

Immobilization of cadmium in soil using magnetic biochar derived from *Eichhornia crassipes*

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Received 24 Sep 2019

Accepted 23 Jun 2020

ABSTRACT: Heavy metal contamination in an environment is a critical problem in Thailand that needs to be addressed urgently, particularly contaminated soil. This research aims to study the adsorption of cadmium ion by unmodified biochar and sodium dodecyl sulfate modified magnetic biochar (SDS-MB) derived from *Eichhornia Crassipes*. The adsorbent and soil characteristics were determined. Observed by scanning electron microscope (SEM), the surface of unmodified biochar (B) was smoother than SDS-MB. The X-ray diffractometer (XRD) pattern showed peaks for iron oxide. The values of point of zero charge (pH_{PZC}) and acid neutralization capability (ANC) were 3 and 1000.3 meq/kg, respectively. The greatest adsorption of cadmium occurred when the pH of the wastewater was 8. The adsorption reached equilibrium within 1 h. It followed Freundlich, Temkin, and Dubinin-Radushkevich isotherm model and the pseudo-second-order kinetic. SDS-MB was mixed with sandy clay loam soil (pH 7.87) contaminated with cadmium 50 mg per kilogram soil at the ratio of 0–5%. The results from the extraction with ethylenediaminetetraacetic acid (EDTA), ammonium acetate, calcium chloride, diethylene triamine pentaacetic acid (DTPA), and sequential extraction method indicated that 5% mixing ratio showed the best ability to reduce cadmium movement in the soil. Cadmium in a form that bound to oxide and a form that bound to organic matter significantly increased.

KEYWORDS: cadmium, *Eichhornia crassipes*, magnetic biochar, sodium dodecyl sulfate, soil remediation

INTRODUCTION

Cadmium is commonly found in many products such as Cd-Ni rechargeable batteries, plastics, ceramics, glasses, enamels, polyvinylchloride, cigarettes, electronic applications, electrical conductivity alloys, heat conductivity alloys, electrical contact alloys, and solar cells [1, 2]. Cadmium has been found contaminated in environments such as near the factory and near the garbage dump. Cadmium is highly toxic. It affects blood, liver, and kidneys and is the cause of the Itai-Itai disease [3, 4]. Cadmium contaminated soil is not suitable for agricultural use, but farmers do not have much choice. They need to grow crops while the land is contaminated. The restoration of cadmium contaminated soil is essential and urgent in order to ensure the safety of the health of people who consume plants grown in the contaminated soil. Adsorption techniques help to reduce the transformation of cadmium from the soil into the biological systems [5, 6] with high efficiency, affordability and *in situ* availability. It is a safe alternative to restoring heavy metal contaminated soil [7]. Substances that are added to stabilize metals in soils can be classified into 4 groups as

follows: group 1 (inorganic substances such as bentonite, phosphate, lime, gypsum, and zeolite, etc.), group 2 (substances derived from industrial processes such as metal sediment, rods, and fly ash, etc.), group 3 (agricultural wastes such as sawdust, corn core, and bean shell, etc.), group 4 (bio-charcoal produced from agricultural waste). Although adding a metal stabilizer will not remove Cd from the soil, it can reduce Cd toxicity and human health risk [8]. Water hyacinths are plants that cause environmental, social, and economic problems [9]. It will be an appropriate solution to solve such problems if all sectors help to find the best way to earn benefit from water hyacinths. Previous researchers have experimented by applying water hyacinths to absorb contaminating metals in wastewater [10, 11] and to remediate soil [12]. They found that the adsorption efficiency was not good enough. There were other researchers producing biochar by passing water hyacinth through the pyrolysis process. Pyrolysis process converted cellulosic carbons, which tend to decompose in the soil, to more stable and slower decomposable aromatic carbons [13, 14]. Biochar was brought to treat wastewater. The adsorption efficiency was

better than that without pyrolysis [15]. Another researcher mixed biochar with sandy soil and investigated Cd adsorption efficiency [16]. The results showed that the higher the mixing ratio of biochar to the soil, the higher the value of Q_m (the maximum amount of adsorbed material per unit mass of sorbent). Some researchers have developed biochar by using many substances such as acid or base, coating with salt or metal oxides and surfactants [17]. At present, attention is focused on making magnetic biochar [18]. Previous researcher has improved the biochar from sorghum straw by making chitosan-biochar/ Fe_2O_3 [19]. It can adsorb Cd ions in the wastewater with Q_m equal to 105.26 mg/g, which is higher than biochar/ Fe_2O_3 without chitosan. SDS is another attractive substance to modify magnetic biochar. This research aims to add value to water hyacinths by producing and comparing biochar, biochar/ Fe_2O_3 , and SDS-biochar/ Fe_2O_3 and applying for soil remediation.

MATERIALS AND METHODS

Preparation of adsorbents

The method was modified from those previously reported [20, 21]. The collection of water hyacinths was from a canal nearby King Mongkut's Institute of Technology Ladkrabang. They were cleaned with water to remove dirt, heated to dry, crushed until they can pass through a 37.5 mm sieve, passed through a pyrolysis process operating at 400 °C for 4 h. The product called unmodified biochar (B). After immersing the crushed water hyacinth in 2.5 M $FeCl_3$ for 3 h and heating at 70 °C for 0.5 h and further heating at 400 °C for 4 h, the magnetic biochar (MB) was a product. The MB was added to 0.01 M SDS, left for 4 h at 50 °C, filtered through 0.45-micrometer filter paper, washed with water, and heated to dry at 100 °C for 24 h. The last product was SDS modified MB (SDS-MB).

Synthetic wastewater preparation

Preparation of 1000 mg/l Cd stock solution was carried out using cadmium (II) nitrate tetrahydrate (AR grade) and double-distilled water. After adjusting the solution pH to 2 using 0.1 M nitric acid, it was kept at 4 °C for preservation.

Adsorbent characterization

The physical characteristics of B, MB, and SDS-MB was studied using Scanning Electron Microscope (SEM) (1455 VP, Leo), and X-ray Diffractometer (XRD) (D8 Advance, Bruker). The pH value at

the zero-point charges was determined by preparing the 0.01 M NaCl solution at various pH values, adding an adsorbent, measuring the solution pH after shaking for 24 h, and plotting the graph between the initial and final pH [18]. The value of acid neutralization capability (ANC) was analyzed by titration method [22].

Adsorption experiments

The experiment was carried out in a batch process by adding an adsorbent to a 500 ml beaker containing 200 ml of cadmium contaminated wastewater. The mixture was stirred at 120 rpm and then filtered. The cadmium concentration in the aliquot was determined by Atomic Adsorption Spectrophotometer (AAS) (AAS200, Perkin Elmer). The system temperature, adsorbent amount, initial cadmium concentration, and initial solution pH were varied as 30–55 °C, 25–700 mg, 10–40 mg/l, and pH 2–9, respectively.

Isotherm, kinetic, and thermodynamic study

Table S1 showed all used equations [23–29].

Soil sample

Soil from Rayong province was collected using the equal interval on the diagonal line method at the soil surface to the depth of 30 cm. The collection was from many points and then mixed. A large piece of debris and weeds were removed from the sampling soil, dried in sunlight, crushed with a mortar, sieved through a 20 mesh sieve, and heated to dry in the oven at 105 °C for 24 h. Soil characterization was as follows: soil texture (hydrometer), moisture (ASTM 2216), pH (pH meter, Consort C860), electrical conductivity (conductivity meter), cation exchange capacity (Ammonium acetate method), loss of ignition (burning at 550 °C and calculating the mass loss), organic matter (Walkley-Black titrations method), nitrate ion (Brucine method), chloride ion (Argentometric method), total phosphate (Molybdovanadophosphate method), sulfate ion (Turbidimetric method), aluminium ion (Colorimetric method), major element (Ca^{2+} , Mg^{2+} and K^+) and total heavy metal (Cd^{2+}) (SW-846 method 3050b). The soil was prepared to contaminate with cadmium 50 mg/kg. The contaminated soil was left for 3 weeks before mixing with SDS-MB. The contaminated soil was then mixed with SDS-MB at the ratio of 0%, 0.5%, 1%, 2% and 5% and further left for 2 weeks. Determination of heavy metal moving in the environment was by single-step extraction with 0.005 M diethylenetriaminepentaacetic acid

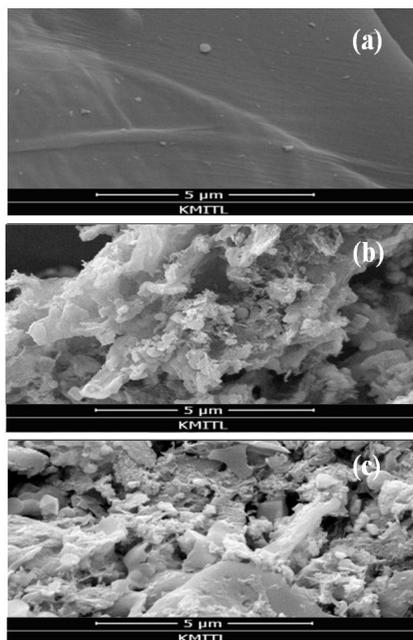


Fig. 1 SEM images of (a) B, (b) MB, and (c) SDS-MB.

(DTPA), 0.01 M CaCl_2 , 0.05 M ethylenediaminetetraacetic acid (EDTA) and 1 M ammonium acetate and sequential extraction. For sequential extraction method, the metal in soil sample was separated into 6 fractions by extraction with 6 types of solution as follows: water (Fraction 1), 1 M magnesium chloride (Fraction 2), 1 M sodium acetate (Fraction 3), 0.04 M hydroxylamine hydrochloride in 25% acetic acid (Fraction 4), 0.02 M nitric acid, 30% hydrogen peroxide and 3.2 M ammonium acetate (Fraction 5), and concentrated nitric acid (Fraction 6) [30]. The determination of the amount of the metal extracted was performed by Atomic absorption spectrometer (AAS).

Statistical analysis

All experiments were performed in triplicate. The one-way analysis of variance (ANOVA) was used to determine the statistically significant (at 95% confidence level) difference between the 2 or more groups of data using SPSS version 23.

RESULTS AND DISCUSSION

Adsorbent characterization

Fig. 1 presented a smooth surface of the unmodified biochar (B) and iron oxide deposition on the surface of the MB. The surface of SDS-MB became smoother (Fig. 1c) than the surface without SDS modification. Adding SDS-MB to the soil will result in the better

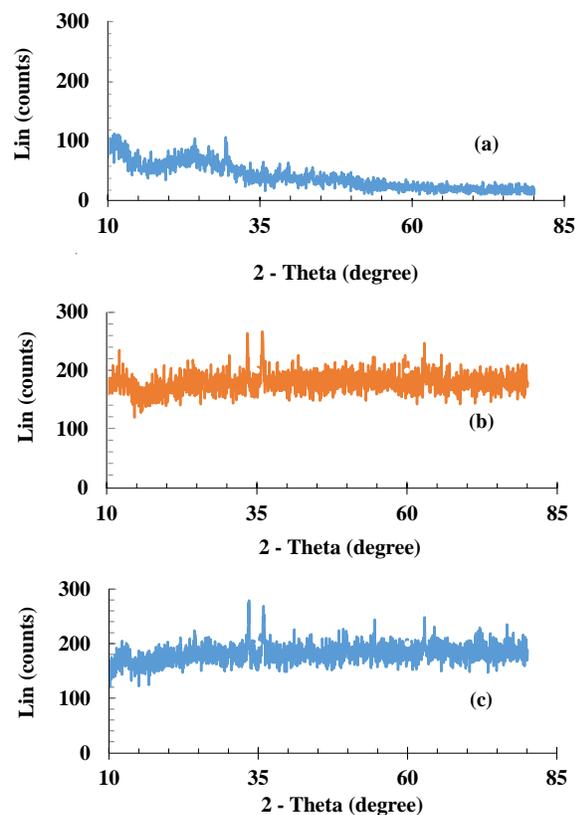


Fig. 2 XRD pattern of (a) B, (b) MB, and (c) SDS-MB.

reduction of metal movement in soil than adding B due to higher porosity. SDS-MB is less porous but more negative charge on the surface than MB.

XRD pattern in Fig. 2b-c showed peaks for iron oxide at 2θ 3.15° , 35.61° , 40.9° , 49.16° , 54.24° , and 62.45° [31].

Effect of pH on adsorption and pH_{PZC} value

The adsorption of 10 mg/l synthetic wastewater was carried out using 25 mg of B, MB, and SDS-MB. The initial solution pH was 2–8, and the system temperature was 30°C (room temperature). Fig. 3 indicated that the opportunity of metal ions in synthetic wastewater to propagate to the adsorbed active site increased with increasing the adsorption time. For unmodified biochar (B), magnetic biochar (MB), and SDS magnetic biochar (SDS-MB), the maximum adsorption obtained when the initial solution pH was 8. The adsorption ability of SDS-MB was the highest. From the point of zero charge (pH_{PZC}) determination, the charge of B, MB, and SDS-MB surface was negative when the pH of the solution was higher than 7.4, 3.1, and 3, respectively. When

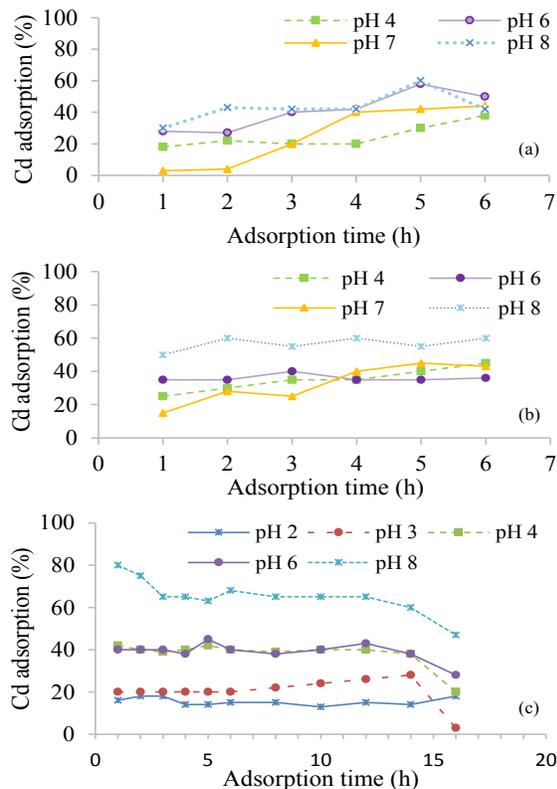


Fig. 3 Cd removal at various solution pH values by (a) B, (b) MB, and (c) SDS-MB.

Table 1 Adsorption isotherm parameters of cadmium by SDS-MB.

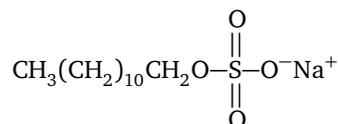
Isotherm		Isotherm	
Langmuir		Dubinin-Radushkevich	
q_{max} (mg/g)	50.00	K_{Dr}	8×10^{-7}
K_L (l/mg)	0.0016	q_D (mg/g)	36.97
R_L	0.9843	E (kJ/mol)	0.7906
R^2	0.0123	R^2	0.9830
Freundlich		Tempkin	
K_F (l/g)	7.7911	b_o (J/mol)	121.95
$1/n$	1.0071	A (l/g)	1.0593
R^2	0.9987	R^2	0.9950
Redlich-Peterson			
K_R (mg/g)	65		
a_R (mg/l)	7.3434		
b_R	0.0081		
R^2	0.0358		

adding SDS-MB to the study soil (pH 7.87), SDS-MB should decrease the movement of Cd in the soil.

Adsorption isotherm study

The consideration was on Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and Redlich-Peterson isotherm to explain the adsorption. Table 1 showed the calculation results.

From Table 1, adsorption of Cd was in accordance with Freundlich, Temkin, and Dubinin-Radushkevich adsorption isotherm models. An explanation from Freundlich isotherm was that the adsorption occurred on the rough and heterogeneous surface. It was a multilayer adsorption. The adsorption mechanism could be both physical and chemical processes. The value of $1/n$ indicated that the adsorption was favorable. Temkin considered effects of some indirect adsorbent/adsorbate interactions on adsorption isotherms and suggested that because of these interactions, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The E value from Dubinin-Radushkevich indicated that the main adsorption mechanism was the physical process. The adsorption capacity calculated by Dubinin-Radushkevich was 36.97 mg/g. From all 3 isotherms, SDS-MB absorbed cadmium by absorbing cadmium into pores (the physical process) and by ion exchange of Na^+ and Cd^{2+} .



Kinetic study

The study of cadmium adsorption kinetic was by varying initial wastewater concentration and system temperature. The consideration was on pseudo-first-order and pseudo-second-order kinetic models. Table 2 presented the calculation results.

Pseudo-second-order model was a better model to explain the adsorption kinetic of SDS-MB. The chemisorption was the rate-limiting step. Cadmium ions were attached to the biochar surface by chemical bonding. The bonding may occur due to the addition of SDS to the biochar surface.

Thermodynamic study

The value of ΔH° , ΔS° , ΔG° at 30 °C, ΔG° at 45 °C, and ΔG° at 55 °C were 6.71 J/mol, 17.32 J/mol.K, -5.24 kJ/mol, -5.50 kJ/mol, and -5.67 kJ/mol, respectively. The positive value of ΔH° indicated that the adsorption was an endothermic process. ΔG° was slightly lessened with the increasing temperature from 30 °C to 55 °C. It confirmed

Table 2 Adsorption isotherm parameters of cadmium by SDS-MB.

Concentration /temperature	Pseudo-first-order			Pseudo-second-order		
	K_1 (1/min)	q_e (mg/g)	R^2	K_2 (g/mg.min)	q_e (mg/g)	R^2
10 mg/l	0.0051	27.96	0.8134	0.0057	27.96	0.9769
20 mg/l	0.0021	52.94	0.3170	0.0087	52.94	0.9887
30 mg/l	0.0023	55.89	0.4030	0.0066	55.89	0.9836
40 mg/l	0.0025	62.45	0.3993	0.0172	62.45	0.9945
30 °C	0.0051	27.96	0.8134	0.0057	27.96	0.9769
45 °C	0.0106	7.44	0.2221	0.0037	7.44	0.7509
55 °C	0.0071	12.17	0.1176	0.0114	12.17	0.7575

Table 3 Soil and SDS-MB characteristics.

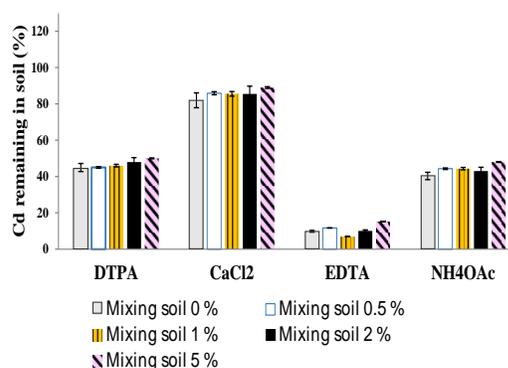
Parameter	Soil sample	SDS-MB
Soil texture	Sandy clay loam	–
Moisture (%)	21	–
pH	7.87	3.67
Electrical conductivity (EC) (mS/cm)	6.53	10.02
Cation exchange capacity (CEC) (cmol/lg)	10.87	4.00
Loss ignition (% LOI)	8.38	3.19
Organic matter (% OM)	3.54	2.97
Nitrate ion (mg/kg)	10.76	14.07
Chloride ion (mg/kg)	2.71	6.97
Total phosphate (mg/kg)	12.51	7.09
Sulfate ion (mg/kg)	45.28	4.70
Aluminium ion (mg/kg)	ND	ND
Major element (mg/kg)		
Ca ²⁺	0.88	0.41
Mg ²⁺	80.0	15.8
K ⁺	65.8	14.3
Cd ²⁺	0.085	0.039
ANC value (meq/kg)	–	1000.3

ND = Not detected.

the endothermic process. The adsorption process was spontaneous at high temperatures and non-spontaneous at low temperatures due to the positive value of both ΔS° and ΔH° . The negative value of ΔG° revealed that the adsorption could occur naturally.

Soil and SDS-MB characteristics

Table 3 showed soil and SDS-MB characteristics. This soil was a sandy clay loam with 72.50%, 5.00%, and 22.50% of sand, silt, and clay, respectively. It is a moderately alkaline soil with pH 7.87. The CEC value is quite high. The LOI value closely relates to OM value. The low OM resulted in low metal in the form of binding to organic matter. Due to

**Fig. 4** Percentage of Cd remaining in soil sample after performing the single-step extraction method.

the low NO_3^- , Cl^- , PO_4^{3-} , SO_4^{2-} , Ca^{2+} , Mg^{2+} , and K^+ concentration in the soil, those ions would not affect the Cd adsorption efficiency. The SDS-MB was acidic. The OM and sulfate came from SDS. Chloride came from the addition of FeCl_3 . The other parameters were from water hyacinth itself. The concentration of Cd^{2+} was low for both soil and SDS-MB. The overall buffering capacity of material can be shown in terms of the acid neutralization capability (ANC) value. The ANC value of SDS-MB was 1000.3 meq/kg which was lower than ANC value for municipal organic waste (4280 meq/kg) and green waste (7100 meq/kg) reported by Venegas et al [22]. Fig. 4 and Fig. 5 showed the results of the single-step extraction and sequential extraction performed after mixing contaminated soil with SDS-MB.

Single-step extraction and sequential extraction

The capacity of EDTA to extract metals was higher than others, so the remaining cadmium in the soil was the lowest (Fig. 4). EDTA was able to ex-

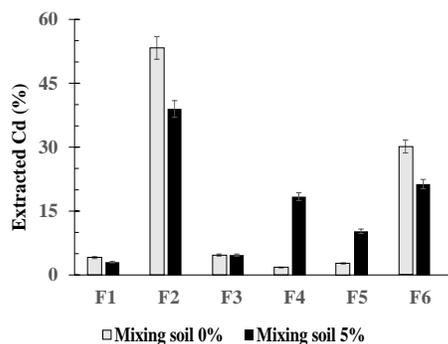


Fig. 5 Percentage of extracted cadmium using a sequential extraction method.

tract metals in a soluble form, an exchangeable form, a carbonate bound form, and partly in Fe-Mn oxide bound form and an organically bound form [32]. Assessing the metal ability to move in the environment, EDTA solution was suitable to be used. Ammonium acetate removed metals in a soluble form and an exchangeable form from soil [33]. Extraction by ammonium acetate was highly recommended to show the exchangeability of metals. DTPA was able to extract metals in a soluble form, an exchangeable form, and partly in organically bound form. Calcium chloride (CaCl_2) removed only metals in a soluble form, so the remaining cadmium in the soil was the highest. DTPA and CaCl_2 could be used to assess the phytoavailability [34]. When adding the SDS-MB to the soil at a ratio of 5%, the value of remaining Cd in the soil was significantly different ($p < 0.05$) from the other ratios. Applying less than 5% may not enough to decrease the movement of Cd in soil. The 5% SDS-MB mixed soil showed the best ability to reduce cadmium movement in the environment and the phytoavailability. The study of a sequential extraction was carried out. In Fig. 5, Fraction 1, Fraction 2, Fraction 3, Fraction 4, Fraction 5, and Fraction 6 indicated metals in a soluble form, an exchangeable form, a form that bound to carbonate, a form that bound to oxide, a form that bound to organic matter, and a residual form, respectively.

Fig. 5 showed that metal in soil was mostly in Fraction 2 (an exchangeable form) due to the high CEC in soil. When mixing SDS-MB with soil at the ratio of 5%, cadmium in Fractions 4 and 5 increased. The amount of iron oxide and organic matter increased when adding SDS-MB to the soil, which caused more cadmium to adhere to iron oxide and organic matter. The metal in an unstable form

(F1+F2+F3) reduced, resulting in the reduction of metal movement in the soil.

CONCLUSION

The application of SDS-MB to remove cadmium from wastewater was a successful, low cost, and environmentally friendly technology. The adsorption capacity of SDS-MB was higher than unmodified biochar. The application of SDS-MB to reduce the movement of Cd in the contaminated soil was possible.

Appendix A. Supplementary data

Supplementary data associated with this article can be found at <http://dx.doi.org/10.2306/scienceasia1513-1874.2020.055>.

Acknowledgements: Authors would like to express gratitude to KMITL Research and Innovation Services (KRIS), King Mongkut's Institute of Technology Ladkrabang for funding this research grant (KREF016009).

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Appendix A. Supplementary data

Table S1 Isotherm, kinetic, and thermodynamic equations.

Isotherm	Linear equation
Langmuir [23]	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \cdot q_m}$ $R_L = \frac{1}{1 + K_L \cdot C_0}$
Freundlich [24]	$\log q_e = \log K_f + \frac{1}{n} \log C_e$
Tempkin [25]	$q_e = \frac{RT}{b_0} \ln A + \frac{RT}{b_0} \ln C_e$
Dubinin-Radushkevich [26]	$\ln q_e = \ln q_D - K_{DR} \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2$ $E = \frac{1}{\sqrt{2K_{DR}}}$
Redlich-Peterson [27]	$\ln \left(K_R \frac{C_e}{q_e} - 1 \right) = b_R \ln C_e + \ln a_R$
Kinetic [28]	Linear equation
The pseudo-first-order	$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303}$
The pseudo-second-order	$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$
Thermodynamic [29]	$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -RT \ln K_c$ $K_c = \frac{q_e}{C_e}$ $\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$

q_t = the amount of adsorbed Cd per unit mass of adsorbent at time t (mg/g) = $\frac{(C_0 - C_t)V}{W}$.

q_e = the amount of adsorbed Cd per unit mass of adsorbent at equilibrium (mg/g) = $\frac{(C_0 - C_e)V}{W}$.

C_t = the Cd concentration in solution at time t (mg/l).

C_0 = the initial Cd concentration in solution (mg/l).

C_e = the Cd concentrations in solution at equilibrium (mg/l).

V = the volume of the solution (l).

W = the adsorbent mass (g).

q_m = the maximum adsorbed Cd amount per unit mass of sorbent (mg/g).

K_L = Langmuir constant (l/mg).

R_L = a dimensionless separation factor or equilibrium parameter.

K_f = Freundlich constant (l/g).

$1/n$ = the value related to the adsorption intensity.

A = Temkin isotherm constant (l/g) corresponding to the maximum binding energy.

b_0 = Temkin constant related to heat of sorption (J/mol).

R = the gas constant (8.314 J/mol.K).

T = the absolute temperature (K).

q_D = the adsorption capacity (mg/g).

K_{DR} = the constant related to mean free energy of adsorption per mole of the adsorbate (mol²/kJ²).

E = the mean adsorption energy (kJ/mol) of the adsorbate.

k_1 = the rate constant for pseudo-first order adsorption (l/min).

k_2 = the rate constant for pseudo-second order adsorption (g/mg.min).

α = the initial adsorption rate (mg/g.min).

β = the constant related to the extent of surface coverage and the activation energy for chemisorptions (g/mg).

K_{id} = the intraparticle diffusion rate constant (mg/g.min^{1/2}).

K_c = the equilibrium constant reflected the adsorbent ability to keep the adsorbate and extent the adsorbate movement within the solution.