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COMPETITIVE ADSORPTION OF Fe^{2+}, Pb^{2+}, AND Zn^{2+} IONS FROM MULTI-METAL ION SOLUTION ON AMMONIUM OXALATE MODIFIED KAOLINITE CLAY

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ABSTRACT

The competitive adsorption of Fe^{2+}, Pb^{2+}, and Zn^{2+} ions from mixed multi-metal aqueous solution on ammonium oxalate-modified kaolinite clay (AOK) was studied to determine the competitive influence of the metal ions on the adsorption of other metal ions. The kaolinite clay was modified by treating it with 0.2 M of ammonium oxalate solution at 50 ^{o}C. The adsorption of the metal ions was carried out using initial concentrations of 20, 35, and 50 mg L^{-1} in both the single and multi-metal ion solutions. The results revealed that at a low concentration of 20 mg L^{-1}, the adsorption capacity for the uptake of the metal ions on AOK is non-competitive. At higher adsorbate concentrations of 35 and 50 mg L^{-1}, the single to multi-metal ions equilibrium adsorption capacity ratio value obtained was less than 1. This indicated an antagonistic effect on competing for the adsorption site in the following order: Pb^{2+} (9.9 mg g^{-1}) > Fe^{2+} (3.85 mg g^{-1}) > Zn^{2+} (2.85 mg g^{-1}). The outcome revealed that ammonium oxalate-modified kaolinite is a potential adsorbent for remediation of multi-heavy metal-laden wastewater with preferentially higher affinity for Pb^{2+} ions than other metal ions.

INTRODUCTION

Industrial and municipal wastewater and agrochemical waste are the major sources of environmental and waterborne pollution globally. Heavy metals are one of the dominant pollutants, especially in iron and steel processing and finishing industrial wastewater [1]. The discharge of heavy metal-laden effluents into water bodies is always at a concentration detrimental to the soil, humans, and aquatic animals. Heavy metal ions are not biodegradable and excessive accumulation in living tissue impedes the biological functions of vital organs resulting in health problems [2]. Several techniques such as membrane separation, electrochemical techniques, adsorption, solvent extraction, advanced oxidation, precipitation, biological techniques, and others have effectively been used for the treatment of wastewater [3-5].

The adsorption technique is considered one of the effective low-cost methods for the removal of heavy metals. Adsorption of heavy metals

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from aqueous solutions has been studied using different adsorbents including clay [6,7]. The use of kaolinite clay for adsorption is worthwhile because of its abundance in deposits as a non-metallic mineral [8]. Kaolinite is a white, soft, and plastic-hydrated aluminum silicate clay mineral with a chemical formula of $Al_2Si_2O_5(OH)_4$. It is the most common member of the kaolin group with dominant type 1:1. It consists of two fundamental crystal sheets tetrahedral or silica and octahedral or alumina sheet. In a unit structure, one octahedral sheet is linked with the apical oxygen ion of the tetrahedral [8]. Simultaneous adsorption of Ni^{2+} and Mn^{2+} ions from aqueous solution into a Nigerian kaolinite clay has been reported [9]. Sodium hydroxide-modified kaolinite has been utilized for the adsorption of heavy metal-laden steel industrial wastewater found to contain Fe^{2+}, Pb^{2+}, $Zn^{2+,}$ and Cr^{6+} ions with concentrations of 309.0, 20.50, 40.40, and 10.90 mg L^{-1} for respectively. After four successive adsorption cycles, the metal ions concentration was removed at approximately 99.77%, 99.95%, 98.91%, and 99.91% for Fe^{2+}, Pb^{2+}, $Zn^{2+,}$ and Cr^{6+} ions respectively [10].

This study focuses on the investigation of competitive adsorption of Fe^{2+}, $Pb^{2+,}$ and Zn^{2+} ions from mixed multi-metal aqueous solution on ammonium oxalate-modified kaolinite clay. Adsorption of the metal ions from a single aqueous metal ion solution on ammonium oxalate-modified kaolinite has been carried out in the previous study [11]. The influence of individual metal ions on the rate of the adsorption of other metal ions from the multi-metal ion system was investigated. The data obtained was used to evaluate the antagonistic effect of the competitive adsorption of heavy metals from the multi-metal ions system.

MATERIALS AND METHODS

Preparation of Ammonium Oxalate Modified Kaolinite

The kaolinite obtained from Argungu, Kebbi State Nigeria was purified using wet sedimentation. A 25 g portion of the 63 µm fraction particle size of the purified clay without any associated minerals was added to a 0.2 M solution of ammonium oxalate. The mixture was stirred with a magnetic stirrer at the rate of 200 revolutions per minute (rpm) for 1 hour at 50 °C and centrifuged at 2500 rpm for 1 hour. The sediment obtained was washed repeatedly with deionized water to a neutral pH and dried at 103 °C [11].

Adsorption from Multi-metal Ion Solution

Adsorption from multi-metal ion solution of Fe^{2+}, Pb^{2+}, and Zn^{2+} ions on AOK was carried out by contacting the adsorbent with 1.0 L of the solutions. The adsorption behavior of the metal ions was studied using initial concentrations of 20, 35, and 50 mg L^{-1} in both the single and multi-metal ion solutions. The constant experimental conditions kept constant include adsorbent particle size of 75 µm, pH of 5.0, agitation speed of 300 rpm, adsorbent dose of 4.0 g L^{-1}, temperature of 55 ^{o}C, and contact time of 240 minutes. In the end, the mixture was centrifuged at 3000 revolutions per minute (rpm) for 30 minutes and the supernatant solution was analyzed using an Atomic Absorption Spectrophotometer (Buck Scientific 210 VGP). The AOK sample was characterized using X-ray Diffractometer, XRD (BRUKER, AXS D8), Fourier Transform Infrared Spectrophotometer, FTIR (Bruker Tensor 27 Platinum ATR-FTIR), and Scanning Electron Microscope, SEM (TESCAN VEGA TS 5136LM).

The adsorption capacity of AOK was determined using the equation:

$$q = \frac{V(C_i - C_x)}{W} \qquad (1)$$

where C_{i} and C_{x} are the concentrations of heavy metal ions before and after adsorption (mg L^{-1}), V is the volume of multi-metal ion solution (L), q is the adsorption equilibrium and w is the weight of AOK (g)

The percentage of heavy metal ions removal was evaluated using the formula:

$$\text{Percentage removal (\%)} = \frac{(C_i - C_x) \times 100}{C_i} \qquad (2)$$

The influence of the mixed metal ions was evaluated using the ratio of metal ion adsorption capacity as a single solution or multi-metal ions system [12]:

$$\frac{q_m}{q_s} \qquad (3)$$

where, q_s and q_m are the equilibrium adsorption capacity in single and multi-metal ion solutions.

The ratio of percentage reduction based on adsorption capacity difference in the single/multi-system was calculated using the equation [12]:

$$\Delta q_x = \frac{q_s - q_m}{q_s} \times 100\% \qquad (4)$$

The total metal ion adsorption (q_T) in the competitive system was calculated by summing up the amount of ions adsorbed [13]:

$$q_T = q_{Fe} + q_{Pb} + q_{Zn} \qquad (5)$$

If the expression $\frac{q_m}{q_s}$ is > 1, the presence of other metal ions enhances the adsorption of the particular ion (synergistic effect), if the ratio is < 1, it indicates an antagonistic effect for the competitive system and if the ratio = 1, the presence of other ions has no effect on adsorption of the particular ion evaluated [13].

RESULTS AND DISCUSSION

Adsorption from Multi-metal Ion Solutions

The adsorption from the single/multi-metal ion solution on AOK was carried out on Fe^{2+}, $Pb^{2+,}$ and Zn^{2+} ions. The adsorption data obtained

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were analyzed using equations 3, 4, and 5 and the results obtained are presented in Table 1. At a low initial solution concentration of 20 mg L^{-1}, the AOK adsorption capacity for Fe^{2+}, $Pb^{2+,}$ and Zn^{2+} were 4.96, 4.96, and 3.88 mg g^{-1} and 4.94, 4.96, and 3.72 mg g^{-1} in the single metal ion system and in the multi-metal ion solution respectively. No significant difference was observed for Fe^{2+} and Pb^{2+}, except for the adsorption capacity for Zn^{2+} ions which reduced slightly from 3.875 to 3.72 mg g^{-1}. The single to multi-metal ion system equilibrium adsorption capacity ratio for both Fe^{2+} and Pb^{2+} was approximately equal to 1 and that of Zn^{2+} was 0.96, with a ratio of adsorption capacity reduction percentage of 0.36, 0.1, and 4.0% respectively. This indicates that the adsorption of a metal ion has no significant effect on the other ions present in the multi-metal ion solution. This was attributed to the fact that at low concentrations, many adsorption sites were available for the ions, hence, the uptake of any particle metal ions is independent of the presence of other ions [14].

As the initial solution concentration was increased to 35 mg L^{-1}, the adsorption capacity of 8.24, 8.71, and 6.90 mg g^{-1} was recorded for Fe^{2+}, $Pb^{2+,}$ and Zn^{2+} ions respectively in the single metal solutions. Their simultaneous adsorption however diminishes significantly in the mixed solution with uptake of 5.075, 7.52, and 3.86 mg g^{-1} at adsorption reduction rate (Δq_x) of 38.41%, 13.66%, and 44.06% for Fe^{2+}, Pb^{2+} and Zn^{2+} ions respectively. The single to multi-metal ion equilibrium adsorption capacity ratio for all the metal ions was less than 1; an indication of an antagonistic effect due to competition for adsorption sites [15].

As the initial concentration was increased to 50 mg L^{-1}, the adsorption capacity of AOK for Fe^{2+}, $Pb^{2+,}$ and Zn^{2+} ions was 11.786, 12.3, and 7.33 mg g^{-1} in the single solution system. Their adsorption in the multi-metal ions solutions reduced to 3.85, 9.9, and 2.85 mg L^{-1} with an adsorption reduction rate of 67.33%, 19.51%, and 60.71 % respectively. The values obtained for single-multi to multi-metal ion equilibrium adsorption capacity ratio for all the metal ions were less than 1; an indication that their interaction is antagonistic due to competition for fewer available adsorption sites.

Total metal ion adsorption capacity (q_T) of 13.615, 16.455, and 16.60 mg g^{-1} were recorded for Fe^{2+}, $Pb^{2+,}$ and Zn^{2+} ions in the multi-metal ion system at initial concentrations of 20, 35, and 50 mg L^{-1} respectively. The results revealed that as the initial concentration increased, the adsorption capacity of AOK also increased. Adsorption capacities of adsorbents usually increase as the concentration of adsorbate increases due to the number of molecules interacting per unit mass of adsorbent. [16,17]. The adsorption of the metal ions from the multi-metal solution was in the following order: Pb^{2+} (9.9 mg g^{-1}) > Fe^{2+} (3.85 mg g^{-1}) > Zn^{2+} (2.85 mg g^{-1}). This order was attributed to the influence of the ionic radius of the metal ions in the following manner: Pb^{2+} (119 pm) > Fe^{2+} (78 pm) > Zn^{2+} (74 pm). Literature reports [18,19] have suggested that the sorption order of ions in a multi-metal ion system is influenced by ionic radii. Hence, the higher the radii of ions, the higher the rate of adsorption. The ability of lead to easily form complexes as a group metal and its high atomic polarizability over Fe^{2+} and Zn^{2+} ions was another factor that may have influenced the higher adsorption capacity of Pb^{2+} ions [20]. The higher rate of adsorption of Fe^{2+} over Zn^{2+} ions was also attributed to the tendency of Fe^{2+} to displace Zn^{2+} from the clay edge site [21].

Table 1. Multi-metal system interaction and rate of adsorption on AOK clay

Initial concentration (mg/L)	20		35		50	
Metal ion	$\frac{q_m}{q_s}$	Δq (%)	$\frac{q_m}{q_s}$	Δq (%)	$\frac{q_m}{q_s}$	Δq (%)
Fe^{2+}	1.0	0.36	0.62	38.41	0.33	67.33
Pb^{2+}	1.0	0.1	0.86	13.66	0.80	19.51
Zn^{2+}	0.96	4.0	0.56	44.06	0.39	60.71

Characterization of Ammonium Oxalate Modified Kaolinite

The XRD patterns of AOK showing the qualitative and quantitative mineralogical phase composition, indicated intense peaks for the interlayer spacing at 12.4, 25, 38.5, 55, and 62.5 2θ respectively (Figure 1). The intensities of the peak were lower than the peaks for the purified form of the kaolinite reported in the previous work [22]. This is an indication that the modifying agents (ammonium oxalate) only interact with the clay at the surface and do not intercalate the interlayer space or affect the crystal structure [23]. The results of FTIR spectra revealed two sharp peaks at 3689.64 and 3619.57 cm^{-1} which represent the stretching of the surface hydroxyl groups of the dioctahedral layer and inner hydroxyl groups located in the plane between the tetrahedral and octahedral sheets of AOK (Figure 2). The absorption peak at 1025.18 cm^{-1} was assigned to the O=C-O symmetric of the oxalate [24]. The surface morphology of AOK before the adsorption of the metal ions from the multi-metal ions solution is shown in Figure 3. The SEM micrograph shows the orientation exhibits predominantly largely filmy flaked particles that are loosely packed with some level of porosity before adsorption. After adsorption, the flaked particles of AOK were found to be dispersed (Figure 4).

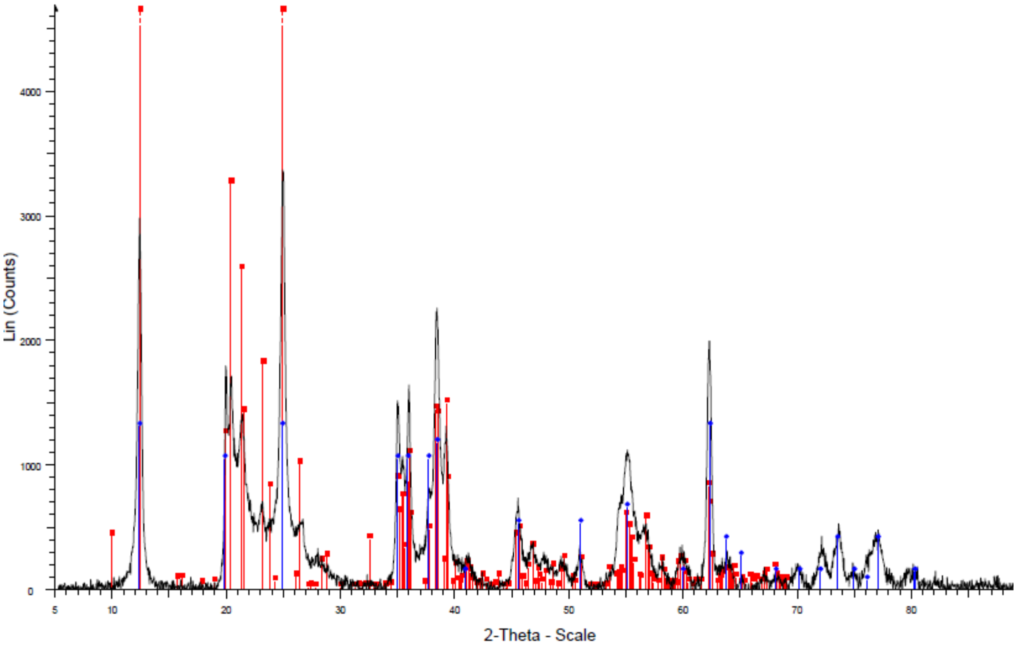

Figure 1 XRD diffractogram of AOK

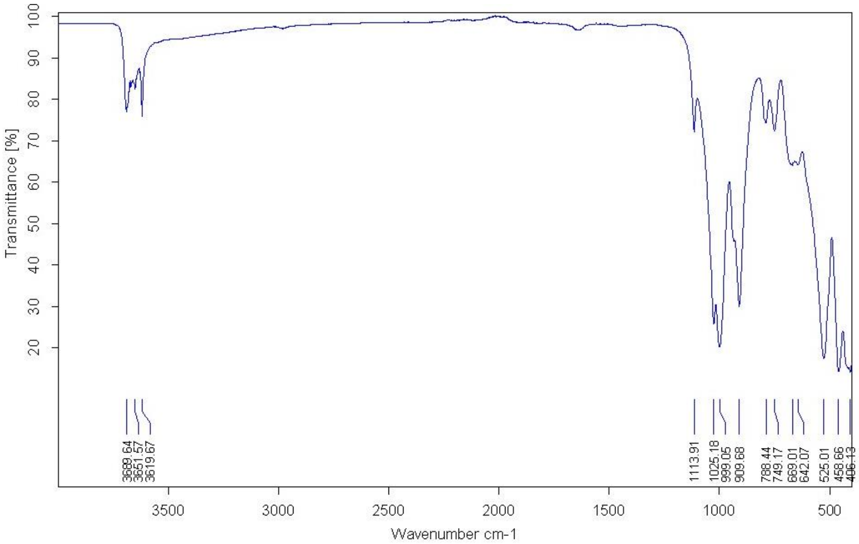

Figure 2 FTIR peak of AOK

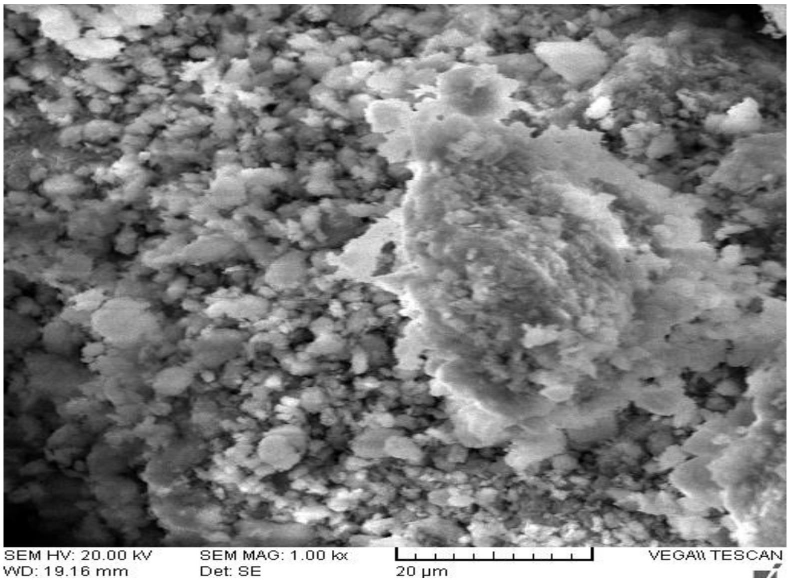

Figure 3 SEM image of AOK before adsorption from multi-metal ion solution

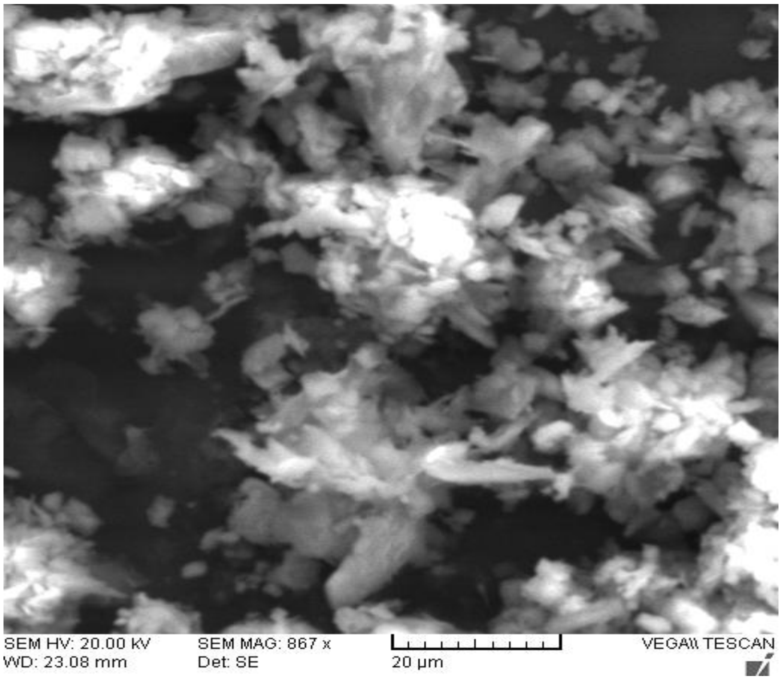

Figure 4 SEM image of AOK after adsorption from multi-metal ion

CONCLUSION

The modified kaolinite (AOK) prepared by treating the clay with 0.2 M ammonium oxalate solution and was found to be effective for the adsorption of heavy metal ions from single and multi-metal ions systems. The microscopic and spectroscopic characterization revealed an interaction of the oxalate only at the surface of the kaolinite with some level of porosity. The AOK showed high adsorption capacity for both the single-metal ions and multi-metal ion solutions of Fe^{2+}, $Pb^{2+,}$ and Zn^{2+} ions. The single to multi-metal system adsorption capacity ratio showed an antagonistic effect because of competition for adsorption sites as the concentration of the metal ions increased from 20 mg L^{-1} to 35 mg L^{-1} and 50 mg L^{-1} respectively. The order of adsorption of the metal ions from the multi-metal solution ($Pb^{2+} > Fe^{2+} > Zn^{2+}$) was attributed to the order of their ionic radius and displacement of the metal ions from the adsorption sites. The adsorption capacity of AOK for the simultaneous uptake of Fe^{2+}, $Pb^{2+,}$ and Zn^{2+} ions from multi-system revealed that pure kaolinite (without any associated mineral) modified with ammonium oxalate is a potential adsorbent for removal of multi-metal ions wastewater with a higher affinity for Pb^{2+} over the other heavy metals.

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