UTILIZATION OF AGRICULTURAL WASTE ADSORBENT FOR THE REMOVAL OF LEAD IONS FROM AQUEOUS SOLUTIONS

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Abstract. This work investigated the potentiality of using chemically modified onion skin waste (CMOSW) as an adsorbent for the removal of lead ions (Pb^{2+}) from an aqueous solution. The material properties were characterized using techniques, such as Brunauer-Emmett-Teller surface area analysis, scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. The effects of adsorbent dosage, contact time, pH and initial Pb^{2+} concentration on the removal efficiency were investigated by experimental tests. The experimental data were analysed by the Langmuir and Freundlich isotherms, while kinetic data obtained at different concentrations were analysed using a pseudo-first-order and pseudo-second-order models. A distinct adsorption of Pb^{2+} was revealed by the SEM results. From the FTIR analysis, the experimental result was corresponded to the peak changes of the spectra obtained before and after the adsorption of Pb^{2+}. The maximum removal efficiency of Pb^{2+} by the CMOSW was $97.3 \pm 0.01\%$ at an optimum CMOSW dosage of 1.4 g/L, contact time of 120 min and solution pH of 6.0. Experimental data obtained fitted well with the Freundlich isotherm model. The kinetics of the Pb^{2+} adsorption by CMOSW appeared to be better described by the pseudo-second-order model, suggesting the chemisorption mechanism dominance.

Keywords: Lead ions, onion skin, adsorption, isotherm, kinetics.

1. Introduction

The increased level of environmental contamination as a result of industrial development by compounds of organic and inorganic sources has become one of the major environmental concerns of many industries [1]. Most water contaminants, such as hydrocarbon, phenolic, dyes, solvent and heavy metals, are soluble chemical substances [2]. These compounds end up in water bodies, causing water and soil pollutions, and thereby constitute threats to plants, animals and human health [1]. However, the presence of toxic heavy metals in industrial effluents gives a cause for environmental concern [3]. Heavy metals are generally toxic, highly soluble in water and can easily find their way into the soil and flowing streams, thereby causing damage to the environment and human health. Lead is known as multifunctional metal, which is a needed element to manufacture pipe, paints, bullets and also one of the essential metals used in the pewter industry [4]. However, a long term exposure to lead ions (Pb^{2+}) can cause mental illness, infertility in women and damage to vital human internal organs [5]. Thus, there is a need to adopt a technology suitable for getting rid of toxic heavy metals and other dissolved contaminants from effluents prior to their discharge into flowing streams. The Nigerian Ministry of Environment recommends 0.01 mg/L as the maximum permitted level of Pb^{2+} in an industrial effluent before its release into surface waters [6] while it has a maximum allowable

limit (sets by World Health Organization, WHO) of 0.003 mg/L in drinking water [7].

However, many wastewater treatment methods have been employed in removing toxic heavy metals from the aqueous environment. These methods include electrocoagulation, reverse osmosis, chemical precipitation, electrochemical reduction, ion-exchange membrane and adsorption [8, 9]. Among these treatment techniques, adsorption seems to be cost-effective, easy and simple to operate [10]. Another advantage of adsorption over other techniques is its capability to treat wastewater pollutants at low concentrations [11]. Some of the porous materials that have been synthesized as adsorbents for the removal of toxic heavy metals include activated carbon, molecular sieve and zeolite. These materials are often used to remove toxic metal ions from contaminated water due to their better surface properties and adsorption capacities [12]. However, they are expensive and challenging to be regenerated and reused. These drawbacks necessitate the need to explore cheap, reusable and biodegradable adsorbents for the removal of toxic metal ions from aqueous solutions. Adsorbents could be obtained from different sources, such as naturally occurring, agricultural biomass and waste materials [13–15]. In order to minimize the wastewater treatment costs and avoid the accumulation of solid waste in the environment, agricultural wastes have been suggested and studied, such as pineapple stem [16], pineapple fruit peel [17], waste tea [18], walnut shell [19], peanut shell [20] and

seed pod [21]. Moreover, onion skins are abundantly available and can be a good source of electrostatically active metal oxides [22].

According to the literature research, a modification of onion skin waste by acid activation is currently being used, and a series of technical challenges are being experienced [23–25]. The promising use of onion skin requires a modification without severely damaging its structure. However, metal oxides, such as an aluminium oxide (Al_2O_3) and silicon oxide (SiO_2), could be used to modify the structure of the adsorbent due to their better textural properties, mechanical and thermal stabilities [26, 27]. The application of Al_2O_3 modified onion skin waste for the removal of heavy metals from aqueous solution is still not well explored.

The aim of the current work was to investigate the potentiality of utilizing onion skin waste as an adsorbent for the removal of lead ions from an aqueous solution. The operational parameters' effect on the uptake efficiency, including initial concentration, pH, adsorbent dosage and contact time, was investigated. The equilibrium adsorption isotherm and kinetics were also studied.

2. METHODOLOGY

2.1. MATERIALS

Onion skin waste was collected from Oja-Oba, Ado-Ekiti, Nigeria. Lead II nitrate (Pb $(NO_3)_2$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and aluminium nitrate (Al$(NO_3)_3$) were all bought from Nizochem Chemical Enterprise, Akure, Nigeria. Pb $(NO_3)_2$ was used as the adsorbate. 1000 mg/L of lead salt solution was prepared by dissolving 1.60 g of (Pb $(NO_3)_2$) in 1 L of deionized water and solutions with different concentrations were prepared from the standard solution.

2.2. PREPARATION AND CHARACTERIZATION OF ADSORBENT

The collected onion skin waste (OSW) were thoroughly washed with clean water to get rid of dirt particles and dried at 110 °C for 24 h. Then, the dried OSW was grinded and finally sieved through a 220 μm mesh size to remove larger parts. In order to prepare a chemically modified onion skin waste (CMOSW) adsorbent, the OSW powder was mixed with Al$(NO_3)_3$ in a ratio of 1:2, and 150 mL of distilled water was added to the resulting solid mixture. Thereafter, the solution was agitated on a hot plate at 75 °C for 12 h and NH_4OH solution was subsequently added dropwise to obtain a basic solution and achieve a complete precipitation. The precipitate was washed severally with deionized water, then dried at 110 °C, and finally calcined at 600 °C for 2.5 h.

A morphological analysis was conducted on the CMOSW sample to evaluate its surface morphology before and after the adsorption of lead ions using a scanning electron microscope (SEM, JEOL-JSM

7650F). The Fourier transform infrared (FTIR) spectrometer (FTIR-1S Shimadzu, Japan) was used to determine the functional groups present on the prepared adsorbent. The spectra were recorded within the range of 4000-400 cm^{-1}. The textural characteristics of the CMOSW samples including specific surface area, total pore volume and pore size distribution were obtained through N_2 adsorption-desorption data at -196 °C using a BELSORP Max surface area and porosity analyser (BEL, Japan). The studied samples were degassed before the analysis at 250 °C for 3 h to remove the adsorbed gases that filled up their pores, and their specific surface areas were computed using the Brunauer-Emmett-Teller (BET) model. The total pore volume and pore size were determined by the Barrett-Joyner-Halenda (BJH) method and studied near the saturation pressure of N_2 (P/P_0 = 0.99).

2.3. ADSORPTION EXPERIMENTS

A required volume of lead salt contaminated water (50 mL) and the needed amount of the prepared adsorbent were charged into 250 mL conical flasks. The mixtures were agitated in a temperature-controlled water bath shaker at 28 ± 2 °C and 200 rpm until an equilibrium was attained. The adsorption of Pb^{2+} ions onto CMOSW was carried out under these operating conditions: initial Pb^{2+} concentration (10-200 mg/L), solution pH (2-10), CMOSW dosage (0.2-1.6 g/L) and contact time (30-180 min).

After the batch adsorption experiment was completed, the adsorbent was removed from the suspension using a centrifuge and the residual Pb^{2+} concentration was measured by an atomic absorption spectrophotometer (Model VGP 210, US). The quantity of Pb^{2+} removed at the equilibrium, q_e (mg/g) and the removal percentage, Y (%) were determined as follows:

$$q_e = (C_o - C_e) \times \frac{V}{m} \tag{1}$$

$$Y = \frac{(C_o - C_e)}{C_o} \times 100\% \tag{2}$$

2.4. ADSORPTION ISOTHERM

Two-parameter isotherm model (Langmuir and Freundlich) was employed in evaluating the experimental data for the Pb^{2+} adsorption by CMOSW. The nonlinear isotherm models are as given by Eqs. 3 and 4.

$$q_e = \frac{q_{max}bC_e}{(1 + bC_e)} \quad \text{(Langmuir model)} \tag{3}$$

$$q_e = k_F C_e^{1/n} \quad \text{(Freundlich model)} \tag{4}$$
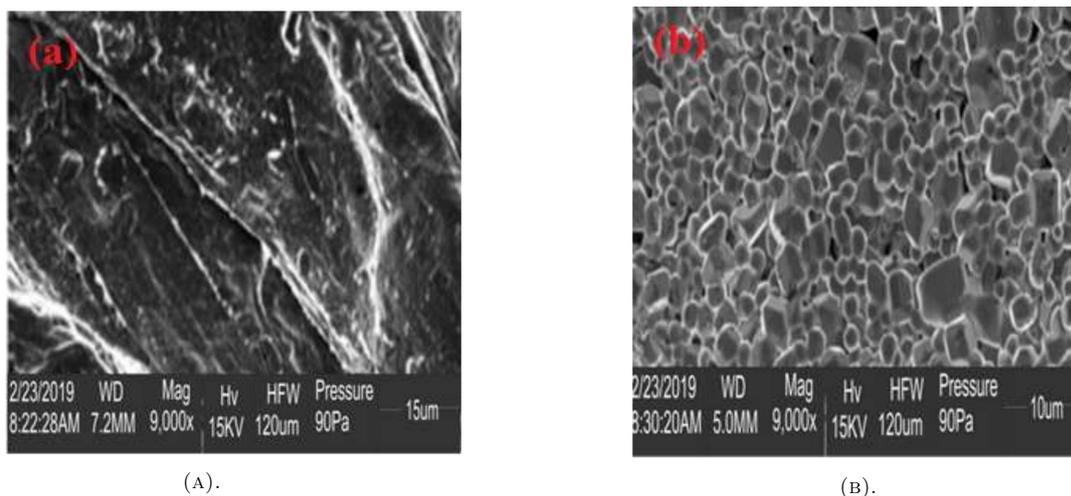
(A).

(B).

FIGURE 1. SEM micrographs of CMOSW sample (a) prior to and (b) after Pb^{2+} ions adsorption.

Separation factor (R_L), a dimensionless parameter, was applied in determining the nature of Pb^{2+} adsorption onto the CMOSW adsorbent. The dimensionless parameter signifies whether the adsorption process is favourable ($0 < R_L < 1$), non-favourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

$$R_L = \frac{1}{(1 + bC_O)} \quad (5)$$

2.5. ADSORPTION KINETICS

Adsorption kinetics describes the rate at which the amount of adsorbate removed varies with time. The kinetic data for the adsorption of the Pb^{2+} onto chemically modified onion skin were analysed using pseudo-first-order and pseudo-second-order kinetic equations.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (6)$$

(Pseudo-first-order)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (7)$$

(Pseudo-second-order)

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF CMOSW ADSORBENT

The morphological structure of the prepared CMOSW before and after the Pb^{2+} adsorption was determined using the SEM analysis, and the micrographs are shown in Figure 1. Figrue 1a revealed that the prepared adsorbent had an almost regular surface containing a long but tiny cavity and pores of different sizes, suggesting a reasonable possibility of a rapid

adsorption of the Pb^{2+} ions. However, upon adsorption of the cation, that large cavity, earlier observed on the fresh CMOSW sample, was filled as a result of the Pb^{2+} adsorption.

The FTIR spectrum of the CMOSW adsorbent before the adsorption of Pb^{2+} is displayed in Figure 2 (a) with several bands at $3496.21\,cm^{-1}$ (O-H stretching vibration), $2968.87\,cm^{-1}$, $2980.24\,cm^{-1}$ (C-H asymmetric and symmetric stretching), $1654.06\,cm^{-1}$ (C=O deformation), $1380.71\,cm^{-1}$ (CH$_3$ deformation), $1086.23\,cm^{-1}$ (-C-NH$_3$ primary aliphatic amine), $652.45\,cm^{-1}$ (C-O-H twist broad) and $458.34\,cm^{-1}$ (C-N-C bending modes). The detection of all these functional groups was an indication that the CMOSW adsorbent was complex. However, upon adsorption of the metal ions (Figure 2 (b)), some peaks shifted, and new bands at $3452.26\,cm^{-1}$ (O-H stretching vibration), $1698.17\,cm^{-1}$ (C=O deformation), and $400.57\,cm^{-1}$ (-C-N-C bending modes) were also formed.
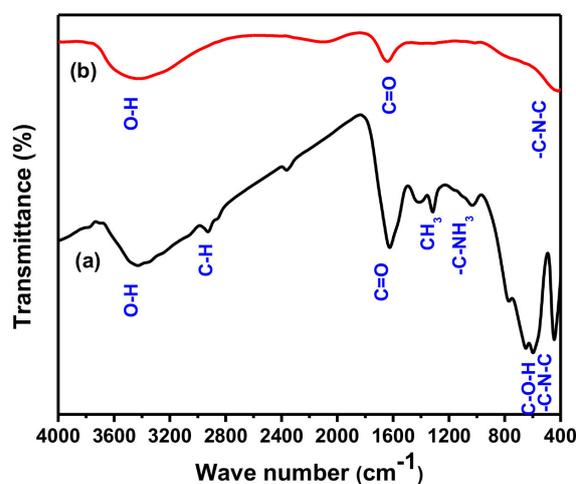

FIGURE 2. FTIR spectra of CMOSW sample (a) prior to and (b) after Pb^{2+} ions adsorption.

Sample	Specific area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
Fresh CMOSW	26.5	0.17	317.9
CMOSW loaded with Pb^{2+}	2.8	0.01	201.7

TABLE 1. Textural characteristics of CMOSW before and after adsorption of lead ions.

Table 1 presents the textural properties of the prepared CMOSW adsorbent before and after the loading of lead ions. The results showed that the fresh adsorbent possessed a large surface area and pore size distribution, and this was an indication that the studied sample had several sorption sites on its surface. The BET surface area of the prepared composite adsorbent was $26.5\,m^2/g$, as seen in Table 1, which was above the surface areas of the acid-modified onion skin ($10.62\,m^2/g$) [23] and garlic waste ($5.62\,m^2/g$) [28]. However, there was a significant reduction in textural properties (surface area, total pore volume and average pore diameter) of the CMOSW sample after the adsorption of Pb^{2+}. These observations were attributed to the agglomeration or overlapping of the sorption sites available for the adsorbates, as corroborated by the SEM result.
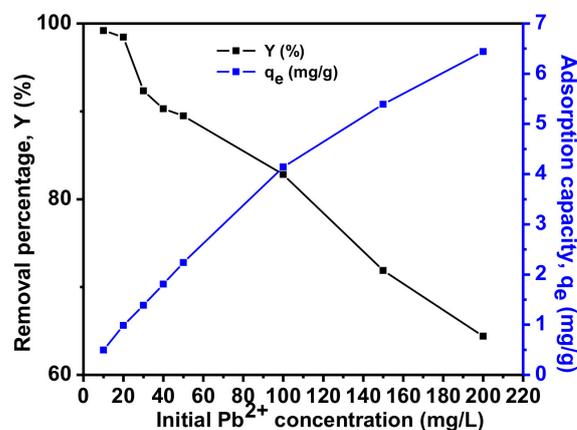
3.2. INFLUENCE OF ADSORPTION PROCESS PARAMETERS

### 3.2.1. INFLUENCE OF INITIAL LEAD IONS CONCENTRATION

The influence of the initial Pb^{2+} concentration (10-200 mg/L) on the adsorption process was investigated by treating the lead salt contaminated solution at room temperature and pH of 6.0 for 120 min using 1.0 g/L of the CMOSW sample. Figure 3 revealed that the removal percentage decreased, and the equilibrium adsorption capacity increased as the lead ions concentration increased. This observation was due to the same number of adsorption sites, which were available for the increasing adsorbate concentration. It could be deduced that at a higher concentration of Pb^{2+} ions, the sorption sites on the CMOSW surface for the electrostatic attraction were occupied by more contaminants, thus leading to an increase in equilibrium uptake capacity of the CMOSW adsorbent and a decrease in the removal percentage of the adsorbate [29]. Similar observations were also reported for an adsorptive removal of heavy metals by *Moringa stenopetala* bark powder [30], prawn shells [31] and paper mill sludge activated carbon [10].

3.2.2. INFLUENCE OF CONTACT TIME

Figure 4 shows the effect of the contact time on the removal percentage and equilibrium adsorption capacity at a fixed Pb^{2+} concentration of 50 mg/L, pH of 6 and a CMOSW dosage of 1.0 g/L. The figure revealed that both the removal percentage and equilibrium adsorption capacity speedily increased with an increase in the contact time and then decreased until an equilibrium was attained. Generally, a prolonged contact time

FIGURE 3. Influence of initial concentration on Pb^{2+} adsorption onto CMOSW.

favours the adsorption process by enhancing the uptake of adsorbate and also increasing the equilibrium sorption capacity of the adsorbent [16]. As seen in the figure, after the contact time reached 120 min, both the removal percentage and the sorption capacity plots became nearly flat, which indicated that the adsorption equilibrium had been reached. This observation agrees with the work reported for a Pb^{2+} removal from aqueous solutions by inactive biomass [5], *Moringa stenopetala* bark [30] and dead anaerobic biomass [32].
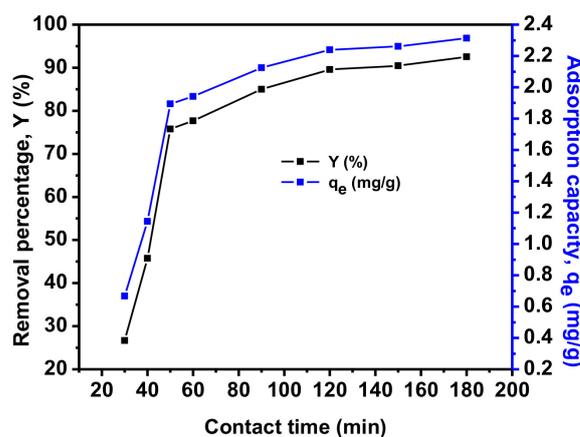
FIGURE 4. Influence of contact time on Pb^{2+} adsorption onto CMOSW.

3.2.3. INFLUENCE OF ADSORBENT DOSAGE

To investigate the influence of the CMOSW dosage on the adsorption of lead ions, we used different quantities

of the CMOSW sample (0.2-1.6 g/L) to treat a lead ion-containing solution at a fixed adsorbate concentration of 50 mg/L, solution pH of 6.0 and a contact time of 120 min. The results showed that the removal percentage of Pb^{2+} increased as the CMOSW loading also increased, while the adsorption capacity exhibited a reverse trend. When the adsorbent dosage rose from 0.2 to 1.6 g/L, the removal percentage increased from 47.98 to 98.24 % because of more active sites for Pb^{2+} ions and the equilibrium sorption capacity decreased from 5.99 to 1.54 mg/g. A similar observation was also reported for a Pb^{2+} ion removal by soil [33].
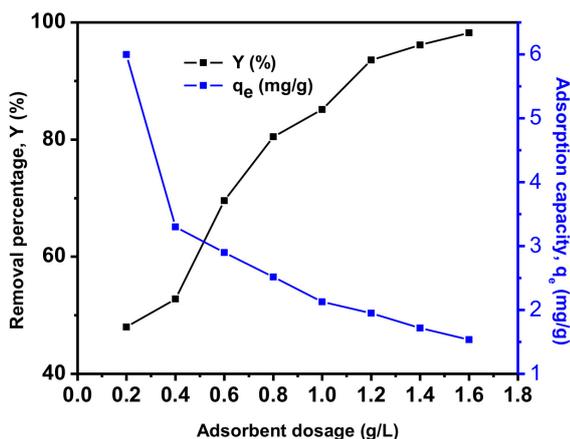

FIGURE 5. Influence of adsorbent dosage on Pb^{2+} adsorption onto CMOSW.

3.2.4. INFLUENCE OF AQUEOUS SOLUTION pH

The influence of pH on the adsorption of lead ions onto a chemically modified onion skin waste was studied at a fixed initial Pb^{2+} concentration of 50 mg/L, a contact time of 120 min and an adsorbent dosage of 1.4 g/L. Figure 6 shows a combined plot of removal percentages and adsorption capacity of Pb^{2+} versus the pH of the simulated solutions. The figure showed that the removal percentages of the cation increased as the pH increased from 2 to 6 and then decreased after the aqueous solution pH exceeded the optimum value. This result indicated that a substantial amount of lead ions could be adsorbed by the CMOSW adsorbent under acidic conditions. In contrast, the adsorption of Pb^{2+} significantly decreases under basic conditions.

3.3. ADSORPTION ISOTHERMS

The non-linear plot of the quantity of Pb^{2+} adsorbed at the equilibrium against the equilibrium concentration for the Langmuir model, Freundlich model and experimental data are displayed in Figure 7. The estimated isotherm parameters, which were obtained from the plot, are presented in Table 2. The best among the models was selected based on the value of the coefficient of determination (R^2). Therefore, the R^2 value (0.9881) suggested that the experimental data better fitted the Freundlich isotherm model.
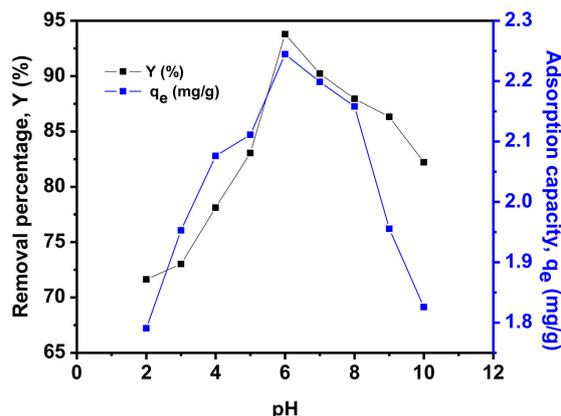
FIGURE 6. Influence of pH on Pb^{2+} adsorption onto CMOSW.

A similar observation was also reported for a Pb^{2+} adsorption by polypyrole-based activated carbon [34] and hazelnut husks based activated carbon [35].

The values of the separation factor and Freundlich exponent for the lead ions, as can be seen in Table 2, suggested favourability and capacity of the Pb^{2+} ions – CMOSW system [36]. By comparing the adequacy of the two isotherm models, it can be concluded that the Freundlich isotherm was suitable to describe the Pb^{2+} adsorption onto the chemically modified onion skin waste.
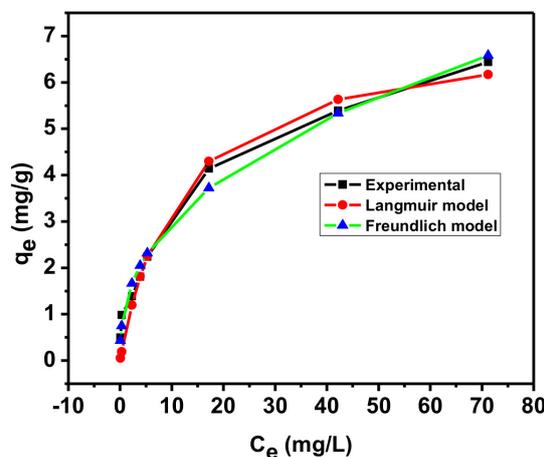

FIGURE 7. Application of two-parameter isotherm to Pb^{2+} adsorption onto CMOSW.

The monolayer adsorption capacity of CMOSW was compared with other reported adsorbents for the adsorption of Pb^{2+} from an aqueous solution at different optimum operational parameters, as shown in Table 3. The Table showed that the CMOSW adsorbent had a strong affinity for the Pb^{2+} removal from an aqueous solution by exhibiting a high maximum uptake capacity of 7.16 mg/g. This value was obtained under the optimum process condition of 50 mg/L initial concentration (C_o), 120 min contact time (t), 1.40 g/L

Isotherm	Value	Unit
Langmuir		
q_{max}	7.16	$mg \cdot g^{-1}$
b	0.09	$L \cdot mg^{-1}$
R^2	0.9847	–
R_L	0.05	–
Average relative error	0.128	–
Freundlich		
k_F	1.19	$Mg \cdot g^{-1}(L \cdot mg^{-1})^{1/n}$
n	2.50	–
R^2	0.9881	–
Average relative error	0.050	–

TABLE 2. Values of two-parameter isotherm constants.

Adsorbent source	q_m (mg/g)	Experimental condition					Reference
		C_o (mg/L)	t (min)	d (g/L)	pH	T (°C)	
Apricot stone	21.38	50	–	1.0	6.0	20	[37]
Hazelnut husk	13.05	200	–	12.0	5.7	18	[35]
Sand	21.78	50	30	2.0	2.0	65	[38]
Groundnut shell	3.428	75	90	8.0	6.0	–	[39]
Soya bean	0.55	–	60	3.0	4.0 ± 0.26	37	[40]
Moringa stenopetala bark	35.71	10	120	1.5	5.0	40	[30]
CMOSW	7.16	50	120	1.4	6.0	28 ± 2	Present study

TABLE 3. Comparison of the adsorption capacities of different adsorbents for Pb^{2+} removal.

adsorbent dosage (d), pH of 6.0, and $28 \pm 2\,°C$ temperature (T). These findings indicated that CMOSW was an efficient adsorbent for lead ions removal from water/wastewater, mostly when compared with those adsorbents derived from groundnut shell [39] and soya bean [40].

3.4. ADSORPTION KINETICS

The plot of $\log(q_e - q_t)$ against t (pseudo-first-order) and t/q_t against t (pseudo-second-order), from which the rate constants (k_1 and k_2) and predicted quantity of Pb^{2+} adsorbed at the equilibrium (q_e) were determined, are shown in Figure 8. The estimated kinetic parameters and R^2 values are given in Table 4. The results revealed that the predicted q_e did not correlate with the observed q_e in the case of pseudo-first-order kinetic. Besides, its R^2 value (0.9773) was lower than that of the pseudo-second-order kinetic model. Therefore, the pseudo-second-order kinetic model was applied to evaluate the obtained adsorption data. The result obtained showed that the predicted q_e was found to be in agreement with the experimental q_e with the value of the coefficient of determination being 0.9996, which rendered it suitable for describing the adsorption kinetics of Pb^{2+} onto CMOSW.
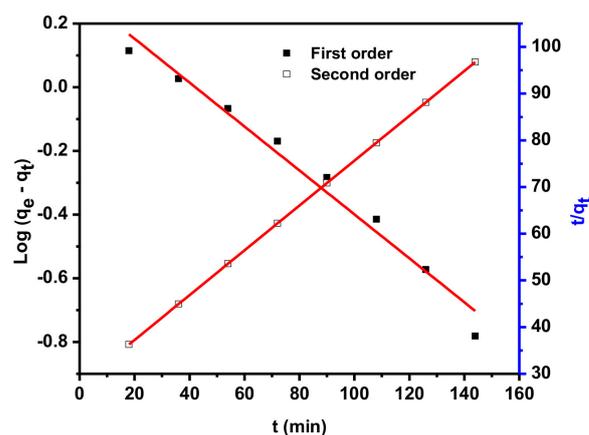
FIGURE 8. Pseudo-first-order and pseudo-second-order kinetics for Pb^{2+} removal by CMOSW.

3.5. ADSORPTION MECHANISM

The lead ions covered the surface and diffused into the pores of the CMOSW adsorbent by capillary force, which was confirmed by the results of the textural properties (surface area and pore size) analysis (Table 1). Thus, the CMOSW adsorbent with better

Kinetic model	Parameter values	Unit
Pseudo-first-order		
q_e (exp)	1.443	$mg \cdot g^{-1}$
q_e (cal)	1.337	$mg \cdot g^{-1}$
k_1	0.016	min^{-1}
R^2	0.9773	–
Pseudo-second-order		
q_e (cal)	1.462	$mg \cdot g^{-1}$
k_2	0.0086	$g \cdot mg^{-1} \cdot min$
R^2	0.9996	–

TABLE 4. Kinetic models and their parameters for Pb^{2+} adsorption onto CMOSW.

textural characteristics would adsorb more lead ions. The capillary force within the mesopore facilitated the diffusion of the metal ions, which enhanced the overall adsorption capacity. Additionally, the electrostatic interaction, which occurred between the lead ions and negative functional groups (O-H and C=O) on the adsorbent surface, also aided the adsorption. Therefore, the adsorptive removal of lead ions by CMOSW involved a synergy between the capillary forces and electrostatic interactions [41].

4. CONCLUSION AND FUTURE RECOMMENDATIONS

This study has revealed that an adsorbent prepared from onion skin was efficient for the removal of Pb^{2+} from an aqueous solution. The Freundlich isotherm model provided a better fit of the equilibrium adsorption data, indicating a multilayer adsorbate-adsorbent system with the dominance of the chemisorption. The maximum removal efficiency of $97.3 \pm 0.01\%$ was achieved at an optimum adsorbent dosage of $1.4\,g/L$, a contact time of $120\,min$ and pH of 6.0. The pseudo-second-order model proved to best describe the kinetic data. The change in the adsorbent structure and peak changes of the spectra after adsorption, as revealed by SEM and FTIR analyses, respectively, suggested a distinct adsorption of the Pb^{2+} onto CMOSW. The removal of Pb^{2+} by CMOSW via an adsorption process experiment led to encouraging results, and we authors wish to achieve the same breakthrough in an adsorption column mode under the conditions applicable to the treatment of industrial wastewater. The current investigation also revealed that CMOSW has a potential as an effective adsorbent for the toxic heavy metals and dye removal.

LIST OF SYMBOLS
C_o initial concentration [mg/L]
C_e equilibrium concentrations [mg/L]
V solution volume [L]
m mass of adsorbent use [g]
q_e amount of metal ion adsorbed at equilibrium [mg/g]

q_{max} maximum adsorption capacity [mg/g]
b Langmuir equilibrium constant
k_F adsorption capacity of the adsorbent [mg/g(L/mg)$^{1/n}$]
n Freundlich exponent
q_t amount of metal ion adsorbed at time t [mg/g]
k_1 rate constant for pseudo-first order model [min^{-1}]
k_2 rate constant for pseudo-second order model [g/mg min]

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