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Adsorption of Malachite Green and Pb^{2+} by KMnO_4 -Modified Biochar: Insights and Mechanisms

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Abstract: In this study, the feasibility and mechanism of Pb^{2+} and malachite green (MG) adsorption from wastewater using KMnO_4 -modified bamboo biochar (KBC) was evaluated. The KBC was characterized by SEM-EDS, XRD, FTIR and XPS. The adsorption results for Pb^{2+} conformed to pseudo-second-order kinetics and the Langmuir model theory. Unlike the case for Pb^{2+} , the Freundlich model better described the adsorption behaviour of MG, indicating that adsorption occurred within multiple molecular layers. Both pseudo-first-order kinetics and pseudo-second-order kinetics fit the MG adsorption data well, indicating that physical adsorption was involved in the adsorption process. In addition, the maximum adsorption capacity for Pb^{2+} /MG was $123.47/1111.11 \text{ mg} \cdot \text{g}^{-1}$, KBC had high adsorption capacities for Pb^{2+} and MG, and the mechanisms of Pb^{2+} adsorption were mineral precipitation, functional group complexation, and cation- π interactions, while the main mechanisms for MG adsorption were pore filling, π - π interactions, and functional group complexation. In this study, KMnO_4 -modified biochar was prepared and used as an efficient adsorbent, and showed good application prospects for treatment of wastewater containing MG and Pb^{2+} .

Keywords: bamboo biochar; KMnO_4 modified; MG; Pb^{2+} ; adsorption mechanism

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1. Introduction

With the rapid development of industrial and agricultural modernization, pollution from heavy metals and organic wastewater has become increasingly serious [1]. As a heavy metal pollutant, Pb wastewater has the characteristics of persistence, nondegradation, and high toxicity [2]. In addition, Malachite Green is a common dye and a controversial antibacterial agent used in aquaculture which acts on the immune system and reproductive system of the human body, causing irreversible damage to human health [3]. These two types of wastewater pose serious threats to the ecological environment as well as to human survival and development. Therefore, pollution from Pb and MG wastewater urgently needs to be controlled.

Common wastewater treatment methods include electroflocculation [4], ion exchange [5], and membrane separation [6]. These methods often have disadvantages, such as high application costs, long treatment cycles, and low efficiencies. Adsorption is the main method used to reduce the content of pollutants in wastewater because of its high efficiency, simple operation, and low cost [7]. Hypercrosslinked cyclodextrin networks [8], Hydrogels [9], carbon balls [10], and biochar are commonly used sorbents. Among them, Biochar is considered to be a good adsorbent material because of its large specific surface area, abundant oxygen-containing surface functional groups, developed pore structure, and high stability [11]. However, the variability of biomass materials and preparation conditions leads to biochar having different pollutant adsorption effects. In comparing the adsorption performance of banana straw and cassava

straw biochar prepared at different carbonization temperatures, Li et al. [12] found that the adsorption capacity of banana straw biochar for Cd^{2+} was much higher than that of cassava straw biochar, and 500 °C was used as the optimum pyrolysis temperature. To improve the adsorption performance of biochar, Ding et al. [13] modified hickory shell biochar with NaOH and realized good selective adsorption and preferential adsorption of Pb^{2+} and Cu^{2+} in a mixed system. Sun et al. [14] used citric acid and oxalic acid to modify eucalyptus biochar with carboxyl functional groups and showed that the maximum adsorption capacity of citric acid-modified carboxylated biochar for methylene blue was $178.5 \text{ mg}\cdot\text{g}^{-1}$. Lu et al. [15] found that loading manganese oxides onto rice straw biochar significantly improved the adsorption of Cu^{2+} and Zn^{2+} , and that the main adsorption mechanisms were complexation and cation- π interactions. Modification of biochar using different techniques can improve such properties of biochar as specific surface area, surface charge, and functional group and pore distribution, which can enhance its capacity for adsorption of pollutants [16]. It has been shown that loading with metal oxides can lead to a larger specific surface area and more active groups, allowing biochar to adsorb pollutants through redox, complexation, and coprecipitation [17–19]. Loading metal oxides (Fe oxides, Mg oxides, Mn oxides, Al oxides, Ti oxides, etc.) onto biochar significantly enhances its adsorption capacity [20]. Jiang et al. [21] showed that manganese oxides exhibited outstanding immobilization potential, good stability after loading, and very low manganese leaching without secondary contamination. KMnO_4 is a strong oxidant commonly used in the water treatment process. It degrades pollutants without secondary pollution, and eventually converts to manganese dioxide through reduction [22]. Pang et al. [23] modified biochar by KMnO_4 and simulated a wastewater environment by adding metal ions such as K^+ , Ca^{2+} , Na^+ and Mg^{2+} , and proved that KMnO_4 -modified biochar has good adsorption performance for heavy metals. Li et al. [24] studied the adsorption of malachite green by KMnO_4 -modified rice straw biochar and discussed the influence of different reaction conditions on the adsorption effect. The above studies showed that the preparation process of KMnO_4 -modified biochar is simple and that the adsorption performance is improved significantly. However, the adsorption performance of biochar in composite systems is rarely reported. Therefore, the adsorption effect and mechanism of KMnO_4 biochar on pollutants in the composite system requires further study.

China has the richest bamboo resources and the largest bamboo forest area in the world, with 6.412 million hm^2 and a reserve of approximately 14 billion plants. While bamboo exhibits good utility in landscaping, building materials, and fibre garments, the level of processing and utilization of bamboo timber is low [25]. Bamboo waste is generally discarded or used as fuel, which causes a waste of resources and serious pollution of the environment. Therefore, in this study we consulted previous studies [26,27] in proposing the preparation of biochar from waste bamboo by oxygen-limited pyrolysis, through which both effective adsorption of organics and heavy metals and utilization of bamboo waste resources can be achieved.

The objectives of this study were to (1) prepare KMnO_4 -modified bamboo biochar as an adsorbent and investigate the effects of solution concentration, pH value, reaction time, coexisting ion strength and reuse times on MG and Pb^{2+} adsorption; and (2) investigate the adsorption mechanism by combining characterization techniques such as SEM–EDS, XRD, XPS, and FTIR in order to provide a theoretical basis for utilization of bamboo biochar for treatment of heavy metals and organic wastewater.

2. Materials and Methods

2.1. Preparation of Biochars

Bamboo biochar (BC) was purchased from Guilin Farmers' Market. The bamboo biochar was crushed and passed through a 0.054 mm screen, washed with $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl, dried, and set aside.

For KMnO_4 -modified biochar (KBC), BC was mixed with $0.33 \text{ mol}\cdot\text{L}^{-1}$ KMnO_4 solution in a conical flask at a solid–liquid ratio of 1:10, sonicated for 10 min, transferred to a

shaker, and shaken at 50 °C for 240 min. Finally, the residue was washed with distilled water until the pH was nearly neutral, filtered, and dried.

2.2. Characterization of the Biochars

The surface morphological features of the biochar were observed using an FEI Inspect F5 field emission scanning electron microscope (SEM, FEI Quanta 200; Thermo Fisher Scientific; Eindhoven, The Netherlands) at a magnification of 500–40,000 $\times$ and an acceleration voltage of 20 kV for the electron beam; elemental compositions were analysed by EDS. A Bruker D8 Advance X-ray diffractometer (XRD, Bruker D8 Advance; Bruker AXS Corporation; Karlsruhe, Germany) was used to scan the biochar at angles of 10–60° and with a speed of 8°/min in order to determine the crystalline structure. Fourier transform spectroscopy (FTIR, Nicolet, Magna550; Thermo Fisher Scientific; Bedford, MA, USA) was used to measure the characteristic functional groups on the surface of the biochar over the wavenumber range 400–4000 cm^{−1}. The binding energies and chemical oxidation states of C, O, N and Pb in the samples were analysed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi, Thermo Fisher Scientific; Bedford MA America). For determination of zero charge (pH_{PZC}) [28], a 0.1 mol·L^{−1} NaCl solution was prepared; 50 mL was placed in a conical flask, the pH was adjusted to 2–12 with 0.1 mol·L^{−1} NaOH and HCl, 0.1 g of KBC was added, and the mixture was shaken in a thermostatic shaker at 25 °C and 150 rpm for 24 h. The final pH (pH_{Final}) values of solutions were measured and plotted against the initial pH to obtain the point of zero charge.

2.3. Adsorption Experiments

All adsorption experiments were carried out in 100 mL stoppered conical flasks. The pH experiments were performed as follows: the pH of MG (1000 mg·L^{−1}) and Pb²⁺ (300 mg·L^{−1}) solutions were adjusted to 2–7 with 0.1 mol·L^{−1} NaOH and HCl, 0.1 g of KBC was added to 50 mL of the above solutions, the resulting solution was shaken at 25 °C and 150 rpm for 360 min, and the adsorption capacity and removal rate were calculated with Equations (1) and (2) after filtration. The adsorption isotherm experiment is an important index with which to evaluate the performance of the adsorbent; the procedure was as follows: 100–1000 mg·L^{−1} MG solution and 50–500 mg·L^{−1} Pb²⁺ solutions were prepared and 0.1 g of KBC was added to 50 mL of the above solutions. The resulting solutions were shaken at different temperatures (25, 35 and 45 °C) for 360 min, then the concentration of the filtrate was measured and the adsorption capacity was calculated. Adsorption isotherms were fitted using the Langmuir model (3), Freundlich model (4), Sips model (5), and Peterson model (6). Adsorption kinetic experiments were the main reference for analysing adsorption saturation times. Briefly, solutions with different concentrations of MG (600, 800, 1000 mg·L^{−1}) and Pb²⁺ (300, 400, 500 mg·L^{−1}) were prepared, 0.1 g of KBC was added to 50 mL of the above solution and shaken at 25 °C and 150 rpm, and the filtrate was collected at different time points (5–360 min). The samples were filtered at 25 °C and 150 rpm, the concentration of pollutants in the filtrate was measured, and the adsorption capacity was calculated. The experimental adsorption kinetic data were fitted using pseudo-first-order [29] (7) and pseudo-second-order [30] (8) models. Cycling experiments were performed according to the results of previous experiments. Briefly, 200 mg·L^{−1} Pb²⁺ and MG solutions and mixed solutions of Pb²⁺ and MG (both at concentrations of 200 mg·L^{−1}) were prepared, 0.1 g of KBC was added to 50 mL of the above solutions, they were shaken for 360 min at 25 °C and 150 rpm, and the filtrate was removed to determine the concentration. The remaining filtrate was collected by a 0.45 μ m filter membrane, and the adsorbent was collected and desorbed with 0.1 mol·L^{−1} NaOH solution, dried and prepared for use. The above experimental operation was repeated, and reusability was measured. In general, wastewater in natural systems contains a variety of coexisting ions; thus, interference experiments with coexisting ions are very important. Interference ions (K⁺, Ca²⁺, Na⁺, Mg²⁺) with concentrations of 0, 10 and 25 mmol·L^{−1} were added to Pb²⁺ (200 mg·L^{−1}) and MG (800 mg·L^{−1}) solutions, respectively, and 0.1 g

of KBC was added to 50 mL of the above solutions, shaken for 360 min at 25 °C and 150 rpm, filtered to measure the Pb^{2+} and MG concentrations, and the adsorption capacity was calculated. The concentration of MG was determined by UV spectrophotometry at a wavelength of 618 nm, and the concentration of Pb^{2+} was determined by flame atomic absorption spectrometry. All experiments were performed in triplicate, and the standard errors were less than 5%.

$$p = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

$$Q = \frac{(C_0 - C_t) \times v}{m} \quad (2)$$

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$Q_e = K_F C_e^{1/n} \quad (4)$$

$$Q_e = \frac{Q_m (K_{RP} C_e)^{n_s}}{1 + (K_{RP} C_e)^{n_{PR}}} \quad (5)$$

$$Q_e = \frac{Q_m (K_{RP} C_e)}{1 + (K_{RP} C_e)^{n_{PR}}} \quad (6)$$

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (7)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (8)$$

where p is the removal rate for pollutant per unit mass of adsorbent, t is the adsorption time in minutes, m is the dosage of adsorbent in g, v is the volume of solution in mL, Q is the adsorption capacity per unit mass of adsorbent, Q_t is the adsorption capacity at time t , Q_e is the theoretical saturation adsorption capacity in $\text{mg} \cdot \text{g}^{-1}$, C_0 is the mass concentration before adsorption, C_t is the mass concentration at time t , C_e is the concentration at adsorption equilibrium in $\text{mg} \cdot \text{L}^{-1}$; K_F and n are Freundlich constants related to adsorption capacity and intensity, K_{PR} (L/mg) is the affinity constant, and n_s describes the surface heterogeneity. K_L is the Langmuir isotherm constant related to the free energy of adsorption ($\text{mg} \cdot \text{L}^{-1}$), while K_1 (min^{-1}) and K_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are the equilibrium rate constants of the pseudo-first-order model and the pseudo-second-order model, respectively.

3. Results and Discussion

3.1. Effect of pH

The pH of any adsorption system has a significant impact on the surface characteristics of the adsorbent as well as on the ionization and speciation of the adsorbate. Changes in the initial solution pH significantly affected MG and Pb^{2+} adsorption onto KBC. Figure 1a shows the pH_{PZC} of BC and KBC; pH_{PZC} refers to the pH value when the surface charge number of biochar is zero. After calculation, the pH_{PZC} of BC and KBC is 7.42/7.78, respectively. In the pH 2–3 range, the adsorption of MG by KBC increased from $252.73 \text{ mg} \cdot \text{g}^{-1}$ to $366.38 \text{ mg} \cdot \text{g}^{-1}$, which may be because the solution pH was less than $\text{pH}_{\text{PZC}} = 7.76$ (Figure 1a); there were positive charges on the surface of KBC, strong electrostatic repulsions between MG and KBC, and the solution contained a high H^+ concentration and a high capacity for protonation [31], resulting in poor adsorption. In the pH 3–7 range, as the pH was increased the number of protons in solution decreased, protonation decreased, and competition with MG for adsorption weakened, leading to higher steady-state adsorption [32,33] (Figure 1b). In addition, Figure 1c shows the variation in Pb^{2+} adsorption capacity for different solution pH values. In the pH 2–3 range, the adsorption of Pb^{2+} increased from $14.02 \text{ mg} \cdot \text{g}^{-1}$ to $95.5 \text{ mg} \cdot \text{g}^{-1}$, and adsorption was stable and remained at a high level for pH 3–7 (Figure 1c). As the solution pH was increased, the H^+ concentration decreased and the competition between Pb^{2+} and H^+ weakened, resulting in an increasing trend for Pb^{2+} adsorption [34,35]. In addition, Mohan et al. [36] showed that at solution

pH values higher than 6.0 Pb^{2+} was almost completely removed, indicating that other mechanisms such as precipitation might affect heavy metal removal.

Figure 1. pH_{PZC} (a) and the effect of initial pH of solution of MG (b) and Pb^{2+} (c).

3.2. Adsorption Isotherm Study

The influence of different concentrations and temperatures on adsorption was investigated, and the equilibrium curves for adsorption of MG and Pb^{2+} by KBC were slightly different (Figure 2). The capacity for adsorption of MG and Pb^{2+} by KBC increased with increasing initial concentration. Sufficient adsorption sites were available on the KBC surface at low initial concentrations. With increasing initial concentration, the adsorption sites were gradually saturated, and the adsorption capacity gradually stabilized. In this paper, four isothermal adsorption models (Langmuir, Freundlich, Sips, and Redlich–Peterson) were used to fit the data and study the distribution of adsorbed molecules in solid and liquid phase equilibrium states (Figure 2a,b); the resulting fitting parameters are shown in Table 1. The results for fitting of the four isothermal adsorption models indicated that adsorption of MG and Pb^{2+} by KBC proceeded differently. The results showed that the R^2 values of the Freundlich model (0.9913, 0.9978, 0.9966) for the MG adsorption process were higher than the R^2 values of the other isotherm model. This showed that the Freundlich model was more suitable for modelling the adsorption of MG, and is consistent with nonhomogeneous multimolecular layer adsorption [37]. The R^2 values of the Langmuir model (0.9997, 0.9997, 0.9998) for Pb^{2+} adsorption were greater than the R^2 values of the other isotherm model. These results showed that the Langmuir model was more suitable for simulating Pb^{2+} adsorption by KBC, and the process involved monolayer adsorption [38]. The theoretical maximum adsorption capacities of KBC for MG and Pb^{2+} calculated by the Langmuir model were 1111.11 $\text{mg}\cdot\text{g}^{-1}$ and 123.47 $\text{mg}\cdot\text{g}^{-1}$, respectively. In addition, the Freundlich model fit parameters of $1/n$ (MG: 0.682, 0.392, 0.405; Pb^{2+} : 0.173, 0.169, 0.161) were all consistent with $0 < 1/n < 1$. It has been shown that adsorption of MG and Pb^{2+} by KBC is easily achieved [39]. The Sips model is based on the Langmuir model and considers the heterogeneity of adsorption sites on the surface of adsorbents. The Redlich–Peterson adsorption equation combines the parameters of the Langmuir and Freundlich adsorption equations. This equation is widely used for adsorption properties between Langmuir adsorption and Freundlich adsorption. The correlation coefficient R^2 of the Sips and Redlich–Peterson models has a small difference, $0.85 < R^2 < 0.999$. The above results show that the adsorption of KBC on MG is heterogeneous multi-molecular layer adsorption, and that of KBC on Pb^{2+} is heterogeneous single-molecular layer adsorption. In order to fully understand the adsorption properties of KBC, we reviewed studies on the adsorption of Pb^{2+} and MG and compared the adsorption properties of different adsorption materials, as shown in Table 2. In terms of preparation processes, this study involves simple preparation and a low risk of secondary pollution. KBC showed effective adsorption performance and provided reference values for the treatment of MG and Pb^{2+} in wastewater.

Figure 2. Isotherm model fitting for adsorption of MG (a), Pb²⁺ (b).

Table 1. Isotherm parameters for adsorption of MG, Pb²⁺.

Pollutants	Temperature (K)	Freundlich Model			Langmuir Model			Sips Isotherm			Redlich–Peterson Isotherm				
		$K_F/(\text{mg}^{1-n} \cdot \text{L}^n \cdot \text{g}^{-1})$	1/n	R ²	$K_L/(\text{L} \cdot \text{mg}^{-1})$	$Q_m/(\text{mg} \cdot \text{g}^{-1})$	R ²	$Q_m/(\text{mg} \cdot \text{g}^{-1})$	K _S	n _s	R ²	$Q_m/(\text{mg} \cdot \text{g}^{-1})$	K _{RR}	n _{RR}	R ²
MG	298	47.29	0.682	0.991	2.267×10^{-3}	1111.11	0.975	1277.197	0.0107	1.187	0.948	1645.521	0.0105	2.704	0.965
	308	140.67	0.392	0.998	6.748×10^{-3}	909.09	0.890	865.806	0.0105	1.529	0.997	1668.761	0.0126	2.351	0.997
	318	132.11	0.405	0.997	6.748×10^{-3}	909.09	0.890	705.576	0.0025	2.566	0.892	1357.782	0.0299	1.915	0.838
Pb ²⁺	298	50.60	0.173	0.731	0.612	121.95	0.9997	109.48	0.600	1.768	0.975	152.748	0.311	1.053	0.934
	308	51.15	0.169	0.594	0.432	121.95	0.9997	144.42	0.626	0.369	0.855	46.184	13.406	0.884	0.848
	318	55.56	0.161	0.808	0.717	123.47	0.9998	124.60	1.016	0.782	0.998	117.386	1.2392	0.992	0.994

Table 2. Comparison of the adsorption capacity of KBC for MG, Pb²⁺ with other reported adsorbents.

Adsorbents	Pollutants	Maximum Adsorption Capacity (mg·g ⁻¹)	References
KMnO ₄ -modified bamboo biochar	Pb ²⁺ /MG	123.47/1111.11	This study
NaOH-modified Hickory shell biochar	Pb ²⁺	53.6	[12]
MnO ₂ -loaded Palm kernel cake residue biochar	Pb ²⁺	46.64	[40]
FeCl ₃ -modified Sugarcane Straw biochar	Pb ²⁺	92.81	[19]
Magnetic activated carbon-cobalt nanoparticles	Pb ²⁺ /MG	312.5/263.2	[41]
Magnetic activated cortaderia selloanafflower spikes	MG	59.5	[42]
CuS nanorods loaded on active carbon	Pb ²⁺ /MG	47.98/145.98	[43]

3.3. Adsorption Kinetics Study

The effects of different reaction times on the adsorption of MG and Pb²⁺ by KBC were investigated for the mechanisms of MG and Pb²⁺ adsorption, respectively, and the results are shown in Figure 3. The adsorption trends of KBC were similar for MG and Pb²⁺. Adsorption of MG and Pb²⁺ by KBC was divided into the fast phase (0–60 min) and the slow phase (60–360 min). In the fast phase, the adsorption capacity increases rapidly with time, and adsorption sites are gradually filled. The adsorption process then enters the slow phase, adsorption sites reach saturation, and the adsorption capacity tends towards a steady state. The MG and Pb²⁺ adsorption processes were fitted by pseudo-first-order and pseudo-second-order models; the fitting results are shown in Figure 3a,b, and the fitting parameters are shown in Table 3. The R^2 values for fitting MG adsorption data with the pseudo-first-order and pseudo-second-order models were relatively close, and the predicted saturation adsorption capacities for both models were close to the actual adsorption capacity, indicating that adsorption of MG by KBC includes both pure physical adsorption and chemical adsorption processes such as electron transfer and ion exchange. The R^2 for fitting Pb²⁺ adsorption data with the pseudo-second-order model was higher

than the R^2 for the pseudo-first-order model, and the maximum adsorption capacities predicted by the model (112.36, 126.58, 119.05 $\text{mg}\cdot\text{g}^{-1}$) were close to the actual adsorption capacities (114.04, 125.02, 123.75 $\text{mg}\cdot\text{g}^{-1}$); this indicated that the pseudo-second-order model was more consistent with the data for KBC adsorption of Pb^{2+} . Therefore, the adsorption of Pb^{2+} by KBC was dominated by chemisorption, including liquid film external diffusion, surface adsorption, and intraparticle diffusion [30].

Figure 3. Kinetic plots for adsorption of MG (a), Pb^{2+} (b).

Table 3. Calculated parameters for kinetic models for the adsorption of Pb^{2+} and MG onto KBC.

Pollutant	Concentration ($\text{mg}\cdot\text{L}^{-1}$)	Pseudo-First-Order			Pseudo-Second-Order		
		$K_1/(1\cdot\text{min}^{-1})$	$Q_e/(\text{mg}\cdot\text{g}^{-1})$	R^2	$K_2/(\text{g}/(\text{mg}\cdot\text{min}))$	$Q_e/\text{mg}\cdot\text{g}^{-1}$	R^2
MG	600	0.0153	257.83	0.998	8.378×10^{-5}	322.58	0.9857
	800	0.014	328.82	0.9896	6.906×10^{-5}	400	0.9927
	1000	0.0177	510.4	0.9954	4.716×10^{-5}	555.56	0.9825
Pb^{2+}	300	0.0115	30.69	0.955	1.886×10^{-3}	112.36	0.9986
	400	0.0128	49.73	0.9667	9.385×10^{-3}	126.58	0.9958
	500	0.0092	44.38	0.9468	1.198×10^{-3}	119.05	0.9973

3.4. Reusability and Stability of KBC

From the perspective of resource utilization, repeated adsorption performance is an important indicator of biochar utility. Manisha et al. [17] found that washing of organics from the surface of KBC by NaOH resulted in adequate removal of organic molecules from the surface. In this study, the pollutants MG and Pb^{2+} were desorbed from KBC with $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaOH, and KBC was cleaned to neutrality with distilled water. The data for regenerative adsorption cycles are shown in Figure 4. The MG removal efficiency decreased from 99.17% to 98.75% after five desorption and adsorption cycles (Figure 4a), indicating confirmation of the reusability of KBC for MG removal; this is consistent with significant pore filling during the adsorption process, which is consistent with Manisha's findings. During desorption and adsorption of Pb^{2+} , the removal efficiency for solution Pb^{2+} by KBC decreased from 84.00% to 76.88%, a change more significant than for MG (Figure 4b). Because Pb^{2+} and MG are more easily adsorbed under alkaline conditions, desorption with NaOH can reduce the acidic functional groups on the surface of biochar and increase the content of alkaline functional groups, which is conducive to the adsorption of the two pollutants [44]; however, NaOH may consume surface manganese oxides and destroy active sites [45], which may be a reason for the decrease in adsorption capacity. Experimental results for the mixed system along with difference analysis results are shown in Figure 4c.

The difference analysis of MG adsorption results between single system and mixed system is not significant, and while the difference analysis of Pb^{2+} adsorption effect is somewhat more obvious, the changes in MG and Pb^{2+} removal rates in different systems are not significant. These results showed that KBC maintained effective adsorption and reusability for removal of both MG and Pb^{2+} under these experimental concentrations. This may be the reason for the different mechanisms for adsorption of MG and Pb^{2+} on KBC: MG is mainly adsorbed through surface pore filling, while Pb^{2+} is adsorbed through functional group complexation and mineral precipitation. The different adsorption mechanisms reduce the extent of competitive adsorption for the two pollutants; thus, selective adsorption of MG and Pb^{2+} were not affected substantially. The above results indicate that KBC has high potential for MG and Pb^{2+} wastewater treatment.

Figure 4. Regeneration study of KBC to MG (a) and Pb^{2+} (b) in single system, mixed system experiment, and difference analysis (c). Capital letters represent the difference between a single system and mixture system; lowercase represent the difference between adsorption times.

3.5. Coexisting Cation Experiment

The complex environment of actual wastewater was simulated by adding K^+ , Ca^{2+} , Na^+ and Mg^{2+} ions at different concentrations; their effects on the adsorption of MG and Pb^{2+} are shown in Figure 5a,b. Figure 5 shows that the trends for MG and Pb^{2+} adsorption in the coexisting cation experiments were similar. MG and Pb^{2+} adsorption decreased slightly with increasing concentrations of interfering cations. The effects of each cation on the adsorption capacity for the target pollutants decreased in the order $Ca^{2+} > Mg^{2+} > Na^+ > K^+$. Because Ca^{2+} and Mg^{2+} are divalent cations and possess higher charges than Na^+ and K^+ , they compete more with MG and Pb^{2+} for adsorption and have more significant effects on adsorption [46]. The KBC adsorption capacities for both pollutants were not disturbed substantially by the coexisting cations, indicating that KBC has better selectivity for MG and Pb^{2+} .

Figure 5. Coexisting cation interference experiment of MG (a) and Pb^{2+} (b).

3.6. Characteristics of KBC

Functional groups often play important roles in the adsorption process; thus, the surface functional groups of the four materials were studied. The FTIR spectra for the four materials are shown in Figure 6a. At 524 cm^{-1} , a characteristic peak for Mn-O appeared in the FTIR spectrum of KBC, indicating that modification with KMnO_4 changed the surface functional groups and successfully loaded manganese oxide [47]. A peak at 3420 cm^{-1} is attributed to the stretching vibration of the -OH bond. The peak position of the -OH stretching vibration was slightly shifted after adsorption. Li et al. [48] believed that the stretching vibration for -OH bonds indicated that a large number of hydrogen bonds affected heavy metal adsorption and promoted ion exchange with heavy metals. The absorption peak at 600 cm^{-1} was attributed to the -C=O group on the aromatic ring [49], which was slightly shifted after adsorption of Pb^{2+} , indicating that there were cation- π interactions between the aromatic ring on the KBC surface and Pb^{2+} during the adsorption process. The stretching vibration peak at 1390 cm^{-1} was mainly from CO_3^{2-} , and its peak value increased after adsorption of Pb^{2+} , which may be related to the formation of lead carbonate precipitates [46,50]. The comparison of spectra for KBC and KBC-MG showed that the absorption peak of C=O changed after adsorption, indicating that aromatic rings on the surface of KBC formed π - π interactions with the aromatic ring of MG. A new absorption peak appeared at 1160 cm^{-1} ; this arose from aromatic ring C-H in-plane bending vibrations, indicating that MG was successfully adsorbed [51]. In conclusion, oxygen-containing functional groups are important for better adsorption of MG and Pb^{2+} on KBC.

To probe surface crystallization of BC and KBC before and after adsorption of MG and Pb^{2+} , XRD analyses were conducted on the four biochars; the results are shown in Figure 6b. The XRD pattern of BC was retrieved and a significant diffraction peak appeared at 26.52° , which was identified as a characteristic peak of C (PDF card number: 26-1 080) by MDI Jade8.5 software. In comparing KBC and BC, the diffraction peak for C was obviously weaker for KBC, and there were no obvious diffraction peaks at 36.56° , 42.44° and 57.18° for $\beta\text{-MnO}_2$ (PDF card number: 42-1 316); hence, no obvious crystalline material was formed on the surface of biochar modified by KMnO_4 , and manganese oxide existed in an amorphous form. The material lattice did not change significantly after MG and Pb^{2+} adsorption, indicating that KBC did not form obvious crystal structures after MG and Pb^{2+} adsorption, though these may exist as compounds with low crystallinity [51,52].

To analyse the chemical and morphological changes in each element during adsorption, XPS analyses were carried out on the four materials, and the results are shown in Figure 6c–g. Figure 6c shows the wide survey spectra for BC, KBC, KBC-MG and KBC- Pb^{2+} . Unlike BC, the Mn 2p peak appeared in the KBC spectrum, indicating successful introduction of manganese on the surface of KBC. The XPS spectra of KBC-MG and KBC-Pb showed strong N 1s and Pb 4f peaks, respectively, indicating that KBC adsorbed Pb^{2+} and MG effectively. Deconvolution was performed for O 1s and C 1s peaks observed before and after adsorption and Pb 4f and N 1s peaks observed after adsorption; the results are shown in Figure 6d–g. The O 1s deconvolution results are shown in Figure 6d. The peaks at 529.6 eV, 531.3 eV, 522.4 eV and 533.6 eV belong to Mn-O, Mn-OH, C-OH and H_2O , respectively [53]. The Mn-O peak intensity weakened after KBC absorbed MG, indicating that Mn-O on the KBC surface participated in MG adsorption and provided a large number of active sites for the adsorption process [54]. The peak for the Mn-OH functional group disappeared, indicating that MG may have undergone a complex reaction with hydroxyl groups during adsorption. The disappearance of the H_2O peak indicated that chemisorbed water was involved in adsorption of MG. The weakening of the Mn-O peak after Pb^{2+} adsorption by KBC indicated that Mn-O on the surface of KBC was involved in Pb^{2+} adsorption, and Song et al. [54] suggested that Mn-O provides a large number of active sites for the adsorption reaction. The disappearance of the peak for the Mn-OH functional group indicated that the hydroxyl group played an important role in Pb^{2+} adsorption. Figure 6e shows the deconvolution results for the C 1s peak. The peak for KBC at 292.7 eV was for

O=C-O, and O=C-O disappeared after adsorption of MG and Pb^{2+} , indicating that O=C-O was involved in adsorption of MG and Pb^{2+} through complexation with functional groups. Figure 6f shows the deconvolution results for the Pb 4f peak of KBC-Pb $^{2+}$. The peaks at 138.7 eV and 143.5 eV were attributed to Pb 4f $_{7/2}$ and Pb 4f $_{5/2}$ ionizations, respectively, and the peak positions were consistent with the binding energy of Pb(OH) $_2$ to PbCO $_3$ [41], proving that Pb^{2+} generates mineral precipitates with mineral anions on the surface of KBC during adsorption. Deconvolution of the N 1s peak of KBC-MG showed that the peak was attributed to C-NH $_2$ and to an aromatic ring C-H (Figure 6g), indicating that MG adsorbed effectively on KBC [51], which is consistent with the FTIR results.

Figure 6. FTIR spectra of four biochars (a), XRD patterns of four biochars (b), wide survey spectra of four biochars, (c) and high-resolution XPS spectrum of O 1s (d), C 1s (e), Pb 4f (f), and N 1s (g).

SEM mapping results for BC (a), KBC (b), KBC-MG (c), and KBC-Pb $^{2+}$ (d) are shown in Figure 7. Figure 7a shows the SEM image for BC; the surface structure appears as a complete block structure with a relatively smooth and undeveloped pore structure. Figure 7b shows the SEM image of KBC; the surface structure is broken, the specific surface area is increased over that of BC, a large number of pores have formed, and a large number of adsorption sites are present [55]. A small area of particulate flocs on the surface was analysed for

manganese oxides [49]. Figure 7c shows the SEM image of KBC after adsorption of MG; the surface pores are filled with blocky material. Sara et al. [51] suggested that KBC adsorbs MG through pore filling. Figure 7d shows the SEM image for KBC after adsorption of Pb^{2+} ; the flocculent precipitate on the surface of KBC could be a mineral precipitate from CO_3^{2-} and Pb^{2+} on the surface of the biochar [52]. The results of EDS mapping showed that the KBC surface was successfully loaded with Mn. The mapping results for KBC- Pb^{2+} and KBC-MG showed that KBC was effective in adsorbing both MG and Pb^{2+} . The elemental distributions of Pb and Mn were similar, indicating that adsorption of Pb^{2+} is closely related to manganese oxides. This result is also consistent with the FTIR analysis. The elemental distributions of N and Mn were not consistent, indicating that pore filling was an important process in MG adsorption by KBC.

Figure 7. The SEM mapping images of BC (a), KBC (b), KBC-MG (c), and KBC- Pb^{2+} (d).

4. Conclusions

In conclusion, the process for adsorption of MG on KBC was consistent with the Freundlich model. Both pseudo-first-order kinetics and pseudo-second-order kinetics fit the MG adsorption data well. The adsorption process for Pb^{2+} was consistent with the Langmuir model and pseudo-second-order kinetic model. The theoretical saturation sorption capacities for MG and Pb^{2+} were $1111.11 \text{ mg}\cdot\text{g}^{-1}$ and $123.47 \text{ mg}\cdot\text{g}^{-1}$, respectively. The efficiencies for removal of MG and Pb^{2+} in solution by KBC reached more than 99% and 75% in the fifth cycling experiment. The differences in removal rates of MG and Pb^{2+} by KBC were not significant in the mixed system as compared to single systems.

The mechanism for adsorption of MG on KBC involved pore filling, π - π interactions, and functional group complexation. The mechanism of Pb^{2+} adsorption by KBC involved mineral precipitation, functional group complexation, ion exchange and cation- π interactions. KBC has good potential as an adsorbent material for the treatment of wastewater containing organic and heavy metal pollutants.

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