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Hydrothermal Synthesis of Multifunctional Biochar-supported SALEN Nanocomposite for Adsorption of Cd(II) Ions: Function, Mechanism, Equilibrium and Kinetic Studies

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Facile hydrothermal synthetic technique was employed for the fabrication of bis(salicylidene)ethylenediamine (SALEN) grafted multifunctional nanocomposite biochar, aiming at the efficient removal of cadmium (Cd). The elemental composition and structure of the composite and the cadmium loaded sorbent were characterized using EDX, FTIR and SEM. Variables affecting cadmium removal such as initial metal ion concentration, contact time and pH were investigated by batch experiment. Maximum adsorption capacity of 8220 mg kg⁻¹ was obtained at optimal pH 5 with percentage removal efficiency of 99.30% for 4480 ppm initial metal ion dosage. The data simulated using the adsorption and kinetic models were fitted well in the Freundlich isotherm implicating multilayer adsorption-chemisorption process and pseudo-second-order kinetic as the rate limiting steps. Critical examination of the adsorption mechanism showed that inner-sphere complexation, ion exchange, co-precipitation and electrostatic attraction are the main driving force in the mechanistic interaction of the Schiff base N₂O₂ surface functionalized nanocomposite biochar with cadmium. The new nanocomposite is of low cost, benign, effective and efficient for the removal of cadmium in comparison with industrial sorbents and other functionalized biomaterials, and highly recommended for decontamination of cadmium polluted sites.

Keywords: Adsorption, Cadmium, Multifunctional biochar nanocomposite, Functionalization, Mechanism

INTRODUCTION

Heavy metals even at low concentrations exert significant health impact on animals and the ecosystem when consumed or interact with the system [1]. Lack of proper treatment or none treatment of municipal wastes and sewages, industrial effluents, agricultural production related waste and general waste water from other sources leads to heavy metal contamination and serious global environmental challenges [2]. Globally, pollution of water sources by heavy metals is undoubtedly a serious challenge in the environment and has imparted adversely on the health of man and livestock [3,4]. Heavy metals are considered as environmental toxicant and non-biodegradable [4,5].

Cadmium, one of the heavy metals, due to the deleterious effect is considered as an important food and water contaminant, and a human carcinogen that adversely affect the human health and the seventh most dangerous element to human health that should be extensively researched [6,7,8]. Health challenges such as hypertension, disruption of central nervous system, psychological imbalance, reproductive malfunctioning, stomach cramps ,malformation of bones, tissues and cartilages and renal dysfunction are attributed to cadmium infiltration into body of animals and plants either by inhalation, ingestion, root uptake or absorption through nanosized complexation, cation exchange or precipitation [1,9]. The occurrence of

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cadmium in combination with other metals such as nickel, copper, lead and zinc in the earth crust and in anthropogenic sources such as coatings, batteries and alloys and plating in industrial synthesis has remained the main source of leakage or seepage of this toxicant into water and food sources [10]. Due to the harmful nature of cadmium, several traditional methods have been applied to remove it from water, food and soil included ion exchange, chemical precipitation, electroplating and membrane separation, cloud point separation, and solvent extraction [11-15]. There are myriads of limitation with the listed techniques ranging from time wastage of operation, matrix effect, outrageous costs, low sensitivity, emulsion formation, low concentration to volume ratio to generation of secondary wastes [16-19]. To overcome these shortcomings, a more reliable, efficient and effective cadmium removal technique which uses a low cost, simple, regenerable, mechanically stable and chemically inert lignocellulosic waste material whose functionality increases with increase in impregnation of dopants is currently the most favoured [17,20]. Biochar is a solid product of the thermochemical conversion of agricultural products such as wood, animal dung, grasses, and agricultural waste residues that has high porosity and large number of surface functional groups profiling it as effective and efficient adsorbent material for sorption of cadmium from water [2]. Saw dust is a waste biomass of wood originated from wood workshops and are readily available, cheap, environmentally friendly that accumulates in the environment as waste. Conversion of saw dust biomass, its immobilization with a dopant to increase the functionality, and exploring the striking adsorbent qualities forms the fulcrum of the applicability of this sorbent in industrial processes.

Conversion of lignocellulosic waste into biochar by carbonization or pyrolysis temperatures between 400-900 °C for the removal of cadmium is currently the research focus because biochar is environmentally friendly, modifiable, and has high surface area. Modified biochar has been used for the removal of heavy metals from environmental matrices with promising results which are observable from increased adsorption capacity due to increased functionality and mechanical stability [17]. Bis(salicylidene)ethylenediamine (SALEN), а tetradentate Schiff base ligand has electron donating and

withdrawing properties and stabilizes metals in low and high oxidation state. The presence of N, and O atoms in the imine moiety and phenyl ring confers a strong complexing character on the ligand when it comes to contact with metals containing vacant orbitals for co-ordination [21]. Immobilization of biochar surface increases the interaction between cadmium and the composite due to increased surface complexation, ion exchange and precipitation owing to increased surface polarity, functionality, chelation property and decreased hydrophobicity [13].

In line with the current research on sustainable development goals, there is need for a reliable, efficient, effective, cost friendly, replicable and environmentally friendly approach for the removal of cadmium from environmental matrices. The objective of this study therefore includes the synthesis of efficient, effective and mechanically stable low cost SALEN immobilized biochar composite of saw dust origin, characterization of the biochar and composite using SEM/EDX and FTIR to understand the structure, composition and mechanism of adsorption of Cd(II) ions, application of the composites for the removal of Cd(II) ions from aqueous solution evaluating the variables of time of contact, initial Cd(II) ions concentration and pH, applying the generated data in simulation of the adsorption isotherms and kinetics of Cd(II) ions removal from aqueous solution and finally comparison of generated data on adsorption capacity of the composite with other works from literature. To achieve the last objective, literature survey was conducted using different search terms such as impregnation, immobilization, doping, functionalization and modification of biochar for adsorption or removal of cadmium from solution using different search engines. The first work based on available record on the use of modified biochar for the removal of cadmium was that of Zhou and coworkers on bamboo biochar modified with chitosan [22]. A total of 35 different works was seen online specifically on the removal of cadmium using impregnated, modified, grafted, immobilized, doped or functionalized biochar. A critical comparison on the adsorption capacity and mechanism of adsorption of the functionalized biochar was presented. Good enough, none of the literature work had used SALEN or Schiff base as a dopant or functionalizing agent for biochar immobilization for the sorption of cadmium from

aqueous solution. In addition, from literature reviewed, no existing work involving the use of Schiff base immobilized saw dust biochar composite exists laying further credence to this novel, green, facile and replicable study. Future work will appraise the physicochemical aspects, characterization, preparation methods and conditions, applicability, reliability and replicability of the method and reusability of the composites.

MATERIALS AND METHODS

Reagents and Materials

The analytical grade reagents used in this study, including carbon tetrachloride, cadmium sulphate, hydrochloric acid, aqueous ammonia, salicyladehyde, sodium hydroxide, ethanol and ethylenediamine, were purchased from Merck company.

The functional group and bonding pattern as well as mechanism of chelation of the activated saw dust biochar (SDB), the SALEN impregnated saw dust biochar composite (SISDBC) and cadmium loaded SALEN impregnated saw dust biochar composite (CLSISDBC) were studied using Cary 630 Agilent Technologies, USA, for functional group determination. The morphology of SISDBC and CLSISDBC was obtained using Bruker® D8 Discover x-ray diffractometer, equipped with a Lynx Eye detector, under Cu-Ka radiation (1¹/₄ 1.5405 Å). Concentration determination of the sample aliquots was done using Buck 205 Scientific Atomic Absorption Spectrometer (AAS). Elemental composition of SISDBC and CLSISDBC was determined using Phenomprox by Phenom-World Eindhoven, Netherlands. Drying and equilibration were done using drying oven (model DHG) and rotary shaker (RF-12 Remi equipment), respectively.

Synthesis and Activation of Saw Dust Biochar

The saw dust was collected in polyethene bags from Abakaliki timber shade, cleaned and washed severally with deionized water and kept under the sun to dry for 7 days and then subjected to a temperature of 90 °C for 12 h in an oven. Exactly 500 g of the oven dried biochar was subjected to N₂ environment pyrolysis in a furnace at the temperature of 550 °C for 2 h as previously reported [23]. The biochar

produced was collected, ground and activated using $0.5\ M$

HCl for 2 h and washed severally to neutral pH with distilled water. The HCl activated biochar was then dried in an oven (Model DHG) at 110 °C for 12 h and the product was collected and kept for further analysis.

Synthesis of the Dopant

Bis(salicylidene)ethylenediamine (SALEN) was according to the literature procedure [24] using ethylenediamine and salicylaldehyde as the precursors in a 1:2 mole ratio. The exothermic process gave yellow product which was recrystallized twice from carbon tetrachloride to yield golden yellow crystals [64.45% yield, M. P.: 121 \pm 1 °C]. The product formed was stored in a container and used when required.

Fabrication of SALEN Impregnated Biochar Composite

The SALEN impregnated saw dust biochar composite (SISDBC) was synthesized by hydrothermal method. Firstly, 5% of SALEN solution was prepared by dissolving 5 g of SALEN in 100 ml of ethanol. In the synthetic process, 20 ml of the SALEN solution was mixed with 5 g of activated rice husk biochar in a beaker. The mixture was agitated for 6 h using mechanical shaker to ensure complete reaction and saturation of the activated saw dust biochar sites. The unadsorbed SALEN was removed by filtration and SISDBC was isolated, washed repeatedly with distilled deionized water and dried in an oven at 110 °C for 3 h. The composite fabricated was kept for further analysis.

Adsorption Experiments

The extraction variables of initial metal ion concentration, time of contact and pH were studied using the batch experimental design.

Variation of initial metal ion concentration: To understand the effect of initial Cd(II) ion concentration on the adsorption of the composite, 0.05 g of the composites was added to 10 ml of different concentrations of Cd(II) solution (0.1, 0.01, 0.001, 0.0001 M) in extraction bottles and at fixed pH of 10 and the mixture was equilibrated at room temperature (30 ± 1 °C) for 60 min using mechanical shaker (100 rpm). The resulting solution was filtered after replicate study and the solution aliquot was analyzed using AAS analysis. Variation of time of contact: The time of contact of the immobilized nanocomposite in relation to Cd(II) ions removal was varied between 30-120 min. In the process, 0.05 g of the biochar was added into 10 ml of 0.0001 M Cd(II) solution maintained at pH 10. The mixture was equilibrated and the extraction bottle removed at intervals of 30, 60, 90 and 120 min. The resulting solution was filtered after replicate measurement and the combined filtrate subjected to AAS determination.

Variation of pH: The adsorption pH was varied between 2-11. In the process, 0.05 g of the nanocomposite was added to 10 ml of each of 0.0001 M Cd(II) ion solution. The mixture was equilibrated at room temperature $(30 \pm 1 \text{ °C})$ for 60 min (100 rpm) and the resulting solution was filtered. The Cd(II) ion in the combined filtrate, after triplicate analysis, was determined using AAS analyzer.

The surface coverage degree (Z), distribution coefficient (K_d), dosage concentration (S), the adsorption capacity (" α "), percentage of Cd(II) ions adsorbed (%), quantity of cadmium adsorbed (qt) at time t, and Cd(II)-ligand adsorption capacity ratio (ω) were evaluated using Eqs. (1)-(7), respectively [17,23].

$$Z = 1 - \frac{C_e}{C_0} \tag{1}$$

 $k_{d} = \frac{amount \ of \ metal \ in \ adsorbent}{amount \ of \ metal \ in \ solution} \times \frac{1}{S}$ (2)

$$S = \frac{m}{V} \tag{3}$$

$$\alpha = \frac{(C_0 - C_e)V}{m} \tag{4}$$

$$%Cadmium \ chelated = \frac{C_0 - C_e}{C_0} \times 100$$
(5)

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{6}$$

$$\omega = \frac{Metal \ adsorption \ capacity}{Surface \ coverage} \tag{7}$$

The variables $C_0 (mg l^{-1})$, $C_e (mg l^{-1})$, $C_t (mg g^{-1})$, V (l)

and m (g) stand for the initial Cd(II) concentration, final concentration of the Cd(II) ion, concentration of Cd(II) ion at time t, volume of aqueous solution and weight of composite, respectively.

Data generated were used to simulate the linear adsorption models of Langmuir and Freundlich and pseudofirst order and pseudo- second order kinetics models while equation of line of best fit was used for evaluating the coefficient of determination (R^2) to arrive at the adequacy and applicability of the models.

RESULTS AND DISCUSSION

EDX Analysis of SDB, SISDBC and CLSISDBC

The EDX analysis gives the weight concentration of the elements present (%) in the SISDBC and CLSISDBC and are presented in Figs. 1 and 2, respectively. As seen in Figs. 1 and 2, the percentage composition of the elements present in SISDBC are 78.16% C, 7.98% O, 3.24% Si, 2.26% Al, 1.85% Ag, 1.76% N, 1.34% Ca, 0.94% K, 0.67% S, 0.61% Fe, 0.55% P, 0.51% Mg and 0.13% Na, while the percentage composition of the elements in CLSISDBC is 73.22% C, 8.53% O, 6.75% Cd, 2.59% Si, 1.98% Al, 1.43% Cl, 1.24% Ca, 0.81% Fe, 0.71% Ti, 0.65% S, 0.59% K, 0.58% P, 0.39% Mg, 0.31% N and 0.21% Na. This clearly shows that 6.75% of cadmium is present in CLSISDBC which was previously absent in SISDBC. It further showed that cadmium was actually adsorbed onto the biochar composite surface either by complexation, cation exchange or precipitation. Table 1 clearly revealed the variation in the elemental composition of SISDBC and CLSISDBC. Increase or decrease in the percentage atomic ratio of the elements such as O, P, Si, N is a strong confirmation of underlying cation exchange process.

The hydrophobicity, surface polar functional group and cation exchange capacity of SISDBC and CLSISDBC are shown in Table 2. The atomic ratio (O/C) of CLSISDBC (Table 2) is 0.166 which is higher than the atomic ratio of SISDBC (0.102). The high atomic ratio of CLSISDBC defines high cation exchange capacity, low hydrophobicity, greater metal chelation ability and greater surface functionality [13,25]. Similarly, decrease in percentage of atomic weight of oxygen implies increased hydrophobicity and justifies greater surface functionality (Shen *et al.,*



1		THE AN		Element	Element	Element	Atomic	Weight
	US The	NY/A	TAN Y	number	symbol	name	Conc.	Conc.
al and			4 4 4 5 15		0	Center	0(00	70.16
E ENT	Sino Maria		2011-6	6	C	Carbon	86.98	/8.16
	123761		CT -CT	8	0	Oxygen	6.66	7.98
2		FALAS.		14	Si	Silicon	1.54	3.24
Frank b	COD /A		100 -0	13	Al	Aluminium	1.12	2.26
AL S				47	Ag	Silver	0.23	1.85
A AND		And St		7	Ν	Nitrogen	1.68	1.76
				20	Ca	Calcium	0.45	1.34
		A STA		19	Κ	Potassium	0.32	0.94
			And the	16	S	Sulfur	0.28	0.67
		A CARLON		26	Fe	Iron	0.15	0.61
				15	Р	Phosphorus	0.24	0.55
	Martin and			12	Mg	Magnesium	0.28	0.51
201/2331		15kV - Map	OCT 22 2019 14:09	11	Na	Sodium	0.07	0.13
100 µm	∢⊺ 537 um							

Fig. 1. EDX image showing the elemental composition of SISDBC.

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	Element number	Element symbol	Element name	Atomic Conc.	Weight Conc.
	6	С	Carbon	86.39	73.22
The Reader of the second	8	0	Oxygen	7.55	8.53
	48	Cd	Cadmium	0.85	6.75
	14	Si	Silicon	1.31	2.59
	13	Al	Aluminium	1.04	1.98
	17	Cl	Chlorine	0.57	1.43
	20	Ca	Calcium	0.44	1.24
	26	Fe	Iron	0.21	0.81
	22	Ti	Titanium	0.21	0.71
	16	S	Sulfur	0.29	0.65
	19	Κ	Potassium	0.21	0.59
	15	Р	Phosphorus	0.27	0.58
	12	Mg	Magnesium	0.23	0.39
	7	Ν	Nitrogen	0.31	0.31
	11	Na	Sodium	0.13	0.21
100 μm 4] 537 μm					

Fig. 2. EDX image showing the elemental composition of CLSISDBC.

Elements	SISDBC%	CLSISDBC%
С	78.16	73.22
0	7.98	8.53
Cd	-	6.75
Si	3.24	2.59
Al	2.26	1.98
Ca	1.34	1.24
Fe	0.61	0.81
S	0.67	0.65
K	0.94	0.59
Р	0.55	0.58
Mg	0.51	0.39
Ν	1.76	0.31
Na	0.13	0.21

Table 1. Percentage of Elemental Composition of SISDBC and CLSISDBC

Table 2. Surface Polar Functional Groups, Cation Exchange Capacity and Hydrophobicity of

 SISDBC and CLSISDBC

	Carbon (C)	Oxygen (O)	Nitrogen (N)	(O + N)/C	O/C
SISDBC	78.16	7.98	1.76	0.125	0.102
CLSISDBC	73.22	8.53	0.31	0.121	0.116

2014). The higher atomic ratios of (O + N)/C for SISDBC (0.125) compared to CLSISDBC (0.121) indicates the greater surface polar groups and greater adsorption capacity due to more binding sites. The presence of the exposed multifunctional surface of the composite leads to conjugation by complexation, cation exchange or precipitation which lowers the surface activity of CLSISDBC. The low atomic ratio of CLSISDBC indicates less pores are exposed due to saturation upon adsorption of cadmium. Critical examination of the composition of

SISDBC indicates high amounts of calcium, potassium and phosphorus implicating the composite as soil amendment agent capable of sequestering heavy metallic and other anionic species that may be trapped on the multifunctional surface.

SEM Analysis of SDB, SISDBC and CLSISDBC

The surface morphology of SISDBC and CLSISDBC characterized using SEM/EDX is presented as micrograph in Figs. 3 and 4, respectively, at different magnifications.



Fig. 3. SEM micrographs of SISDBC at different magnifications.

The microporous SEM images of SISDBC contained irregular porous surface that is conspicuous, rough and highly corrugated with enough micropores that could lead to increased adsorption of matrixes which is consistent with other studies [26,27].

The SEM micrograph of CLSISDBC looks well

dispersed and observed as clusters of small particles not initially contained in SISDBC. These clusters of patches granular polymers in the macropore were originally absent in the composite, and present after adsorption of Cd(II), suggesting that the porous multifunctional surface has actually captured the contaminant which could have existed



Fig. 4. SEM micrographs of CLSISDBC at different magnifications.

as cadmium compound layer.

FTIR Analysis of SDB, SISDBC and CLSISDBC

The mechanism of adsorption of Cd(II) ions on the SALEN impregnated sawdust nanocomposite could be explained by the interactions of the surface functional

groups or bonds on the multifunctional nanocomposite surface [28]. The major functional groups in the saw dust biochar (SDB), SISDBC and the after sorption of Cd(II) ions (CLSISDBC) were identified, assigned to various groups and are presented in Figs. 5, 6, 7 and Table 3. The peaks at 3634, 3678 and 3809 cm⁻¹ were assigned to

Table 3. FTIR Absorption Bands (cm ⁻)) of SDB, SISDBC and CLSISDBC
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Assignment	SDB	SISDBC	CLSISDBC
H ₂ O (Rocking, twisting or wagging vibration)			3809.3,3678
			3634
-OH	3186.9	3242.8	3324.8
С-Н	2922.2	2922.2	2885.0
			2780.6
С=О	1684.8	1871.1	1982.9
Aromatic ring vibration	1580.4	1558.0	1561.8
C-N stretching vibration of amine group		1420	1423
C-O, C=C and C-C-O stretching vibration (ether)	1032.5	1148.0	1207
P-O stretching vibration of PO ₃ ⁴⁻		1017	1021.3
Si-O deformation and stretching modes	872.2	752.9	752



Fig. 5. FTIR absorption bands (cm⁻¹) of activated SDB.



Fig. 6. FTIR absorption bands (cm⁻¹) of activated SISDBC.



Fig. 7. FTIR absorption bands (cm⁻¹) of activated CLSISDBC.

rocking, twisting or wagging vibration of water molecules after adsorption nanocomposite (CLSISDBC) [29] which was absent in the SDB and SISDBC. The Peak at 3186.9 cm⁻¹ for SDB was shifted to 3242.8 cm⁻¹ for SISDBC and to 3324.8 cm⁻¹ for CLSISDBC and was assigned to the O-H stretching vibrations of free hydroxyl group due to inter and intramolecular hydrogen bonding and O-H carboxylic group bands common in lignocellulosic polymeric species [27]. The asymmetric C-H stretching vibration of the aliphatic acid group was observed as bands positioned at 2922.2, 2922.2 and 2885. 0 cm⁻¹ for SDB, SISDBC and CLSISDBC, respectively. The peak at 2780.6 cm⁻¹ which appeared only in the spectra of CLSISDBC was assigned to C-H bond of aliphatic group due to symmetric stretching vibration of CH₂ group [22,28,29]. The stretching vibration of C=O bond resulting from non-ionic carboxyl groups (-COOH, COOCH₃) was observed as peaks centered at 1684.8, 1871 and 1982.9 cm⁻¹ for SDB, SISDBC and CLSISDBC, respectively, and assigned to the esters of the carboxylic acid group and symmetric or asymmetric ionic carboxyl group vibration (-COO-) [30]. The peaks at 1420 and 1423 cm⁻¹ for SISDBC and CLSISDBC, respectively, assigned to the amine group of the SALEN grafted into the biochar, were absent in SDB. The peaks at 1032.5, 1148 and 1207 cm⁻¹ for SDB, SISDBC and CLSISDBC, respectively, were assigned to C-O, C=C or C-C-O stretching vibration of ether group of cellulose, hemicellulose or lignin and could have probably arisen from polysaccharide [31]. The stretching vibration of P-O bond assigned to PO₃⁴⁻ was observed at 1017 and 1021.3 cm⁻¹ for SISDBC and CLSISDBC, respectively, while the peak at 872, 752, 752 cm⁻¹ were assigned to the Si-O deformational or bending vibration of SDB, SISDBC and CLSISDBC, respectively. Participation of P-O and Si-O bonds in the adsorption was further confirmed from the EDX analysis as shown in Table 1, with changes in the atomic ratios of O, P and Si. Observation was made on significant spectral band shift of O-H stretching vibration of free hydroxyl group (Table 3). The difference between the peaks of SISDBC and CLSISDBC for O-H stretching vibration was 82 cm⁻¹ indicating the strong inner-sphere cation complexation interaction between the fabricated biochar composite and cadmium. Similarly, the high spectral band shift as observed

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in the stretching vibration of C=O between the SISDBC and CLSISDBC was also a strong indication that cation exchange may also be in control of the mechanism of adsorption with a little allowance of cation π -bonding [32]. Dominant adsorption mechanism may be due to the interaction of the surface functional group with the cation and due to the multifunctionality of the nanocomposite, improved Cd(II) removal was observed. Immobilization fine tunes and modifies biochar surface functional sites and always is mediated by tuneable properties of the biochar such as porosity, chemical inertness and high adsorption capacity. The covalent cation π -linkages of the hydroxides, metal oxides or amino groups in the surface of the functionalized biochar composite could be due to the dopant or conjugant effect.

Influence of Initial Concentration of Cd(II) Ions

Study of initial metal ion concentration in adsorption experiment is very important as it significantly gives direction on the relative ability or extent of preconcentration and removal ability of metal ions from solution of a named adsorbent [29]. It shows the quantity of metal ions that will be sorbed from solution at given extraction conditions and how variation in the concentration of metal ions in solution drives the extraction profile. The effect of initial concentration of Cd(II) ions adsorbed on the surface of the nanocomposite is illustrated in Figure 8. The percentage of Cd(II) ions adsorbed onto the nanocomposite increased linearly from 4.48 ppm to maximum at 448 ppm at pH 5 and equilibration for 60 min at 301 ± 1 °C. As the concentration of Cd(II) ions increased, exposed sites of the nanocomposite were gradually filled due to surface electrostatic interaction, cation exchange, intermolecular hydrogen bonding, precipitation or surface complexation, and upon saturation there was absence of more exposed surface and regress or steady state adsorption [13,29].

Effect of Shaking Time

Influence of time of contact on the removal of metal ions from solution is germane and significantly affects the adsorbent efficiency [29]. The variation of time of contact for the removal of Cd(II) ions from solution using SISDBC at pH of 5 and initial Cd(II) ion concentration of 4.48 ppm is shown in Fig. 9. It is evident from Fig. 6 that the amount



Fig. 8. Effect of initial Cd(II) ions concentration on the adsorption of Cd(II) onto SISDBC.



Fig. 9. Effect of initial time of contact on the adsorption of Cd(II) onto SISDBC.

of Cd(II) ions adsorbed increased as the time of contact increased from 30 min until equilibrium was attained at 60 min. Further increase in equilibration and shaking time leads to regress in the amount of Cd(II) adsorbed. The regress in the amount of Cd(II) adsorbed above 60 min

equilibration time may be due to concentration effect engineering the desorption of dopant molecules on the surface of the nanocomposite into the adsorption solution [23].

Effect of pH on the Removal of Cd(II) Ions from Aqueous Solution Using SISDBC

The pH of a solution remains the most important factor that determines the sorption efficiency and mechanism of the interaction of the nanocomposite and the metal ions. The pH of sorptive solutions to a great extent influences the chemical nature (speciation) of the metal ions and characteristics of nanocomposite sorbent [29]. The influence of pH on the removal percentage of Cd (II) ions on the interaction of SISDBC with the aqueous Cd(II) ions solution is shown in Fig. 10. It is evident from Fig. 7 that adsorption increases with increase in pH from 2-4 with a dip at pH 6 probably due to ion exchange processes predominantly controlling the sorption at the pH ranges. Possibility of formation of Cd(OH)⁺ due to reduced electrostatic repulsion between Cd(II) and the nanocomposite surface functional group leads to increase the adsorption capacity at the pH 5 and 7. Between pH 8-9, a regress was observed in adsorption capacity which could be due to precipitation of Cd(II) ions in the form of Cd(OH)₂ [33]. Adsorption percentage was seen to be highest at pH of 10 probably because of the electrostatic attraction between the positively charged metal ions and the negatively charged nanocomposite surface functional groups and formation of stable metal hydroxo species. At low pH, deprotonation of the carboxylate group, ligand degradation, demetallation and competitive complexation between the H^+ and SISDBC were prominent [23,34].

Mechanism of Adsorption

Five different mechanistic processes govern the mechanism of adsorption of metal ions from aqueous solution and include complexation, cation exchange, electrostatic chemical interactions. reduction and precipitation [34]. In this study, spectra shift of the hydroxyl group observed was an indication of complexation interaction and co-precipitation leading to the formation of cadmium hydroxide, cadmium oxide and cadmium ammine carbon dots linkages [34]. The complexation observed was highly significant as the functional group in the nanocomposite interacts with the metal ion as shown in Eqs. (8)-(10). Therefore, the variation of FTIR wavelength of O-H from 3242.8 to 3324.8 cm⁻¹ confirmed that Cd(II) was likely bonded to free hydroxyl group through innersphere complexation common among other divalent cations [31]. Complexation of Cd(II) through N atom of the imine could be a possibility and is illustrated in Eq. (11) confirming the wavelength shift from 1420 to 1423 cm⁻¹. In addition, co-precipitation could also be possible due to the interaction between Cd(II) and PO34- (Eq. (12)) clearly shown by the wavelength variation from 1017 to 1021.3 cm⁻¹. Formation of Cd(OH)₂ and Cd₃(PO₄)₂ remains a strong possibility as shown in Eqs. (12) and (13), respectively, and the FTIR analysis is consistent with EDX characterization result. The formation of Cd₃(PO₄)₂ is usually associated with water molecules and this further justifies the presence of the peaks at 3634, 3678 and 3809 cm⁻¹ assigned to rocking, twisting or wagging vibration of water molecules in the after adsorption nanocomposite (CLSISDBC) which were absent in both SDB and SISDBC. This observation is consistent with other studies on the interaction of Cd(II) with PO₃⁴⁻ and further implicated co-precipitation as a mechanism for cadmium adsorption onto the nanocomposite [35].

Spectra shift of the C=O group from 1871.1 to 1982.9 cm⁻¹ indicates cation exchange as also a plausible mechanism for the removal of Cd(II) from aqueous solution and further confirmed by the EDX analysis (Figs. 1, 2 and Table 1) [34];

$$2R_1COO^-(s) + M^{2+}(aq) \longleftrightarrow [(R_1COO^-)_2 M^{2+}](s)$$
(8)

$$2R_1O^{-}(s) + M^{2+}(aq) \longleftrightarrow [(R_1O^{-})_2M^{2+}](s)$$
(9)

$$2R_2OH(s) + M^{2+}(aq) \xleftarrow{} (R_2O^-)_2 M^{2+}](s) + 2H^+ \qquad (10)$$

$$M^{n+} + nRNH_2 \to M(RNH_2)^{n-}$$
(11)

$$Cd^{2+} + 2OH^{-} \to Cd(OH)_2 \tag{12}$$

$$2Cd^{2+} + 2(PO_4)^{3+} \to Cd_3(PO_4)_2 \tag{13}$$

where R_1 represents the surface of the SDB, R_2 the surface of SISDBC, M the metal ion (cadmium) and R an alkyl or aryl group.

Previous work on the chelation of Cd(II) with SALEN shows that it forms extractable complex of the type



Fig. 10. Effect of pH on the removal of Cd(II) ions from aqueous solution using SISDBC at pH 5.

pН



Fig. 11. Langmuir adsorption isotherm.

Cd(H₂SAL) [21]. The quantitative removal of Cd(II) from aqueous solution at pH 10 using the nanocomposite could be as a result of complexation of Cd(II)with the dissociated HSAL⁻ and SAL²⁻ on the surface of the biocomposite. At

higher pH of 10 and above and in the dissociated form, H_2SAL impregnated composite complexes with Cd(II) through the lone electron pair on the oxygen and nitrogen atoms of the SALEN moiety and imine group, respectively.

When the ligand exists in the protonated form predominantly observed at lower pH, [H₄SAL]²⁺ or $[H_3SAL]^+$ is prominent and the immobilized H_2SAL on the surface of the composites may co-ordinate with the Cd(II) to form protonated cationic complex. Competitive interaction of Cd(II) and the hydronium ions in solution at pH 2-4 may likely cause cationic complex degradation, demetallation and instability and regress in the amount of Cd(II) adsorbed. Competitive interaction between the Cd(II) and the hydronium ions diminishes at pH 5 and stable cationic complex was formed with manifestable increase in the quantity of Cd(II) removed. The species M²⁺ and M(OH)⁺ are dominant at pH 5 and pKa of Cd(II) is 10.1 as shown in Eqs. (14)-(16) but the extraction efficiency was predominantly higher at pH 10 [32]. At pH of 10, highest quantity of Cd(II) was adsorbed probably due to the formation of stable metal hydroxo species which significantly enhanced the removal of Cd(II).

$$M^{2+} + nH_2O \to M(H_2O)_n^{2+}$$
 (14)

$$M(H_2O)_n^{2+} \leftrightarrow [M(H_2O)_{n-1}(OH)]^+ + H^+$$
 (15)

$$M^{2+} + nH_2O \xleftarrow{K_a} [M(H_2O)_{n-1}(OH)]^+ + H^+$$
(16)

The mechanisms driving the adsorption of Cd mainly involve ion exchange, inner-sphere complexation, coprecipitation and electrostatic attraction. The major mechanisms include inner-sphere complexation, ion exchange and co-precipitation

Langmuir and Freundlich isotherms

The data from the adsorption experiment were fitted into the Langmuir and Freundlich adsorption isotherms. The linear form of Langmuir and Freundlich adsorption isotherm is shown in Eqs. (17) and (18), respectively. The Langmuir and Freundlich model plots of ce/qe versus ce and $\log q_e vs$. $\log c_e$ are shown in Figs. 11 and 12, respectively, with the isotherm parameters and regression coefficients presented in Table 5. Adsorption capacity is a very important factor to consider in any adsorption system as defines the effectiveness of any adsorption system. The maximum adsorption capacity of the SALEN immobilized saw dust biochar for the sorption of cadmium was 8220 mg kg⁻¹ that was favourably comparable with metal oxide, amine, sulphur and general basic or alkali based impregnated biochar composites as shown in Table 5. The co-ordination affinity of the nanocomposite functionalized surface with cadmium is described by the Langmuir constant (K_L) (Eq. (19)) obtained as the intercept of the Langmuir plot as 0.038 ml mg⁻¹. This binding site affinity is paramount in evaluating the equilibrium parameter (R_L) which defines the extent of affinity for the sorbent-sorbate interaction [32-42].

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{17}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{18}$$

$$R_{L} = \frac{1}{1 + K_{L}C_{0}}$$
(19)

Here, C_0 represents initial Cd(II) ions concentration and K_L is the Langmuir constant, q_m is maximum adsorption capacity, n is the Freundlich adsorption strength and K_F is Freundlich adsorption capacity.

The nature of Langmuir isotherm model is determined by R_L value. If $R_L = 0$, the isotherm is irreversible, if $R_L > 1$, it is unfavourable, if $R_L = 1$, it is linear but if $0 < R_L < 1$ then it is favourable. Simulation of the data and evaluation using the relation in Eq. (19) revealed R_L to be in the range of 0.0058-0.854 giving credence that the adsorption of cadmium onto the functionalized saw dust biochar was favourable. Based on the value of regression coefficient (R^2) (0.6903), it could be suggested that experimental data could not fit well into the Langmuir isotherm. Though the R_L shows possibility of monolayer coverage with uniform and equivalent adsorption sites common in adsorption involving functionalized biochar, the data were not well simulated by this model [10].

Evaluating the Freundlich adsorption model shows the adsorption capacity (K_F) determined at 303 ± 1 K to be 0.000039 mg^{1-1/n}L^{1/n}g⁻¹. The degree of nonlinearity of the adsorption and concentration regarded as Freundlich adsorption strength (n) was evaluated to be 0.188. The value of n implicates the adsorption process to either be



Fig. 12. Freundlich adsorption isotherm.



Fig. 13. Pseudo-first-order kinetic model.

chemisorption of physisorption. Accordingly, if n = 1, the adsorption process was linear, if n < 1, adsorption process was chemisorption while if n > 1, adsorption process was physisorption [20]. On the account of the value of n < 1, the process could be basically chemisorption. The regression

coefficient (R^2) value was 0.9736 which suggested close fit of the experimental data into the Freundlich isotherms better than the Langmuir model. The process is basically multilayer with little allowance for monolayer adsorption and is consistent with other studies involving removal of



Fig. 14. Pseudo- second-order kinetic model.

Table 4. Isotherms, Kinetic Parameters and I	Regressi	on Constants
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Models	Parameter 1	Parameter 2	R^2
Langmuir	$q_{\rm m} ({\rm mg \ kg^{-1}}) = 8220$	$b(l mg^{-1}) = 0.038$	0.6903
Freundlich	n = 0.188	$K_F(mg^{1-1/n}l^{1/n}g^{-1}) = 0.000039$	0.9736
Pseudo-first-order	$q_e (mg kg^{-1}) = 1231$	$K_1 (min^{-1}) = 25.83$	0.9950
Pseudo-second-order	$q_e (mg kg^{-1}) = 12706$	$K_2 (g mg^{-1} min^{-1}) = 0.0443$	0.9987

heavy metals from aqueous solution using impregnated biochar [20,35-56].

Adsorption Kinetics

The pseudo-first-order and pseudo-second-order kinetic models (Eqs. (20) and (21), respectively) were used to evaluate and simulate data to determine the rate controlling step of the adsorption of cadmium onto the functionalized biochar. The plots of $log(q_e - q_t)$ against time (t) for pseudo-first-order and t/qt against t for pseudo-second-order kinetic model respectively are shown in Figs. 13 and 14, respectively. The kinetic parameters of equilibrium rate constants K₁ (min⁻¹) and K₂ (g mg⁻¹ min⁻¹) and adsorption

capacity values are shown in Table 4. Evaluating the kinetic model parameters shows that adsorption process favoured pseudo-second-order kinetics with pseudo-first-order kinetic not much pronounced. The equilibrium rate constant for pseudo-second-order kinetics (K_1 (min⁻¹)) was 25.83 min⁻¹ with q_e (mg g⁻¹) as 1231 mg kg⁻¹ and R² value as 0.995 while the equilibrium rate constants of the linearized pseudo-second-order kinetic model (K_2) (g mg⁻¹ min⁻¹) and adsorption capacity (q_e) were evaluated to be 0.0443 and 12706 mg kg⁻¹, respectively with R² value of 0.9987. Pseudo-second-order model simulated the data better based on the R² values and other constants and clearly shows that electron pair donor-acceptor exchange and other minor

Table 5.	Comparison of	the Adsorption	Capacity an	d Sorption	Mechanism of	Impregnated	Saw Dust Bioch	nar and other
	Biochars Comp	osites for Sorpti	on of Cd(II)	Ions from A	Aqueous Solutio	on		

S/N	Biochar source	Dopant	pН	Adsorption	Mechanism	Ref.
				capacity		
1	Bamboo	Chitosan	-	-	-	[22]
2	Sugar bagasse	Chitosan	-	-	-	[22]
3	Hickory wood	Chitosan	-	-	-	[22]
4	Peanut hull	Chitosan	-	-	-	[22]
5	Rice straw	Sulphamethazole	5	3412 mg kg ⁻¹	Precipitation and	[37]
					complexation	
6	Empty fruit	Iron oxide	5	62.5 mg g ⁻¹	-	[38]
	bunch					
7	Pristine	KMnO ₄	-	28.1 mg g ⁻¹	Surface adsorption	[39]
8	Hickory wood	NaOH	-	62.5 mg g ⁻¹	-	[40]
9	Coconut shell	FeCl ₃	-	-	-	[41]
10	Rape straw	KMnO ₄ , FeCl ₃ , NaOH	-	81.10 mg g ⁻¹	Complexation	[42]
11	Corn straws	Ammonia	-	1.76	Cation π -bonding and	[32]
				mmol g ⁻¹	complexation	
12	Aerobically	MnO_2	-	45.8 mg g ⁻¹	Electrostatic attraction	[43]
	composted				and ion exchange	
	swine manure					
13	Eucalyptus leaf	Zero-valent iron	-	-	-	[44]
	residue					
14	Pristine	H_3PO_4	-	-	Complexation	[45]
15	Biomass ash	3-Aminopropylt riethoxysilane	5	23.95 mg g ⁻¹	-	[46]
16	Ulva fasciata	Polysaccharide	5	2.9 mg g^{-1}	-	[46]
17	Unclassified	3-Mercaptopropyltrimethyoxy-	3-8	-	-	[33]
	green waste	silane				
18	Pristine	KMnO ₄	-	-	Complexation, cation π -	[48]
					interaction, electrostatic	
					attraction	

Table 5. Continued

19	Coal (lignite)	Polyacrylamide-hydrogel	-	24.72 mg g ⁻¹	Ionic attraction	[49]
20	Tea	Mg, Fe, Mn, Al	-	70-100	-	[50]
				mg g ⁻¹		
21	Rice husk	Cystamine dihydrochloride	5-7	81.02 mg g ⁻¹	Surface attraction/	[18]
					complexation	
22	Reed	Ferrous ammonium sulphate	-	2.9 mg g ⁻¹	-	[51]
23	Corn straw	$MnFe_2O_4$	5	127.83	Complexation/ion	[19]
				mg g ⁻¹	exchange	
24	Spent coffee	Sodium dodecyl sulphate	-	10.67 mg g ⁻¹	-	[52]
25	Pristine	Chlorophosphate	-	-	precipitation	[7]
26	Chicken feather	H_3PO_4	-	7.84 mg g ⁻¹	Electrostatic attraction,	[53]
					precipitation and	
					complexation	
27	Rice husk	Fe(NO ₃) ₃ /KMnO ₄	5	79 mg g^{-1}	-	[54]
28	Pennisetum	KMnO ₄ /H ₂ O ₂	-	41.18-90.32	-	[55]
	sp.straw			mg g ⁻¹		
29	Rice sraw	Citric acid	-	68.7 mg/g	-	[5]
30	Kiwi branch	Mg-Fe Layered Double Hydroxide	-	25.6 mg g ⁻¹	-	[56]
31	Wheat straw	CS ₂ /NaOH	-	-	Precipitation	[20]
32	Bamboo	NH ₃ /ZnCl ₂	7	44.54 mg g ⁻¹	-	[4]
33	Recycled	Na_2S	-	63.5 mg g ⁻¹	-	[36]
	plating waste					
	water					
34	Water hyacinth	MnO_2	6.5	66.48-151.43	Complexation,	[31]
				mg g ⁻¹	precipitation and cation	
					exchange	
35	Carrot pulp	Thiourea	-	4122.7	-	[8]
				mg kg ⁻¹		
36	Corn cob	$ZnCl_2/H_3PO_4$	-	-	-	[6]
37	Saw dust	SALEN	5	8220 mg kg ⁻¹	Complexation, cation	This
					exchange and	work
					precipitation	

interactive processes like dipole-dipole attraction and hydrogen bonding may likely be the rate controlling step during the sorbent-sorbate interaction [32]. The high value of R^2 is a further confirmation of chemisorption and complexation between the multifunctional surface of the composite with the sorbate or ion exchange in the sorption process. The adsorption process shows chemisorption as the main rate controlling step with little allowance for physisorption and this observation is consistent with other studies [5,32-40].

$$\log(q_e - q_t) = \log q_e - (\frac{k_1}{2.303})t$$
(20)

$$\frac{t}{q_t} = \frac{1}{K_2} q_e^2 + \frac{t}{q_e}$$
(21)

CONCLUSIONS

Hydrothermal method was used to fabricate a low cost, efficient and green multifunctional nanocomposite. The composite was characterized synthesized using physicochemical techniques and applied for the removal of Cd(II) ion from aqueous solution. The mechanism for the removal of Cd(II) ions was mainly based on the innersphere complexation, ion exchange and precipitation. The kinetic studies indicated chemisorption as a rate limiting step while the data simulated into isotherm model were fitted well into the Freundlich isotherm model indicating multilayer adsorption processes. For the first time, the study succeeded in impregnating a Schiff bis base (SALEN) into the porous surface of saw dust biochar to increase the surface functionalities and cadmium removal ability of the nanocomposite. The results obtained indicated that the prepared nanocomposite is efficient and effective for the removal of Cd(II) ions from aqueous solution.

Conflict of Interest

The authors declare no conflict of interest in the manuscript submission.

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