGC and APC is by physical adsorption, as indicated by its E values: 6.51 and 5.91 kJ/mol, respectively. However, the DKR isotherm did not fit either Cd²⁺ and Mn²⁺ for AGC and APC carbons.

4. Conclusions

Activated carbon is effective for the removal of heavy metal ions from an aqueous solution. The adsorption capacity is improved with surface modification and oxidation. However, most of the reported studies focused on a single or a binary metal ion adsorption from the solution. Therefore, gaps remain in understanding the effect of oxidized surface functional groups on the interaction and adsorption mechanisms of heavy metals from multiple ions solution. The purpose of this work is to bridge part of this gap by evaluating and modeling competitive adsorption of Ni²⁺, Cr⁶⁺, Mn²⁺, and Cd²⁺ on both activated carbon, AC, and acid-treated activated carbon in granular and powder forms, AGC and APC, respectively.

Oxidation of activated carbon influenced the competitive adsorption of heavy metal ions Ni²⁺, Cr⁶⁺, Mn²⁺, and Cd²⁺ from an aqueous solution. The adsorption capacity of oxidized activated carbon increased for Cr⁶⁺ but decreased for the ions Ni²⁺, Mn²⁺, and Cd²⁺. The high selectivity of Cr⁶⁺ over other present ions is due to its smaller size and higher ionic potential leading to a faster diffusion to the pores and a stronger attraction to the surface acidic groups. The faster adsorption of Cr⁶⁺ to the acidic groups will hinder the diffusion of other ions to the pores due to the allocation of these acidic groups at the edges of the pores. The Langmuir model did not fit the competitive adsorption of heavy metal ions on oxidized activated carbon since both its assumptions: a homogenous surface with equivalent energy and that there is no interaction between the adsorbed ions, are not valid for the heterogenous surface of AGC and APC. The Freundlich isotherm fitted Cr⁶⁺ and to a lesser extent, Ni²⁺, but not Mn²⁺ or Cd²⁺. The DKR model indicated physical adsorption of Cr⁶⁺ and ion exchange adsorption for Ni²⁺ and Cd²⁺ on AC. It changed to ion exchange for Cr⁶⁺ and physical adsorption for Ni²⁺ on AGC and APC. Mn²⁺ showed

the least attraction to the oxidized activated carbon. The results of this work can be used to tailor and modify adsorption processes for selective removal and separation of heavy metal ions from aqueous solutions based on the interaction of ions with surface functional groups and the differences in their sizes and ionic potential.

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References

- Patel, N.; Chauhan, D.; Shahane, S.; Rai, D.; Ali Khan, M.Z.; Mishra, U.; Chaudhary, V.K. Contamination and Health Impact of Heavy Metals. In *Water Pollution and Remediation: Heavy Metals*; Inamuddin, A.M.I., Lichtfouse, E., Eds.; Environmental Chemistry for a Sustainable World; Springer International Publishing: Cham, Switzerland, 2021; pp. 259–280, ISBN 978-3-030-52421-0.
- Jaramillo, J.; Gómez-Serrano, V.; Álvarez, P.M. Enhanced Adsorption of Metal Ions onto Functionalized Granular Activated Carbons Prepared from Cherry Stones. *J. Hazard. Mater.* **2009**, *161*, 670–676. [[CrossRef](#)] [[PubMed](#)]
- Obasi, P.N.; Akudinobi, B.B. Potential Health Risk and Levels of Heavy Metals in Water Resources of Lead–Zinc Mining Communities of Abakaliki, Southeast Nigeria. *Appl. Water Sci.* **2020**, *10*, 184. [[CrossRef](#)]
- Fallahzadeh, R.A.; Ghaneian, M.T.; Miri, M.; Dashti, M.M. Spatial Analysis and Health Risk Assessment of Heavy Metals Concentration in Drinking Water Resources. *Environ. Sci. Pollut. Res.* **2017**, *24*, 24790–24802. [[CrossRef](#)] [[PubMed](#)]
- Sharma, S.K. *Heavy Metals in Water: Presence, Removal and Safety*; Royal Society of Chemistry: London, UK, 2014; ISBN 978-1-78262-017-4.
- Alfvén, T.; Elinder, C.-G.; Hellström, L.; Lagarde, F.; Järup, L. Cadmium Exposure and Distal Forearm Fractures. *J. Bone Miner. Res.* **2004**, *19*, 900–905. [[CrossRef](#)] [[PubMed](#)]
- Järup, L.; Åkesson, A. Current Status of Cadmium as an Environmental Health Problem. *Toxicol. Appl. Pharmacol.* **2009**, *238*, 201–208. [[CrossRef](#)]
- Zhang, Y.; Chen, J.; Shi, W.; Zhang, D.; Zhu, T.; Li, X. Establishing a Human Health Risk Assessment Methodology for Metal Species and Its Application of Cr⁶⁺ in Groundwater Environments. *Chemosphere* **2017**, *189*, 525–537. [[CrossRef](#)]
- Das, N.; Mathew, L. Chromium Pollution and Bioremediation: An Overview. In *Biomangement of Metal-Contaminated Soils*; Springer: Berlin/Heidelberg, Germany, 2011; pp. 297–321.
- National Toxicology Program. *Report on Carcinogens*; U.S. Department of Health and Human Services, Public Health Service: Research Triangle Park, NC, USA, 2016.
- Das, K.K.; Reddy, R.C.; Bagoji, I.B.; Das, S.; Bagali, S.; Mullur, L.; Khodnapur, J.P.; Biradar, M.S. Primary Concept of Nickel Toxicity—An Overview. *J. Basic Clin. Physiol. Pharmacol.* **2018**, *30*, 141–152. [[CrossRef](#)]
- O’Neal, S.L.; Zheng, W. Manganese Toxicity Upon Overexposure: A Decade in Review. *Curr. Environ. Health Rep.* **2015**, *2*, 315–328. [[CrossRef](#)]
- Michalke, B.; Halbach, S.; Nischwitz, V. Speciation and Toxicological Relevance of Manganese in Humans. *J. Environ. Monit.* **2007**, *9*, 650–656. [[CrossRef](#)]
- Zhou, Q.; Yang, N.; Li, Y.; Ren, B.; Ding, X.; Bian, H.; Yao, X. Total Concentrations and Sources of Heavy Metal Pollution in Global River and Lake Water Bodies from 1972 to 2017. *Glob. Ecol. Conserv.* **2020**, *22*, e00925. [[CrossRef](#)]
- Xará, S.; Delgado, J.; Almeida, M.F.; Costa, C. Laboratory Study on the Leaching Potential of Spent Alkaline Batteries Using a MSW Landfill Leachate. *J. Mater. Cycles Waste Manag.* **2013**, *15*, 61–72. [[CrossRef](#)]
- Karnchanawong, S.; Limpitprakan, P. Evaluation of Heavy Metal Leaching from Spent Household Batteries Disposed in Municipal Solid Waste. *Waste Manag.* **2009**, *29*, 550–558. [[CrossRef](#)] [[PubMed](#)]
- Zhang, C.; Cai, X.; Xia, Z.; Jin, X.; Wu, H. Contamination Characteristics of Heavy Metals in a Small-Scale Tanning Area of Southern China and Their Source Analysis. *Environ. Geochem. Health* **2020**. [[CrossRef](#)] [[PubMed](#)]
- Soliman, N.K.; Moustafa, A.F. Industrial Solid Waste for Heavy Metals Adsorption Features and Challenges; a Review. *J. Mater. Res. Technol.* **2020**, *9*, 10235–10253. [[CrossRef](#)]
- Oruko, R.O.; Selvarajan, R.; Ogola, H.J.O.; Edokpayi, J.N.; Odiyo, J.O. Contemporary and Future Direction of Chromium Tanning and Management in Sub Saharan Africa Tanneries. *Process Saf. Environ. Prot.* **2020**, *133*, 369–386. [[CrossRef](#)]

20. Gotvajn, A.Ž.; Tišler, T.; Zagorc-Končan, J. Comparison of Different Treatment Strategies for Industrial Landfill Leachate. *J. Hazard. Mater.* **2009**, *162*, 1446–1456. [\[CrossRef\]](#)
21. Wang, S.; Kalkhajeh, Y.K.; Qin, Z.; Jiao, W. Spatial Distribution and Assessment of the Human Health Risks of Heavy Metals in a Retired Petrochemical Industrial Area, South China. *Environ. Res.* **2020**, *188*, 109661. [\[CrossRef\]](#)
22. Kadhum, S.A. A Preliminary Study of Heavy Metals Pollution in the Sandy Dust Storms and Its Human Risk Assessment from Middle and South of Iraq. *Environ. Sci. Pollut. Res.* **2020**, *27*, 8570–8579. [\[CrossRef\]](#)
23. Aghel, B.; Mohadesi, M.; Gouran, A.; Razmegir, M.H. Use of Modified Iranian Clinoptilolite Zeolite for Cadmium and Lead Removal from Oil Refinery Wastewater. *Int. J. Environ. Sci. Technol.* **2020**, *17*, 1239–1250. [\[CrossRef\]](#)
24. Salem, M.A.; Bedade, D.K.; Al-Ethawi, L.; Al-waleed, S.M. Assessment of Physiochemical Properties and Concentration of Heavy Metals in Agricultural Soils Fertilized with Chemical Fertilizers. *Heliyon* **2020**, *6*, e05224. [\[CrossRef\]](#)
25. Song, Y.; Li, H.; Li, J.; Mao, C.; Ji, J.; Yuan, X.; Li, T.; Ayoko, G.A.; Frost, R.L.; Feng, Y. Multivariate Linear Regression Model for Source Apportionment and Health Risk Assessment of Heavy Metals from Different Environmental Media. *Ecotoxicol. Environ. Saf.* **2018**, *165*, 555–563. [\[CrossRef\]](#)
26. Alvarez-Bastida, C.; Martínez-Miranda, V.; Solache-Ríos, M.; Linares-Hernández, I.; Teutli-Sequeira, A.; Vázquez-Mejía, G. Drinking Water Characterization and Removal of Manganese. Removal of Manganese from Water. *J. Environ. Chem. Eng.* **2018**, *6*, 2119–2125. [\[CrossRef\]](#)
27. Cerrato, J.M.; Reyes, L.P.; Alvarado, C.N.; Dietrich, A.M. Effect of PVC and Iron Materials on Mn(II) Deposition in Drinking Water Distribution Systems. *Water Res.* **2006**, *40*, 2720–2726. [\[CrossRef\]](#)
28. Li, W.; Gu, K.; Yu, Q.; Sun, Y.; Wang, Y.; Xin, M.; Bian, R.; Wang, H.; Wang, Y.; Zhang, D. Leaching Behavior and Environmental Risk Assessment of Toxic Metals in Municipal Solid Waste Incineration Fly Ash Exposed to Mature Landfill Leachate Environment. *Waste Manag.* **2021**, *120*, 68–75. [\[CrossRef\]](#)
29. Vongdala, N.; Tran, H.-D.; Xuan, T.D.; Teschke, R.; Khanh, T.D. Heavy Metal Accumulation in Water, Soil, and Plants of Municipal Solid Waste Landfill in Vientiane, Laos. *Int. J. Environ. Res. Public Health* **2019**, *16*, 22. [\[CrossRef\]](#)
30. Abu-Daibes, M.; Qdais, H.A.; Alsyouri, H. Assessment of Heavy Metals and Organics in Municipal Solid Waste Leachates from Landfills with Different Ages in Jordan. *J. Environ. Prot.* **2013**, *2013*, 344–352. [\[CrossRef\]](#)
31. Bolisetty, S.; Peydayesh, M.; Mezzenga, R. Sustainable Technologies for Water Purification from Heavy Metals: Review and Analysis. *Chem. Soc. Rev.* **2019**, *48*, 463–487. [\[CrossRef\]](#)
32. Lin, S.-H.; Juang, R.-S. Heavy Metal Removal from Water by Sorption Using Surfactant-Modified Montmorillonite. *J. Hazard. Mater.* **2002**, *92*, 315–326. [\[CrossRef\]](#)
33. Erdem, B.; Özcan, A.; Gök, Ö.; Özcan, A.S. Immobilization of 2,2'-Dipyridyl onto Bentonite and Its Adsorption Behavior of Copper(II) Ions. *J. Hazard. Mater.* **2009**, *163*, 418–426. [\[CrossRef\]](#)
34. Akar, S.T.; Sayin, F.; Yilmazer, D.; Akar, T. Removal of Cadmium and Manganese by an Ecofriendly Biomass. *CLEAN—Soil Air Water* **2016**, *44*, 202–210. [\[CrossRef\]](#)
35. Cao, F.; Lian, C.; Yu, J.; Yang, H.; Lin, S. Study on the Adsorption Performance and Competitive Mechanism for Heavy Metal Contaminants Removal Using Novel Multi-Pore Activated Carbons Derived from Recyclable Long-Root Eichhornia Crassipes. *Bioresour. Technol.* **2019**, *276*, 211–218. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Tran, T.N.; Kim, D.-G.; Ko, S.-O. Adsorption Mechanisms of Manganese (II) Ions onto Acid-Treated Activated Carbon. *KSCE J. Civ. Eng.* **2018**, *22*, 3772–3782. [\[CrossRef\]](#)
37. Mohan, D.; Chander, S. Single Component and Multi-Component Adsorption of Metal Ions by Activated Carbons. *Colloids Surf. A Physicochem. Eng. Asp.* **2001**, *177*, 183–196. [\[CrossRef\]](#)
38. Rivera-Utrilla, J.; Sánchez-Polo, M.; Gómez-Serrano, V.; Álvarez, P.M.; Alvim-Ferraz, M.C.M.; Dias, J.M. Activated Carbon Modifications to Enhance Its Water Treatment Applications. An Overview. *J. Hazard. Mater.* **2011**, *187*, 1–23. [\[CrossRef\]](#)
39. Liu, X.; Xu, X.; Dong, X.; Park, J. Competitive Adsorption of Heavy Metal Ions from Aqueous Solutions onto Activated Carbon and Agricultural Waste Materials. *Pol. J. Environ. Stud.* **2019**, *29*, 749–761. [\[CrossRef\]](#)
40. Berber-Mendoza, M.S.; Martínez-Costa, J.I.; Leyva-Ramos, R.; Amezcua Garcia, H.J.; Medellín Castillo, N.A. Competitive Adsorption of Heavy Metals from Aqueous Solution onto Oxidized Activated Carbon Fiber. *Water Air Soil Pollut.* **2018**, *229*, 257. [\[CrossRef\]](#)
41. Kavand, M.; Kaghazchi, T.; Soleimani, M. Optimization of Parameters for Competitive Adsorption of Heavy Metal Ions (Pb⁺², Ni⁺², Cd⁺²) onto Activated Carbon. *Korean J. Chem. Eng.* **2014**, *31*, 692–700. [\[CrossRef\]](#)
42. Coughlin, R.W.; Ezra, F.S. Role of Surface Acidity in the Adsorption of Organic Pollutants on the Surface of Carbon. *Environ. Sci. Technol.* **1968**, *2*, 291–297. [\[CrossRef\]](#)
43. Franz, M.; Arafat, H.A.; Pinto, N.G. Effect of Chemical Surface Heterogeneity on the Adsorption Mechanism of Dissolved Aromatics on Activated Carbon. *Carbon* **2000**, *38*, 1807–1819. [\[CrossRef\]](#)
44. Abu-Daibes, M.A.; Pinto, N.G. Effect of Surface Oxygen Complexes of Activated Carbon on Phenol Adsorption from Single and Mixed Non-Aqueous Solvents. *Sep. Sci. Technol.* **2004**, *39*, 2997–3009. [\[CrossRef\]](#)
45. Radovic, L.R.; Moreno-Castilla, C.; Rivera-Utrilla, J. Carbon Materials as Adsorbents in Aqueous Solutions. *Chem. Phys. Carbon* **2000**, *27*, 227–405.
46. Rivera-Utrilla, J.; Sánchez-Polo, M. Adsorption of Cr(III) on Ozonised Activated Carbon. Importance of C π —Cation Interactions. *Water Res.* **2003**, *37*, 3335–3340. [\[CrossRef\]](#)

47. Covelo, E.F.; Couce, M.L.A.; Vega, F.A. Competitive Adsorption and Desorption of Cadmium, Chromium, Copper, Nickel, Lead, and Zinc by Humic Umbrisols. *Commun. Soil Sci. Plant Anal.* **2004**, *35*, 2709–2729. [\[CrossRef\]](#)
48. Sposito, G. *The Chemistry of Soils*; Oxford University Press: Cambridge, MA, USA, 2008; ISBN 978-0-19-531369-7.
49. McBride, M.B. *Environmental Chemistry of Soils*; Oxford University Press: New York, NY, USA, 1994; ISBN 978-0-19-507011-8.
50. Iwanaga, M.; Yoshida, H.; Amano, Y.; Machida, M. Reduction of Cr(VI) Varying with the Surface Properties of Activated Carbon. *J. Environ. Chem.* **2013**, *23*, 19–23. [\[CrossRef\]](#)
51. Módenes, A.N.; Espinoza-Quñones, F.R.; Palácio, S.M.; Kroumov, A.D.; Stutz, G.; Tirao, G.; Camera, A.S. Cr(VI) Reduction by Activated Carbon and Non-Living Macrophytes Roots as Assessed by K β Spectroscopy. *Chem. Eng. J.* **2010**, *162*, 266–272. [\[CrossRef\]](#)
52. Shannon, R.D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767. [\[CrossRef\]](#)
53. Nightingale, E.R. Phenomenological Theory of Ion Solvation. Effective Radii of Hydrated Ions. *J. Phys. Chem.* **1959**, *63*, 1381–1387. [\[CrossRef\]](#)
54. Pauling, L. *The Nature of the Chemical Bond . . .*; Cornell University Press: Ithaca, NY, USA, 1960; Volume 260.
55. El-Khaiary, M.I. Least-Squares Regression of Adsorption Equilibrium Data: Comparing the Options. *J. Hazard. Mater.* **2008**, *158*, 73–87. [\[CrossRef\]](#)
56. Dhaouadi, F.; Sellaoui, L.; Reynel-Ávila, H.E.; Landín-Sandoval, V.; Mendoza-Castillo, D.I.; Jaime-Leal, J.E.; Lima, E.C.; Bonilla-Petriciolet, A.; Lamine, A.B. Adsorption Mechanism of Zn²⁺, Ni²⁺, Cd²⁺, and Cu²⁺ Ions by Carbon-Based Adsorbents: Interpretation of the Adsorption Isotherms via Physical Modelling. *Environ. Sci. Pollut. Res.* **2021**, *28*, 30943–30954. [\[CrossRef\]](#)
57. Al-Anber, M.A. Thermodynamics Approach in the Adsorption of Heavy Metals. In *Thermodynamics—Interaction Studies—Solids, Liquids and Gases*; Piraján, J.C.M., Ed.; IntechOpen Limited: London, UK, 2011; pp. 737–764, ISBN 978-953-307-563-1.
58. Dubinin, M.M.; Stoeckli, H.F. Homogeneous and Heterogeneous Micropore Structures in Carbonaceous Adsorbents. *J. Colloid Interface Sci.* **1980**, *75*, 34–42. [\[CrossRef\]](#)
59. Hutson, N.D.; Yang, R.T. Theoretical Basis for the Dubinin-Radushkevitch (D-R) Adsorption Isotherm Equation. *Adsorption* **1997**, *3*, 189–195. [\[CrossRef\]](#)
60. Igberase, E.; Osifo, P.; Ofomaja, A. The Adsorption of Pb, Zn, Cu, Ni, and Cd by Modified Ligand in a Single Component Aqueous Solution: Equilibrium, Kinetic, Thermodynamic, and Desorption Studies. *Int. J. Anal. Chem.* **2017**, *2017*, 1–15. [\[CrossRef\]](#) [\[PubMed\]](#)
61. Krishna, B.S.; Murty, D.S.R.; Jai Prakash, B.S. Thermodynamics of Chromium(VI) Anionic Species Sorption onto Surfactant-Modified Montmorillonite Clay. *J. Colloid Interface Sci.* **2000**, *229*, 230–236. [\[CrossRef\]](#) [\[PubMed\]](#)
62. Mobasherpour, I.; Salahi, E.; Pazouki, M. Comparative of the Removal of Pb²⁺, Cd²⁺ and Ni²⁺ by Nano Crystallite Hydroxyapatite from Aqueous Solutions: Adsorption Isotherm Study. *Arab. J. Chem.* **2012**, *5*, 439–446. [\[CrossRef\]](#)
63. Vijayaraghavan, K.; Padmesh, T.; Palanivelu, K.; Velan, M. Biosorption of Nickel(II) Ions onto Sargassum Wightii: Application of Two-Parameter and Three-Parameter Isotherm Models. *J. Hazard. Mater.* **2006**, *133*, 304–308. [\[CrossRef\]](#)
64. Wang, C.-C.; Juang, L.-C.; Lee, C.-K.; Hsu, T.-C.; Lee, J.-F.; Chao, H.-P. Effects of Exchanged Surfactant Cations on the Pore Structure and Adsorption Characteristics of Montmorillonite. *J. Colloid Interface Sci.* **2004**, *280*, 27–35. [\[CrossRef\]](#)

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