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KOH Treated Biochar: An Improved Material for the Removal of Aqueous Contaminants

By: Cody Layne

A Thesis,

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Acknowledgements

Firstly, I would like to thank Dr. Todd Mlsna for allowing me to conduct my undergraduate research in his laboratory for over a year and for helpfully advising me in matters, both academic and not, throughout my time at Mississippi State University. I would also like to thank my amazing graduate student, Amali Herath, for helping me to conduct and understand my research. I am also very appreciative of my thesis committee members for reviewing my work and providing their thoughts. Lastly, I am very grateful to Mississippi State University's Department of Chemistry for helping to fund, educate, and equip me to be able to complete this research.

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Chapter 1 Introduction

1.1 Background

Industrial processes such as chrome plating, the manufacture of dyes and pigments, leather and wood preservation, and the production of textiles all produce a large amount of hazardous waste which must be treated to remove its dangerous aqueous contaminants.[1] Chemical precipitation is one option to remove these contaminating molecules from industrial wastewaters, but this still leaves the issue of waste disposal and the fact that some pollutants are difficult to remove by this method.[2] One common prospect of contaminant removal is through adsorption on to substances such as peat, graphene, or activated carbon. However, activated carbon is quite expensive to produce on a realistic scale[2], peat has a characteristically low surface area[10], and graphene is also very expensive[11]. A promising, more economically sustainable alternative has quickly emerged as a cause of research for scientists known as biochar.

Biochar is the product of the pyrolysis of biomass in an oxygen-free environment, and it has been found to have many noteworthy uses in agriculture and environmental conservation research.[3] Biochar's unique chemical and physical properties have proven its exceptional ability to remove contaminants through sorption studies.[3] The carbon-rich functional groups present in biochar contributes to its high pH, negative charge, and the capacity for cation exchange and surface complexation useful in adsorbing metals.[12] Biochars have also been shown to contain mineral components including quartz, calcite, and sylvite which can also aid in metal sorption through electrostatic interactions and ion exchange.[12] More current investigations aim to modify the structure and surface of biochar to enhance its adsorptive properties, commonly through treatment with either acid or base.[4] Other types of modification processes have been studied using both chemical and physical methods, and many reports focus on maximizing biochar's potentials as a solution to remove harmful metal ions from waste or water purification.[4]

1.2 Modifications of Biochar

A variety of strong acids have been used to modify biochar which has been shown to aid in metal ion contaminant removal by adding acidic functional groups to the biochar surface such as carboxylic acids or alcohols.[4] The functional groups are believed to help biochar participate in surface complexation and cation exchange with aqueous metals.[4] Acid-modified biochar has shown adsorption capabilities of heavy metals comparable or even better than those of commercially available activated carbon.[4] Base activation of biochar, often with KOH and NaOH, has shown to increase surface basicity as well as tremendously increase pore size and surface area.[4] Maximizing the latter two parameters leads to greater sorption capacities in biochar.

1.3 Aqueous Contaminants

Common environmental contaminants including chromium, lead, rhodamine B, and cadmium were used in this study to evaluate the adsorptive abilities of two novel engineered biochars.

1.3.1 Chromium

This report studies a modified biochar's ability to remove chromium because it is a common industrial waste product which poses serious health problems. Chromium ions are common wastes from a variety of manufacturing processes including those listed above: chrome plating, the manufacture of dyes and pigments, leather and wood preservation, and the production of textiles.[1] Chromium is toxic, especially chromium (VI), as it is a known carcinogen and negatively affects the respiratory system.[5] Because of this toxicity, the American Water Works Association mandates that the maximum levels of chromium safely allowed in drinking water must not exceed 0.1 ppm.[6]

1.3.2 Lead

Pb(II) is known to be one of the most toxic elements to humans as it is a neurotoxin and causes cognitive disabilities.[7] Lead is also one of the most persistent toxic chemicals in the environment because it is not biodegradable.[7] Many industrial processes including mining, electro-plating, lead smelting, and metal-finishing industries produce significant amounts of lead in their waste.[8] Common techniques of water treatment such as reverse osmosis, filtration, sedimentation, coagulation, and flocculation to remove Pb^{2+} are neither environmentally nor economically sustainable because they produce large quantities of chemical and biological sludge, lead to the formation of metal hydroxides, and involve high energy consumption.[7]

1.3.3 Rhodamine B

Rhodamine B is another analyte used to study the adsorption capacities of the novel biochars produced for this study. Rhodamine B (RB) is a fluorescent-based xanthine dye which is very commonly used as a tracer in the pharmaceutical industry.[9] RB is also found in the wastewater of other industries including textile, leather, jute, and food processes.[10] Residual dyes in industrial wastewaters are the primary causes of color contamination.[10] Color in wastewater must be removed because it limits photosynthetic activity, hinders the growth of aquatic life, and can chelate with metal ions producing complexes which can be toxic to fish and other organisms.[10] Additionally, dye contamination as low as 1.0 ppm can cause coloring of drinking water, making it unpotable.[10]

1.3.4 Cadmium

Cadmium is toxic, and because it is non-biodegradable it will bioaccumulate through the food chain causing further problems.[13] Common industries which contribute to cadmium pollution through their wastes include mining and smelting, and other cadmium pollution sources include municipal sewage and agricultural products such as fertilizer and pesticides.[13] Many of the previously stated waste treatment process are also used to remove aqueous cadmium, but adsorption processes using biochar are particularly useful as they are relatively simple, environmentally friendly, and cost effective.[13]

Chapter 2 Materials and Methodology

2.1 Preparation of KOH Modified Biochar

Douglas-fir biochar (DFBC), donated by Biochar Supreme, was treated with KOH by soaking it in a solution made from KOH pellets dissolved in deionized (DI) water. The mixture was prepared in a ratio of 1 part untreated biochar, to four parts KOH pellets, to 5 parts DI water. The mixture was stirred for 1 hour, and then heated in a muffle furnace at 700 °C. The resulting modified biochar, KOH-BC, was washed until neutral pH and dried in an oven at 80 °C. The biochar was then ground and sieved into particle sizes between 0.1 and 0.5 mm. The DFBC being tested against the KOH-BC was also ground to this same particle size range.

2.2 Point of Zero Charge Analysis

The surface charge of both DFBC and the modified KOH-BC was determined through point of zero charge analysis. At this pH, the surface of the biochar exhibits zero net electric charge. 25 mg of biochar were placed in 25 mL of 0.01 M NaCl that was adjusted to pH values ranging from 2.0 to 10.0, using 0.1 M HCl or 0.1M NaOH. The biochar was mixed in these solutions in an orbital shaker for 24 hours and then filtered. The resulting filtrates' equilibrium pH after mixing was then tested and plotted against the initial solutions' pH to determine the point of zero charge of both biochars.

2.3 Thermogravimetric Analysis

Both DFBC and KOH-BC were studied through thermogravimetric analysis (TGA) to understand their respective thermal stabilities and decomposition temperatures. The analysis was carried out using a Mettler TGA/DSC thermogravimetric analyzer (TGA/DSC 1, STARe System, METTLER TOLEDO, USA) at a heating rate of 10 ℃/minute from 50 ℃ to 1,000 ℃ under an atmosphere of oxygen and nitrogen mixture (50 mL/minute).

2.4 Imaging Characterization of the Biochars

Characterization of both biochars was done to compare the changes in both elemental composition and surface level dimensions. The scanning electron microscope (SEM) images were obtained by coating the samples on a carbon stub attached to carbon tape and mounted into the JEOL sample holder. The samples were prepared for TEM analysis by mixing 10 mg of biochar with 0.5 mL of distilled water and sonicating for 2 minutes. One drop of this suspension was placed on the carbon film on a mesh copper grid the day before TEM and EDS analysis. The surface areas were examined by an N_2 BET, Micromeritics Tristar II Plus surface area analyzer. The N_2 adsorption isotherms were examined using the Dubinin-Astakhov equation to determine pore volume.

2.5 Chromium Removal

2.5.1 Chromium pH Studies

To determine the optimal solution pH for the biochar to remove chromium, potassium dichromate solutions at 50 ppm were adjusted to varying pH levels ranging from 2.0 to 11.0. 25 mL of each of these solutions was mixed with 25 mg of both DFBC and KOH-BC for 24 hours at room temperature (25 ℃). The biochars were then filtered out, and percentage removal of chromium ions was determined through UV-Vis spectrophotometry at wavelength 350 nm for both types of biochar.

2.5.2 Chromium Kinetic Studies

Once the ideal pH to remove the contaminant was discovered, solutions of 75, 100, and 150 ppm chromium were made and adjusted to the specific pH value for all further studies. 25 mg biochar was then placed in vials with 25 mL of the three solutions and mixed in the orbital shaker for varying times ranging from 3 minutes to 8 hours. Once the desired time of mixing was reached the samples were quickly filtered, and the adsorption capacity of chromium was tested for each type of biochar at every mixing time, again using UV-Vis analysis. The ideal mixing time was then determined and used for further studies.

2.5.3 Chromium Adsorption Studies

Lastly, the ideal chromium solution concentration and mixing temperature were determined through adsorption studies. 25 mg of the two types of biochar were mixed with a chromium solution at the previously determined ideal pH and mixing times, but this time concentrations were varied from 25 ppm to 400 ppm. This process was done at three different temperatures, adjusting mixing temperature from 25, 35, and 45 °C. The filtrates were again tested for remaining concentrations to determine both optimal solution concentration and temperature for percentage removal for both biochar types. Other studies have reported adsorption capacities for chromium using activated carbon of only about 8 mg/g, but KOH-activated biochar has proven to far exceed these results.

2.6 Lead Removal

2.6.1 Lead pH Studies

To determine the optimal solution pH for the biochar to remove lead ions, solutions of lead nitrate at 350 ppm were adjusted to varying pH levels ranging from 2.0 to 6.0. 25 mL of each of these solutions was mixed with 25 mg of both DFBC and KOH-BC for 24 hours at room temperature (25 °C). The biochars were then filtered out, and percentage removal of chromium ions was determined through AAS for both types of biochar.

2.6.2 Lead Kinetic Studies

Once the ideal pH to remove the contaminant was discovered, solutions of 100 ppm lead were made and adjusted to the specific pH value for all further studies. 25 mg of biochar were then placed in vials with 25 mL of the lead solution and mixed in the orbital shaker for varying times ranging from 3 minutes to 8 hours. Once the desired time of mixing was reached the samples were quickly filtered, and the adsorption capacity of lead was tested for each type of biochar at every mixing time, again using AAS analysis. The ideal mixing time was then determined and used for further studies.

2.6.3 Lead Adsorption Studies

Then, the ideal lead solution concentration and mixing temperature were determined through adsorption studies. 25 mg of the two types of biochar were mixed with a lead solution at the previously determined ideal pH and mixing times, but this time concentrations were varied from 25 ppm to 400 ppm. This process was done at three different temperatures, adjusting mixing temperature from room temperature (25 °C), to 35 °C, and 45 °C. The filtrates were again tested for remaining concentrations of lead to determine both optimal solution concentration and temperature for percentage removal for both biochar types.

2.7 Rhodamine B Removal

2.7.1 Rhodamine B pH Studies

To determine the optimal solution pH for the biochar to remove lead ions, solutions of the dye at 50 ppm were adjusted to varying pH levels ranging from 2.0 to 11.0. 25 mL of each of these solutions was mixed with 25 mg of both DFBC and KOH-BC for 24 hours at room temperature (25 ℃). The biochars were then filtered out, and percentage removal of chromium ions was determined through UV-Vis Spectrophotometry at wavelength 554 nm for both types of biochar.

2.7.2 Rhodamine B Kinetic Studies

Once the ideal pH to remove the contaminant was discovered, solutions of 50, 75, and 100 ppm were made and adjusted to the specific pH value for all further studies. 25 mg of biochar were then placed in vials with 25 mL of the three solutions and mixed in the orbital shaker for varying times ranging from 3 minutes to 8 hours. Once the desired time of mixing was reached the samples were quickly filtered, and the adsorption capacity of lead was tested for each type of biochar at every mixing time, again using UV-Vis analysis. The ideal mixing time was then determined and used for further studies.

2.7.3 Rhodamine B Adsorption Studies

Then, the ideal Rhodamine B solution concentration and mixing temperature were determined through adsorption studies. 25 mg of the two types of biochar were mixed with a

Rhodamine B solution at the previously determined ideal pH and mixing times, but this time concentrations were varied from 25 ppm to 400 ppm. This process was done at three different temperatures, adjusting mixing temperature from 25 ℃, to 35 °C, and 45 °C. The filtrates were again tested for remaining concentrations of dye to determine both optimal solution concentration and temperature for percentage removal for both biochar types.

2.8 Cadmium Removal

2.8.1 Cadmium pH Studies

To determine the optimal solution pH for the biochar to remove lead ions, solutions of cadmium nitrate tetrahydrate at 100 ppm were adjusted to varying pH levels ranging from 2.0 to 7.0. 25 mL of each of these solutions was mixed with 25 mg of both DFBC and KOH-BC for 24 hours at room temperature (25 ℃). The biochars were then filtered out, and percentage removal of cadmium ions was determined through AAS for both types of biochar.

2.8.2 Cadmium Kinetic Studies

Once the ideal pH to remove the contaminant was discovered, solutions of 25 ppm cadmium were made and adjusted to the specific pH value for all further studies. 25 mg of biochar were then placed in vials with 25 mL of the cadmium solution and mixed in the orbital shaker for varying times ranging from 3 minutes to 6 hours. Once the desired time of mixing was reached the samples were quickly filtered, and the adsorption capacity of cadmium was tested for each type of biochar at every mixing time, again using AAS analysis. The ideal mixing time was then determined and used for further studies.

2.8.3 Cadmium Adsorption Studies

Then, the ideal cadmium solution concentration and mixing temperature were determined through adsorption studies. 25 mg of the two types of biochar were mixed with a cadmium solution at the previously determined ideal pH and mixing times, but this time concentrations were varied from 50 ppm to 600 ppm. This process was done at three different temperatures, adjusting mixing temperature from 25 ℃ (room temperature), to 35 °C, and 45 °C. The filtrates were again tested for remaining concentrations of cadmium to determine both optimal solution concentration and temperature for percentage removal for both biochar type

Chapter 3 Results and Discussion

3.1 Biochar Characterizations

Table 1: Surface-structural differences in biochar before/after KOH treatment

Biochar	**Pore size (Å)**	**Pore volume (cm^3/g)**	**Surface area (m^2/g)**
DFBC	18.6	0.249	535
KOH-BC	25.6	0.672	1049

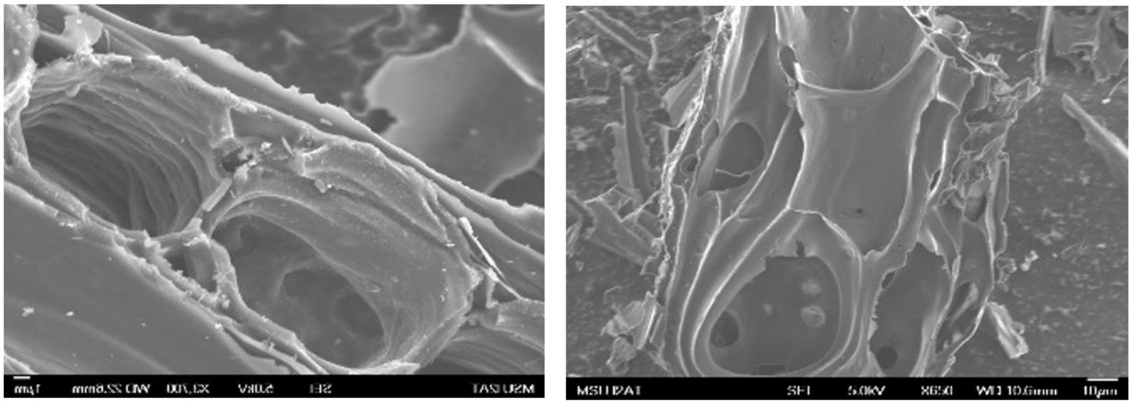


Figure 1: SEM images of DFBC

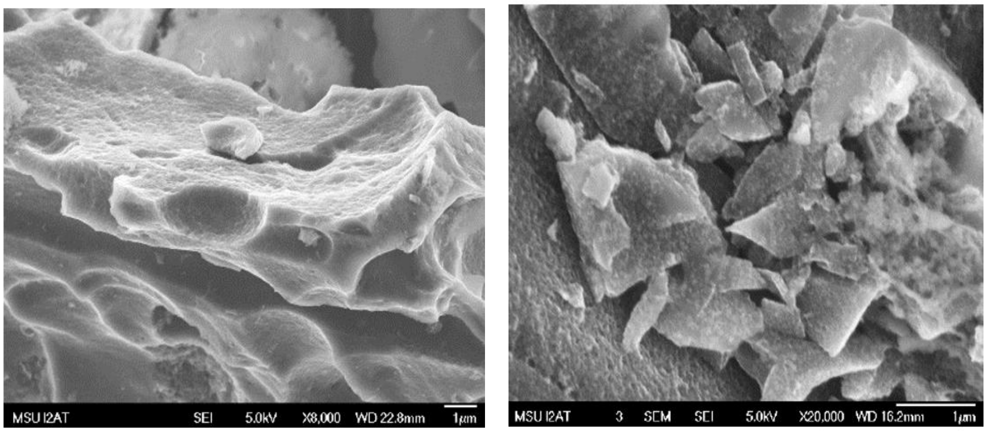


Figure 2: SEM images of KOH-BC

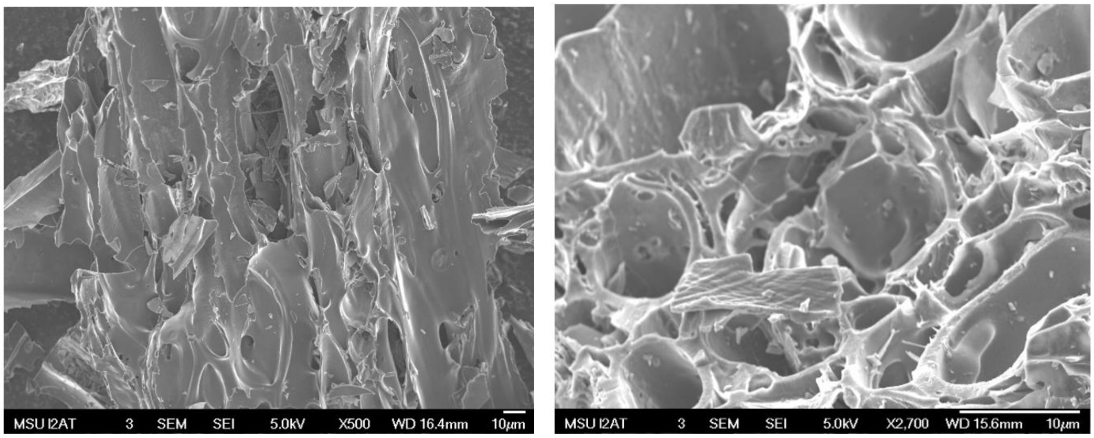


Figure 3: SEM images of KOH-BC and absorbed Chromium

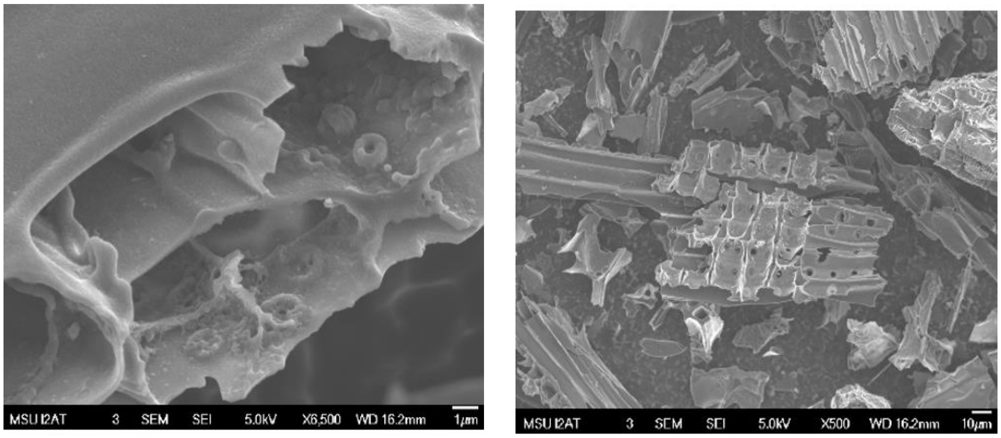


Figure 4: SEM images of KOH-BC and absorbed Lead

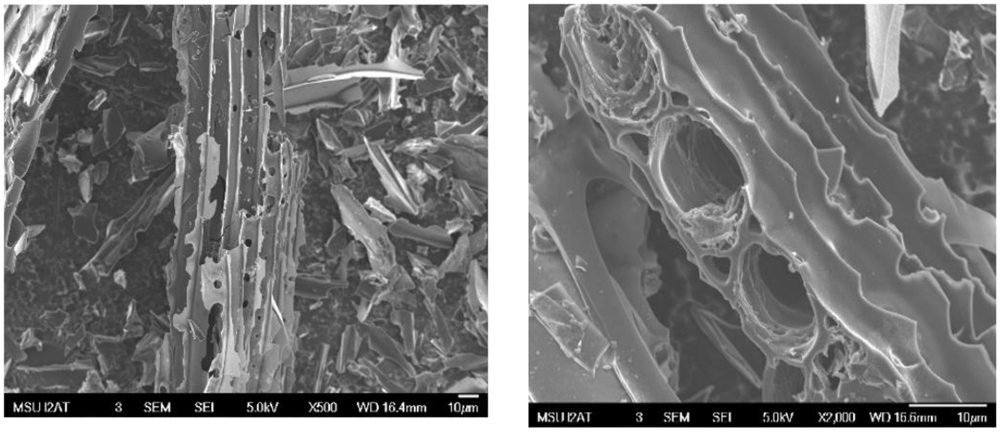


Figure 5: SEM images of KOH-BC and absorbed Rhodamine B

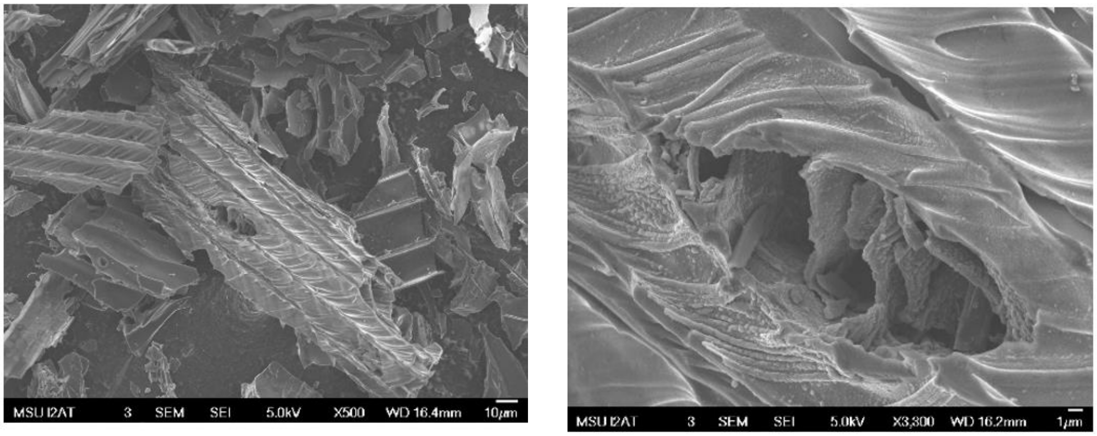


Figure 6: SEM images of KOH-BC and absorbed Cadmium

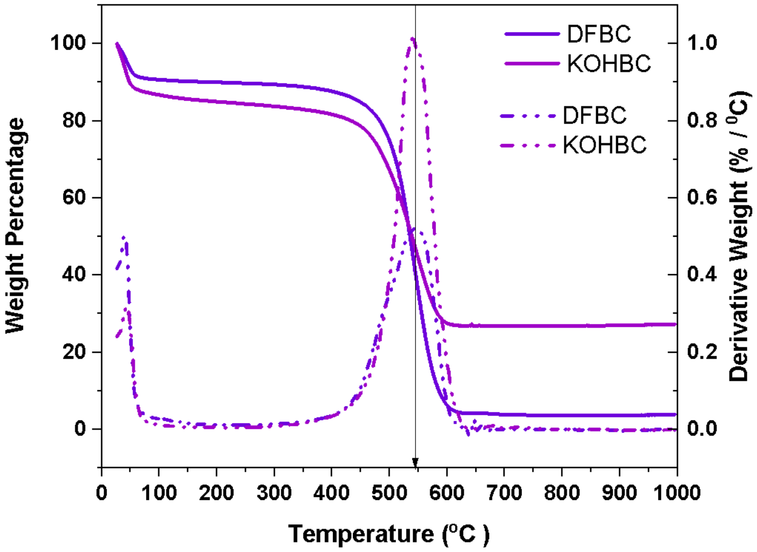


Figure 7: TGA results of DFBC and KOH-BC

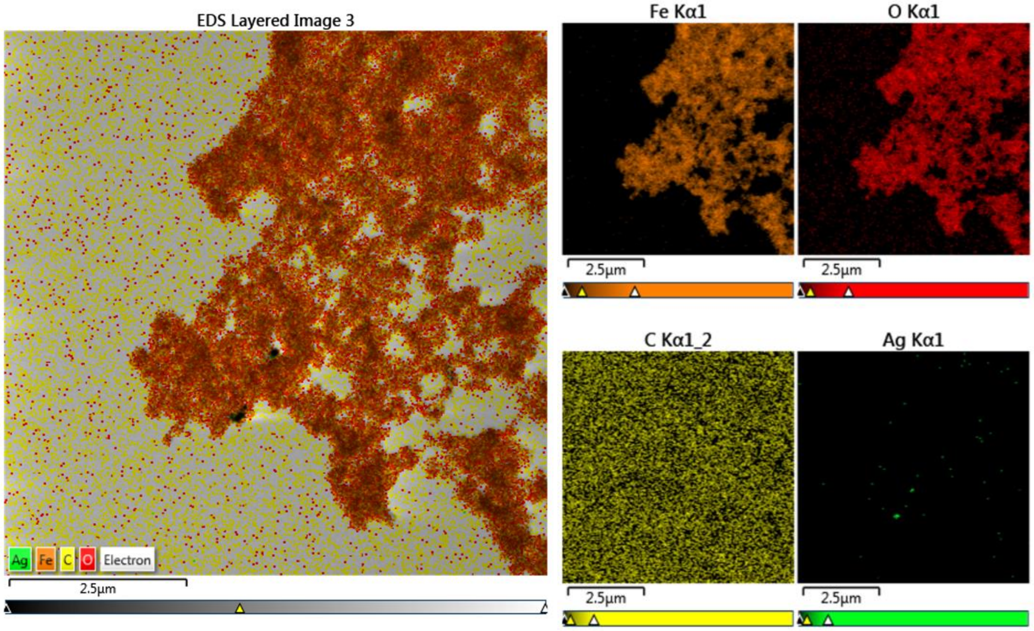
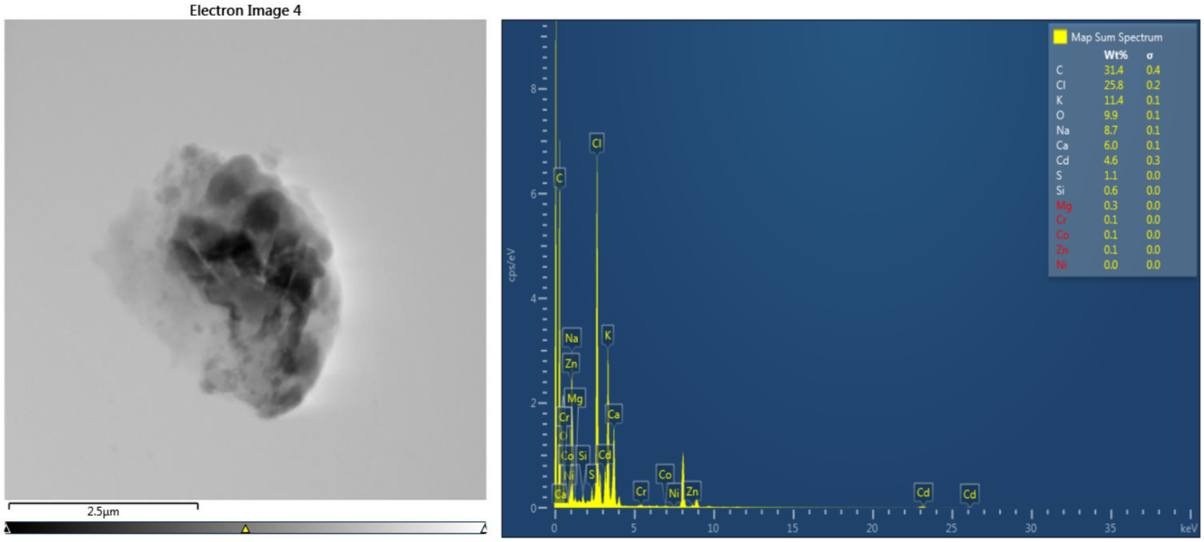


Figure 8: TEM images of elemental distribution DFBC



Map Sum Spectrum

	Wt%	σ
C	31.4	0.4
Cl	25.8	0.2
K	11.4	0.1
O	9.9	0.1
Na	8.7	0.1
Ca	6.0	0.1
Cd	4.6	0.3
S	1.1	0.0
Si	0.6	0.0
Mg	0.3	0.0
Cr	0.1	0.0
Co	0.1	0.0
Zn	0.1	0.0
Ni	0.0	0.0

Figure 9: TEM images of elemental distribution of KOH-BC

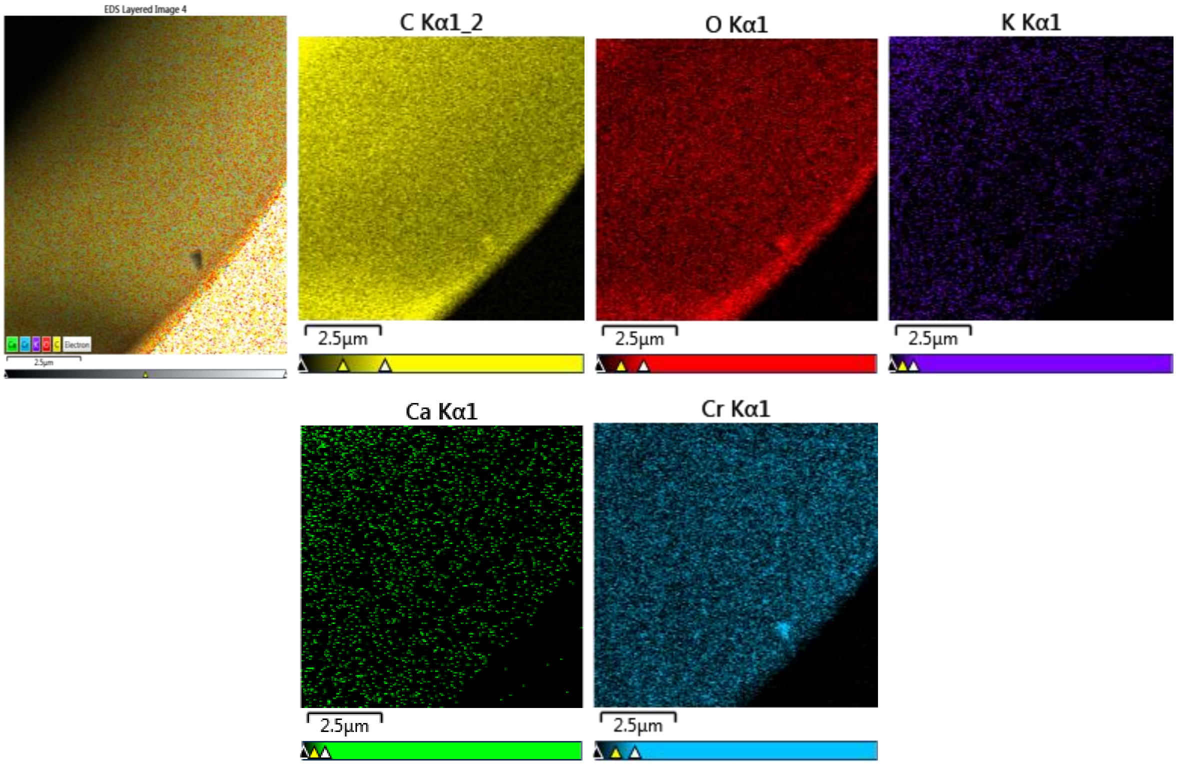


Figure 10: TEM images showing the elemental distribution of KOH-BC with absorbed Chromium

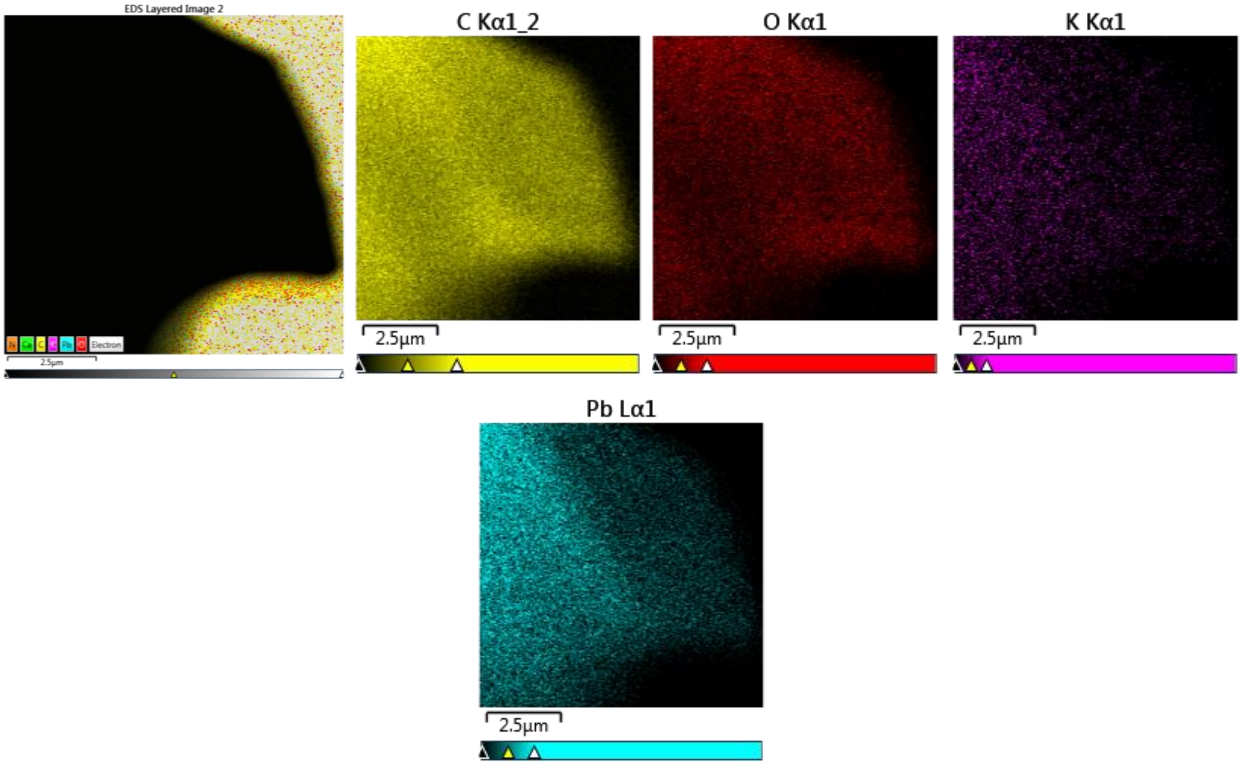


Figure 11: TEM images showing the elemental distribution of KOH-BC with absorbed Lead

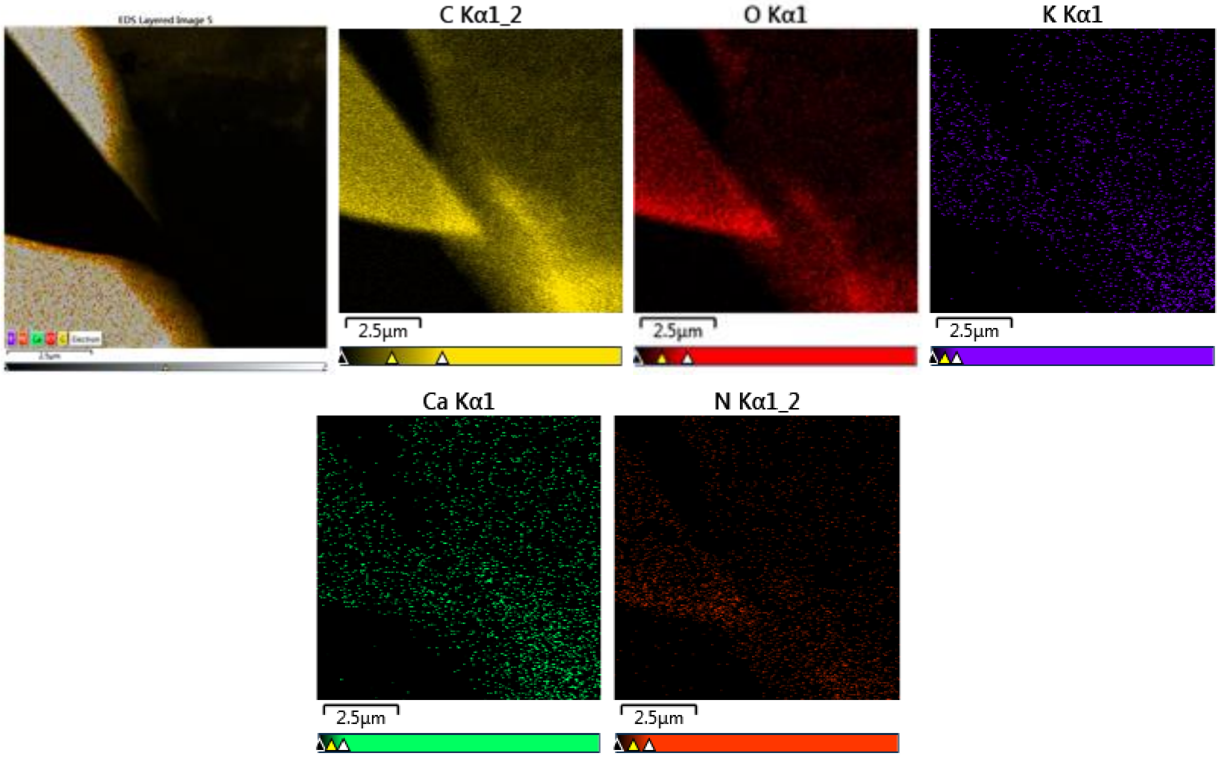


Figure 12: TEM images showing the elemental distribution of KOH-BC with absorbed Rhodamine B

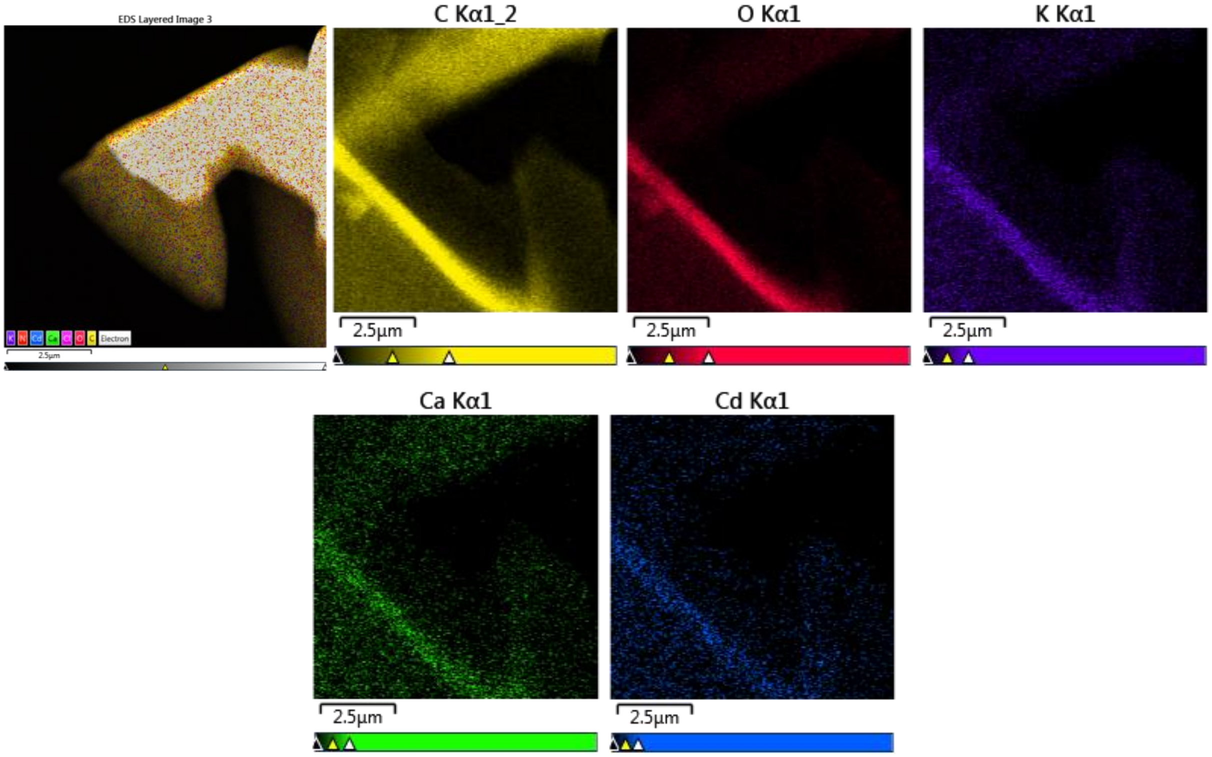


Figure 13: TEM images showing the elemental distribution of KOH-BC with absorbed Cadmium

Scanning electron microscope (SEM) images support that the KOH treatment drastically increases the surface porosity of the biochar. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) also confirmed that after KOH modification the biochar's weight percentage of potassium increased from negligible amounts to 11.4%. Thermogravimetric analysis revealed that both DFBC and KOH-BC decompose at the same temperature (approximately 550 °C). However, KOH-BC exhibited a greater thermal stability at higher temperatures than the untreated biochar, as less modified biochar decomposed as temperature was increased beyond 550 °C. The TEM images confirm that after mixing, the KOH-BC absorbed each of the contaminants from solution.

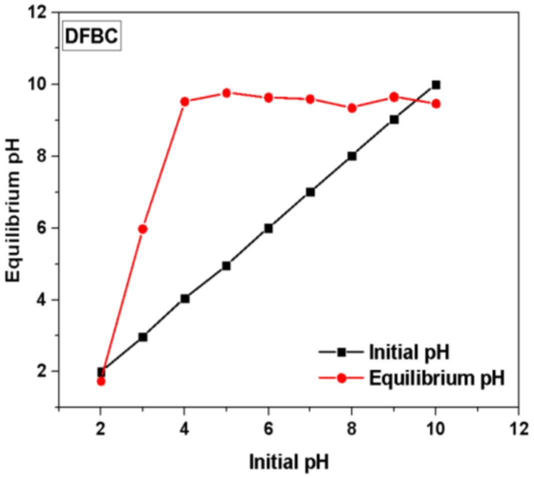


Figure 14: Point of zero charge data for DFBC, carried out in 0.01 M NaCl

As evidenced by the point at which the two lines intersect, the surface charge of DFBC is zero at about pH 9.5.

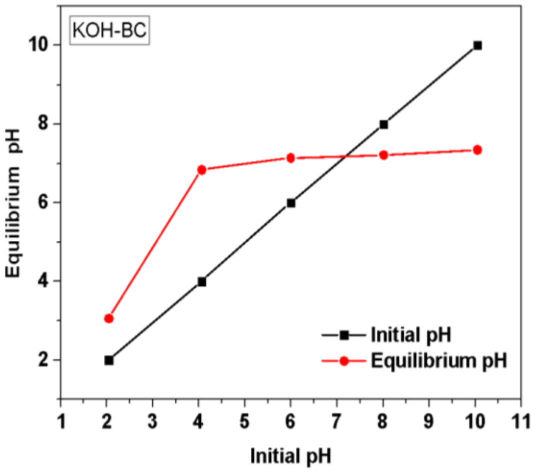


Figure 15: Point of zero charge data for KOH-BC, carried out in 0.01 M NaCl

Interestingly, the surface charge of the KOH modified biochar reaches zero at only about pH 7.25.

3.2 Chromium Removal

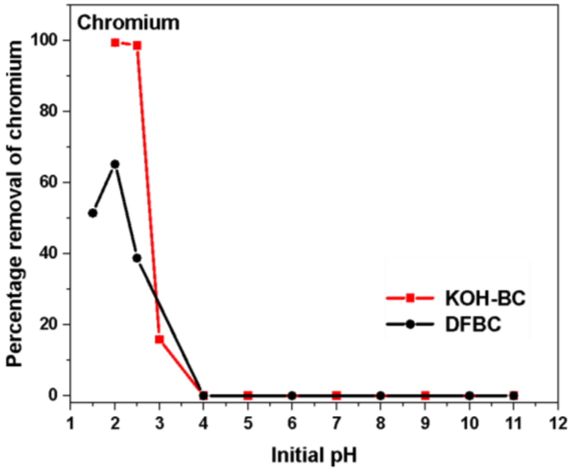


Figure 16: Percentage removal of chromium from 50 ppm Cr at increasing pH

As the initial chromium solution's pH increased from 2.0 to more basic pH values, the percentage removal of chromium (VI) ions drastically decreased to near zero for both KOH-BC and DFBC. While both types of biochar were best suited to remove chromium at low pH values, KOH-BC removed far more chromium than the untreated biochar (over 30% more removal at pH 2). From this data the optimal solution pH was identified as 2.0.

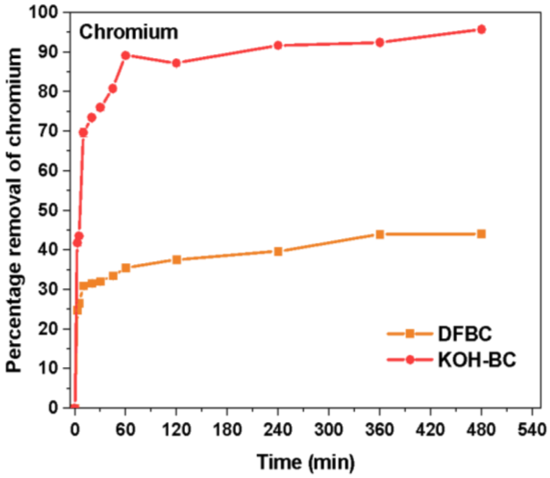


Figure 17: Percentage removal of Chromium with increasing mixing time from the kinetic studies

As the mixing time was increased from 3 minutes to 480 minutes the percentage removal of chromium first saw a sharp rise and then leveled off to a much more gradual increase over time. Again, at every time the KOH-BC consistently removed far more chromium from solution than DFBC (around 50% more ion removal). The optimal mixing time was chosen as 120 minutes as the KOH-BC was able to remove around 85% of the chromium ions by this point.

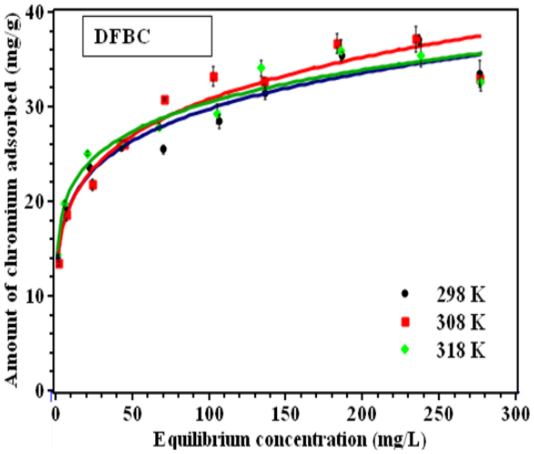


Figure 18: Average Chromium adsorption by DFBC with increasing concentration and temperature

As shown in the graph, as the chromium ion concentration was increased the amount of chromium adsorbed per gram of DFBC increased. Error bars shown are from three replicate samples. However, as temperature was increased from 298 K up to 318 K there was not a clear or notable increase in adsorption capability. Also, the DFBC adsorption data exhibited a Freundlich adsorption behavior which suggests multiple layers of ions adsorbing to the biochar.

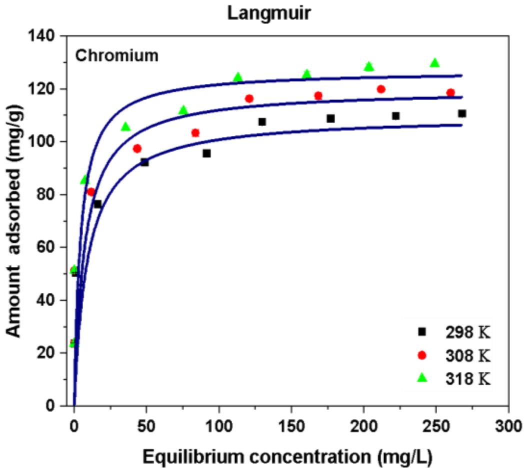


Figure 19: Average chromium adsorption by KOH-BC with increasing concentration and temperature (Langmuir model)

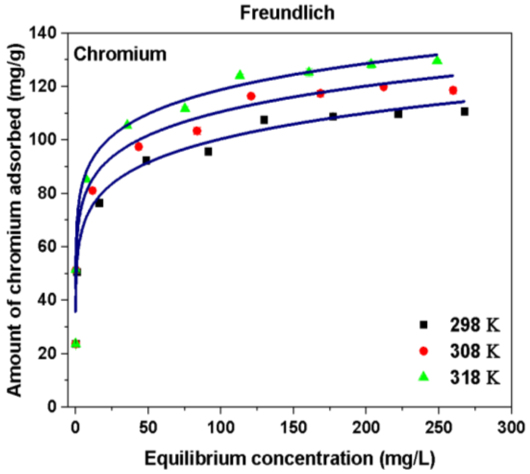


Figure 20: Average chromium adsorption by KOH-BC with increasing concentration and temperature (Freundlich model)

The KOH-BC exhibited linear relationships with both increasing temperature and ion concentration with increasing adsorption capacities. Error bars shown are from three replicate samples. Modifying the biochar caused the adsorption to clearly increase by relatively sizable amounts as temperature was increased. The KOH-BC also more closely exhibited a Freundlich model adsorption behavior, suggesting a multiple layers of ion adsorption.

Table 2: Chromium Adsorption Studies Data for Langmuir/Freundlich Isotherm Models

Analyte	**Adsorbent**	**Isotherm Parameters**		**Temperature**		
				298 K	308 K	318 K
Chromium	KOH-BC	Langmuir	Q° (mg/g)	113.7	120.1	127.2
			b	0.09	0.14	0.23
			R^2	0.99	0.92	0.91
	DFBC		Q° (mg/g)	28.1	32.5	33.5
			b	0.48	0.20	0.77
			R^2	0.97	0.99	0.98
	KOH-BC	Freundlich	K_f (mg/g)	54.5	63.5	70.1
			n	7.53	8.29	8.73
			R^2	0.99	0.99	0.99
	DFBC		K_f (mg/g)	12.5	14.4	16.2
			n	5.22	5.83	7.43
			R^2	0.99	0.98	0.99

3.3 Lead Removal

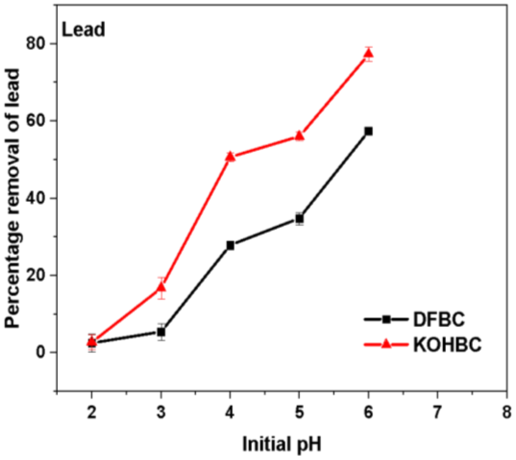


Figure 21: Percentage removal of Lead from 350 ppm Pb at increasing pH

As the initial lead solution's pH increased from 2.0 to less acidic pH values, the percentage removal of lead ions steadily increased from near zero for both KOH-BC and DFBC to respectable values. While both types of biochar were best suited to remove chromium at increasing pH values, KOH-BC removed far more chromium than the untreated biochar (around 20% more removal at pH 6). From this data the optimal solution pH was identified as 6.0.

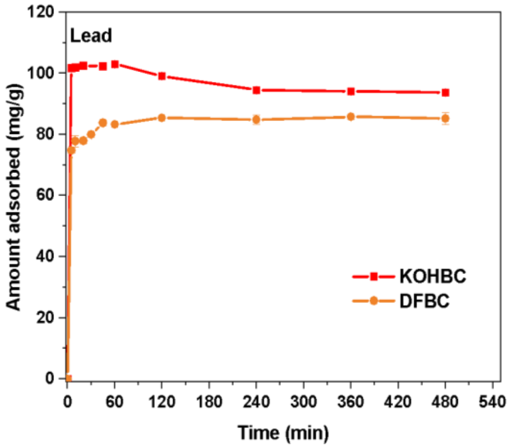


Figure 22: Lead adsorption with increasing mixing times from the kinetic studies

As the mixing time was increased from 3 minutes to 480 minutes the percentage removal of lead first saw a sharp rise and then reached a plateau. Again, at every time the KOH-BC consistently removed more chromium from solution than DFBC . The optimal mixing time was chosen as 60 minutes as the KOH-BC was able to adsorb around 20 more mg lead per gram of biochar than DFBC at this time.

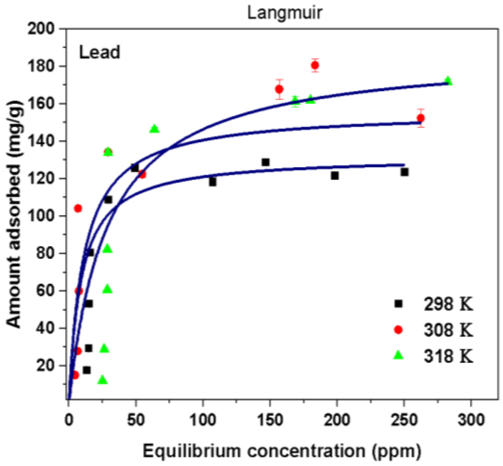


Figure 23: Average lead adsorption by KOH-BC with increasing concentration and temperature (Langmuir model)

The KOH-BC exhibited an increase in adsorption capacity with increasing ion concentration. As temperature increased the relationship towards adsorption of lead is less clear, but both the 35 ℃ and 45 ℃ trials adsorbed more than those at 25 ℃. Error bars shown are from three replicate samples. The KOH-BC with lead also more closely exhibited a Langmuir model adsorption behavior, suggesting a single layer of ion adsorption.

Table 3: Lead Adsorption Studies Data for Langmuir/Freundlich Isotherm Models

Analyte	**Adsorbent**	**Isotherm Parameters**		**Temperature**		
				298 K	308 K	318 K
Lead	KOH-BC	Langmuir	Q° (mg/g)	132.10	156.15	188.15
			b	0.11	0.09	0.04
			R^2	0.99	0.98	0.99
	DFBC		Q° (mg/g)	78.25	81.26	84.21
			b	0.20	0.21	0.19
			R^2	0.99	0.99	0.98
	KOH-BC	Freundlich	K_f (mg/g)	28.51	37.29	40.25
			n	3.41	3.49	3.51
			R^2	0.79	0.79	0.72
	DFBC		K_f (mg/g)	18.34	21.68	23.10
			n	3.48	3.88	4.12
			R^2	0.91	0.71	0.84

3.4 Rhodamine B Removal

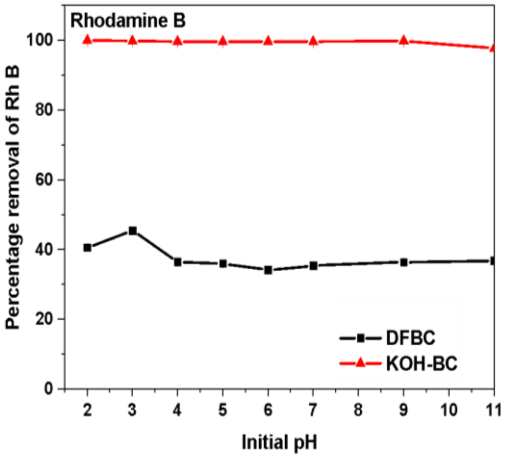


Figure 24: Percentage removal of Rhodamine B from 50 ppm Rh-B at increasing pH

As the initial Rhodamine B solution's pH increased from 2.0 to basic pH values, the percentage removal of Rhodamine B remained near 100 percent for KOH-BC and remained relatively close to 40 percent for DFBC. KOH-BC removed far more Rhodamine B than the untreated biochar (around 60% more removal at most pH values). From this data the optimal solution pH was identified as 2.0.

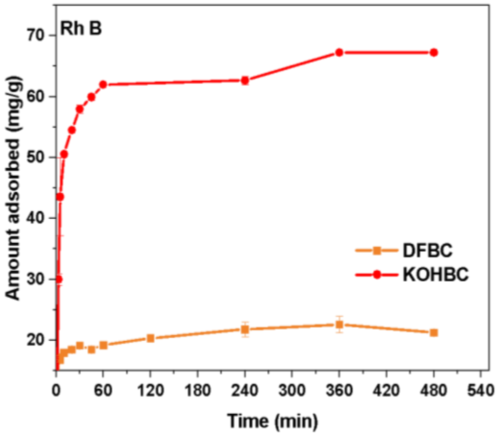


Figure 25: Rhodamine B adsorption with increasing mixing times from the kinetic studies

As the mixing time was increased from 3 minutes to 480 minutes the percentage removal of dye first saw a sharp rise and then leveled off to a much more gradual increase over time. Again, at every time the KOH-BC consistently removed far more Rhodamine B from solution than DFBC (over 40% more dye removal at one hour). The optimal mixing time was chosen as 240 minutes as the KOH-BC was able to remove around 65% of the Rhodamine B by this point.

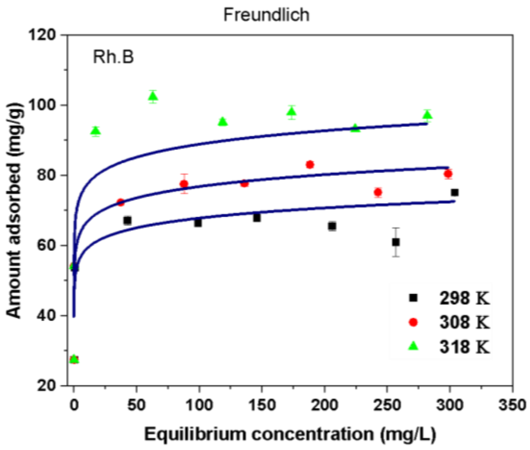


Figure 26: Average Rhodamine B adsorption by KOH-BC with increasing concentration and temperature (Freundlich model)

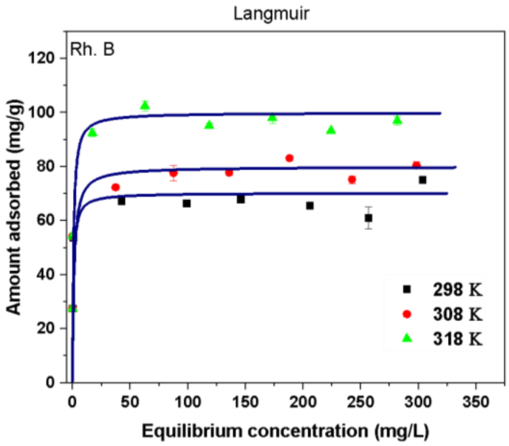


Figure 27: Average Rhodamine B adsorption by KOH-BC with increasing concentration and temperature (Langmuir model)

The KOH-BC exhibited linear relationships with both increasing temperature and ion concentration with increasing adsorption capacities towards Rhodamine B. Error bars shown are from three replicate samples. Modifying the biochar caused the adsorption to clearly increase by relatively sizable amounts as temperature was increased. The KOH-BC and DFBC also more closely exhibited a Langmuir model adsorption behavior, suggesting a single layer of dye adsorption.

Table 4: Rhodamine B Adsorption Studies Data for Langmuir/Freundlich Isotherm Models

Analyte	**Adsorbent**	**Isotherm Parameters**		**Temperature**		
				298 K	308 K	318K
Rhodamine B	KOH-BC	Langmuir	Q° (mg/g)	70.2	80.2	100.3
			b	1.26	0.75	1.21
			R^2	0.99	0.99	0.99
	DFBC		Q° (mg/g)	24.6	26.9	30.2
			b	0.27	0.23	0.15
			R^2	0.97	0.99	0.98
	KOH-BC	Freundlich	K_f (mg/g)	51.4	57.6	67.0
			n	16.53	16.03	16.31
			R^2	0.99	0.99	0.99
	DFBC		K_f (mg/g)	14.6	15.2	15.8
			n	9.94	9.27	9.11

			R^2	0.99	0.91	0.89

3.5 Cadmium Removal

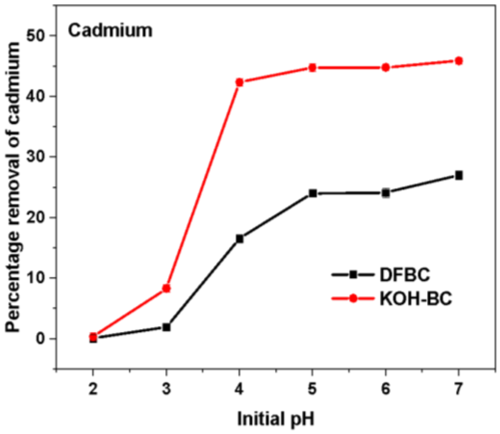


Figure 28: Percentage removal of Cadmium from 100 ppm Cd at increasing pH

As the initial cadmium solution’s pH increased from 2.0 to neutral pH values, the percentage removal of cadmium increased for both KOH-BC and DFBC. KOH-BC removed far more cadmium from solution than the untreated biochar (around 20% more removal at pH 6.0). From this data the optimal solution pH was identified as 6.0.

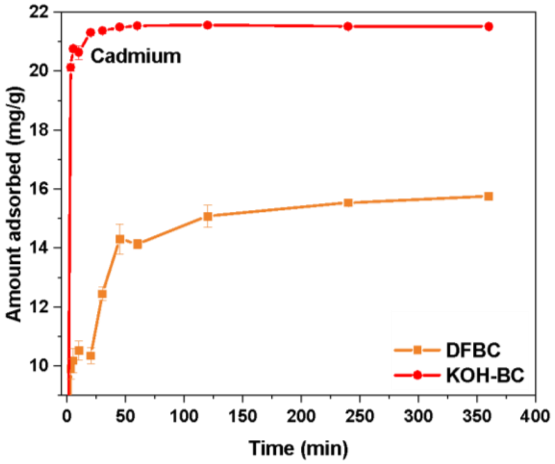


Figure 29: Cadmium adsorption with increasing mixing times from the kinetic studies

As the mixing time was increased from 3 minutes to 360 minutes the percentage removal of cadmium first saw a sharp rise and then plateaued. Again, at every time the KOH-BC consistently removed far more cadmium from solution than DFBC (around 7 more mg cadmium per gram of biochar than DFBC at one hour). The optimal mixing time was chosen as 60 minutes as the KOH-BC was able to remove around 21.5 mg of cadmium per gram of biochar by this point.

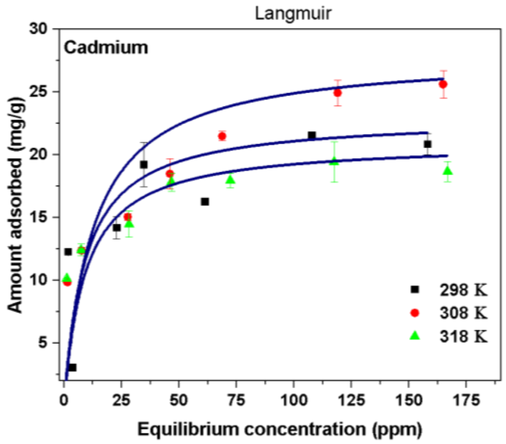


Figure 30: Average cadmium adsorption by KOH-BC with increasing concentration and temperature (Langmuir model)

The KOH-BC exhibited an increase in adsorption capacity with increasing ion concentration. However, as temperature increased the relationship towards adsorption of lead is less clear; the 35 °C trials adsorbed more than those at 45 °C or those at 25 °C. Error bars shown are from three replicate samples. The KOH-BC with cadmium also more closely exhibited a Langmuir model adsorption behavior, suggesting a single layer of ion adsorption.

Table 5: Cadmium Adsorption Studies Data for Langmuir/Freundlich Isotherm Models

Analyte	**Adsorbent**	**Isotherm Parameters**		**Temperature**		
				298 K	308 K	318 K
Cadmium	KOH-BC	Langmuir	Q° (mg/g)	23.25	29.00	19.14
			b	0.18	0.18	0.18
			R^2	0.99	0.99	0.99
	DFBC		Q° (mg/g)	25.66		
			b	0.15		
			R^2	0.99		
	KOH-BC	Freundlich	K_f (mg/g)	6.99	7.75	9.75
			n	4.39	4.25	7.27
			R^2	0.97	0.98	0.98
	DFBC		K_f (mg/g)	7.71		
			n	3.70		

			R^2	0.81		

Chapter 4 Conclusions

KOH treated biochar has proven to be much more effective at removing harmful wastes such as chromium (VI), lead, Rhodamine B, and cadmium from solution than untreated commercial biochar. Imaging and microscopy techniques showed that the KOH treatment increased the biochar's surface area and porosity. Thermogravimetric analysis suggests the modification process also improves the biochar's thermal stability. Point of zero charge analysis reveals that the net surface charge of the biochar reaches zero at a lower pH after KOH treatment. Multiple mechanisms including electrostatic interactions, cation replacement, and hydrogen bonding are likely involved in the adsorption of the different analytes tested in this study. Batch sorption studies showed that under a variety of different conditions KOH-BC had a much higher adsorption capacity than DFBC for chromium, lead, rhodamine B and cadmium. The conditions found to maximize chromium adsorption by KOH-BC were at pH 2.0, 120 minutes of mixing, and maximized solution concentration and mixing temperature. The conditions found to maximize lead adsorption by KOH-BC were at pH 6.0, 60 minutes of mixing, and maximized solution concentration. The conditions found to maximize Rhodamine B adsorption by KOH-BC were at pH 2.0, 240 minutes of mixing, and maximized solution concentration and mixing temperature. The conditions found to maximize cadmium adsorption by KOH-BC were at pH 6.0, 60 minutes of mixing, and maximized solution concentration. The relationships between adsorption of lead and cadmium with increasing mixing temperatures were inconclusive and may require further analysis. Further studies are also required to determine the KOH-BC's thermodynamic parameters.

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