



Simultaneous adsorption–precipitation characterization as mechanisms for metals removal from aqueous solutions by cement kiln dust (CKD)

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Received 21 March 2014; Accepted 6 October 2014

ABSTRACT

Isotherm equations are useful for simulating adsorption data, but they cannot be easily adapted to simulate the precipitation phase. This work presents a new analytical isotherm model, based on the mass conservation principle, which can distinguish between the adsorption and precipitation mechanisms when both these processes occur simultaneously. This model was validated with the results of batch experiments conducted at the appropriate conditions using cement kiln dust as a reactive adsorbent on two metal species: copper and zinc. Thus, a new experimental procedure was established for description of the precipitation process. The developed model was found to be more representative than the conventional models in characterization of the relationship between the total sorption (adsorption–precipitation) and residual concentration of the contaminant. This model can be potentially integrated with several contaminant transport codes such as COMSOL Multiphysics 3.5a (2008), which only considers the adsorption phase. Thus, a reasonable agreement between the developed model predictions and experimental results for pure adsorption, pure precipitation, and combination of adsorption–precipitation processes was recognized.

Keywords: Heavy metals; Precipitation; Adsorption; Contamination; Isotherm; Cement kiln dust

1. Introduction

Adsorption/desorption and precipitation/dissolution are the main mass transfer mechanisms that govern the treatment processes of heavy metals using cement kiln dust (CKD). Several theoretical and experimental studies in the past 2 decades have investigated these mechanisms. Unfortunately, none of these studies could clearly distinguish between these two

mechanisms. Several studies dealing with CKD as an adsorbent material depended on its fine texture and the oxide compositions and suggested that pure adsorption within a certain limits of pH serves as the control mechanism [1,2]. However, this is not an accurate characterization because the treatment process is affected by the pH of the solution, which can be raised in several cases, and consequently, heavy metal hydroxides can precipitate. Other studies analyzed the treatment process as a pure precipitation due to the

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high lime content of CKD [3–5]. While the last studies termed the treatment process as an interaction between CKD and the contaminants without recognizing the removal achieved by adsorption or precipitation and their individual contribution when they both occur simultaneously [6,7].

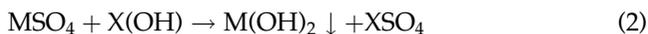
Hence, there is a need to develop an analytical isotherm model that can distinguish between adsorption and precipitation mechanisms when both occur simultaneously. This model can be potentially integrated into large-scale advection–dispersion equation to describe the contaminant transport in the soil-saturated zone. In addition, several contaminant transport codes such as COMSOL Multiphysics 3.5a (2008) (which predefines the adsorption by linear, Freundlich, or Langmuir model [8]) can be modified in conjunction with the presently developed model.

Accordingly, the objective of this study was to derive an analytical framework, based on the mass conservation principle, for modeling simultaneous adsorption–precipitation mass transfer mechanisms and distinguishing between them. The application of this model was demonstrated using adsorption and precipitation experimental datasets of copper (Cu) and zinc (Zn) onto a CKD-reactive material.

2. Derivation of the simultaneous adsorption–precipitation equation

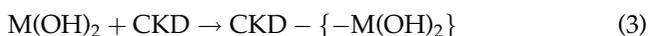
CKD can be chemically classified as a high heterogeneous material, and therefore, dissolved metals in the aqueous solution can be removed by adsorption and precipitation [9,10]. It is preferable to adopt a stepwise operation manner for description of these mechanisms in order to characterize the precipitation phase and the simultaneous adsorption–precipitation phase. The difference between these phases can be represented by the adsorption phase, as follows [11]:

(1) Precipitation by metal (*M*) hydrolysis



where *X* : K, Na, *M* : Cu, Zn

(2) Adsorption of metal onto CKD particles



The amount of metal ion retained in the CKD phase, q_e , as a result of pure adsorption can be calculated as follows [12]:

$$q_e = \frac{V(C_o - C_{eq})}{m} \quad (4)$$

where C_o is the initial concentration of metal in the solution (mg/L), C_{eq} is the equilibrium concentration of metal in the solution (mg/L), V is the volume of solution (L), and m is the mass of CKD (g).

Initially, the metal with a given mass is dissolved in the aqueous phase, given by VC_o . At equilibrium, a portion of this mass ($=VC_{eq}$) remains in the solution and the complementary portion ($=mq_{eeq}(C_{eq})$) is adsorbed onto the reactive material as follows:

$$VC_o = mq_{eeq}(C_{eq}) + VC_{eq} \quad (5)$$

Precipitation can be represented by the formation of the metal hydroxide (M-OH) when adsorption–precipitation occurs simultaneously, as explained in Eq. (2). To complete the present derivation, Eq. (4) can be rewritten as below to represent the apparent adsorption (q_{eapp}), which is reflected by the total amount of metal removed by simultaneous adsorption–precipitation without distinguishing between their individual contribution:

$$q_{eapp} = \frac{V(C_{10} - C_{1f})}{m} \quad (6)$$

where C_{10} and C_{1f} are the initial ($t = 0$) and final equilibrium ($t = \infty$) concentrations of the metals in the solution (in mg/L). The main equations describing the simultaneous equilibrium of adsorption–precipitation are given below:

$$\begin{aligned} \text{Total mass of } M &= \{\text{mass remaining as dissolved ions in solution}\} \\ &+ \{\text{adsorbed mass}\} + \{\text{precipitated mass}\} \end{aligned} \quad (7)$$

Or;

$$VC_{10} = VC_{1f} + \{\text{adsorbed mass}\} + \{\text{precipitated mass}\} \quad (8)$$

By rearrangement, adsorbed mass can be calculated as given below:

$$\{\text{adsorbed mass}\} = VC_{10} - VC_{1f} - \{\text{precipitated mass}\} \quad (9)$$

This quantity also can be written by means of adsorption as given below:

$$\{\text{adsorbed mass}\} = m q_e(C'_{1f}) \tag{10}$$

where $q_e(C'_{1f})$ is the value of adsorption after return of the metal released from the precipitation phase into the aqueous solution (where there is no precipitation), i.e.:

$$C'_{1f} = C_{1f} + C_{1fp} \tag{11}$$

where C'_{1f} represents the equilibrium residual concentration of metal in the solution in absence of precipitation and C_{1fp} is the precipitated portion of metal. This portion can be evaluated as given below:

$$C_{1fp} = C_{10} - C'_{1f} \tag{12}$$

where C'_{1fp} is the residual concentration of metal in absence of adsorption. Hence, Eq. (12) can be rewritten as given below:

$$C'_{1f} = C_{1f} + C_{10} - C'_{1fp} \tag{13}$$

Consequently,

$$\begin{aligned} q_e &= \frac{V(C_{10} - C'_{1f})}{m} \text{ or } q_e(C'_{1f}) \\ &= \frac{V(C_{10} - C_{1f} - C_{10} + C'_{1fp})}{m} \text{ or } q_e(C'_{1f}) \\ &= \frac{V(C'_{1fp} - C_{1f})}{m} \end{aligned} \tag{14}$$

This derivation distinguishes between the adsorbed and precipitated fractions of the removed metal. For validation of this derivation, two sets of batch tests were conducted, (i) for evaluating the total (apparent) adsorption–precipitation when both the processes occur simultaneously and (ii) for evaluating the pure precipitation.

3. Sorption isotherms

Plotting the isotherm data describing the adsorption experiments, and finding the best fitting is important. Two-parameter isotherms such as those described by Freundlich (1906), Langmuir (1916), Temkin (1934), BET (1938), Flower-Guggenheim (1939), Hill-de Boer (1946–1953), Kiselev (1958), Dubinin–Radushkevich (1960), and Elovich (1962) can be applied separately for pure adsorption or pure precipitation. Some of these isotherms can be linearized as listed in Table 1. In addition, three-parameter isotherms such as Redlich–Peterson (1959), Radke–Prausnitz (1972) and Sips (1984) can be applied for adsorption to select a more reasonable combination isotherm for simulating the total adsorption–precipitation process [13–16].

4. Materials and methods

4.1. Mediums and contaminants

The by-product CKD (collected from the Al-Najaf Al-Ashraf Cement Factory, Al-Najaf, Iraq) was used as a reactive material in the batch experiments. The chemical composition of this material is summarized in Table 2.

Table 1
Two and three-parameter single-component isotherm models and their linearization [13–16]

Isotherm	Form	Plot
Freundlich	$q_e = KC_e^{1/n}$	$\ln q_e$ vs. $\ln C_e$
Langmuir	$q_e = \frac{q_m b C_e}{1 + b C_e}$	$\frac{C_e}{q_e}$ vs. C_e
Temkin	$q_e = \frac{RT}{b} \ln(K_T C_e)$	q_e vs. $\ln C_e$
Dubinin–Radushkevich	$q_e = q_D \exp\left(-B_D \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2\right)$	$\ln q_e$ vs. $\left(\ln\left(1 + \frac{1}{C_e}\right)\right)^2$
BET	$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e) \left[1 + (C_{BET} - 1) \left(\frac{C_e}{C_s}\right)\right]}$	$\frac{C_e}{q_e(C_s - C_e)}$ vs. $\frac{C_e}{C_s}$
Redlich–Peterson	$q_e = \frac{K_K C_e}{1 + a_s C_e^{\beta_s}}$	$\ln\left(K_K \frac{C_e}{q_e} - 1\right)$ vs. $\ln(C_e)$
Radke–Prausnitz	$q_e = \frac{K_{RP} C_e}{1 + \left(\frac{K_{RP}}{F_{RP}}\right) C_e^{1-N_{RP}}}$	—————
Sips	$q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	$\beta_s \ln(C_e)$ vs. $\ln\left(\frac{K_s}{q_e}\right)$

Table 2
The chemical composition of CKD

Constituents	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	L.O.I ^a	Na ₂ O	K ₂ O	Na ₂ O eq. ^b
Composition (wt.%)	13.38	5.87	1.61	40.35	3.08	8.83	21.8	2.63	4.23	5.42

^aLoss on ignition.

^bNa₂O + 0.658 K₂O.

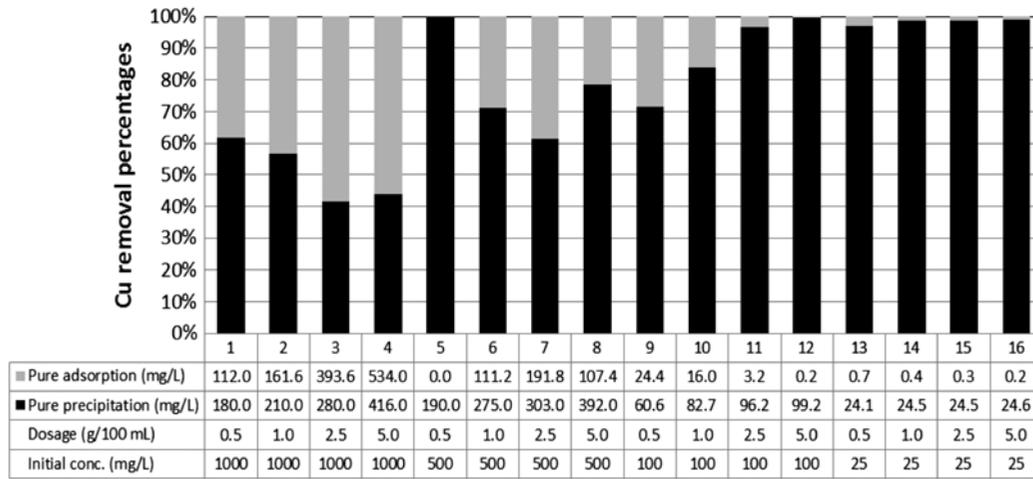


Fig. 1. Percentage and concentration of copper ions removed by pure adsorption and pure precipitation onto CKD particles.

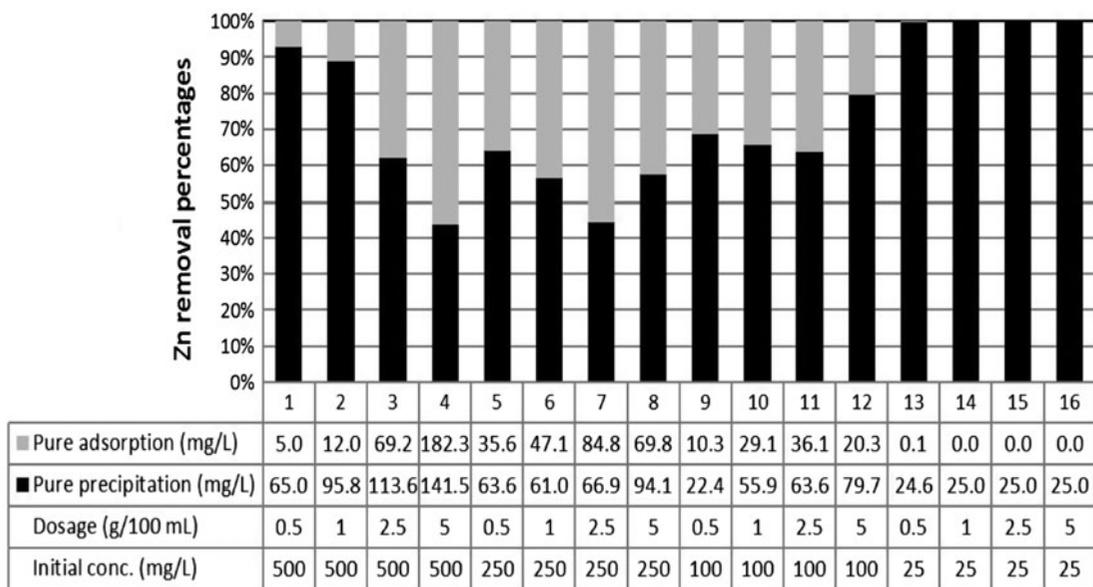


Fig. 2. Percentage and concentration of zinc ions removed by pure adsorption and pure precipitation onto CKD particles.

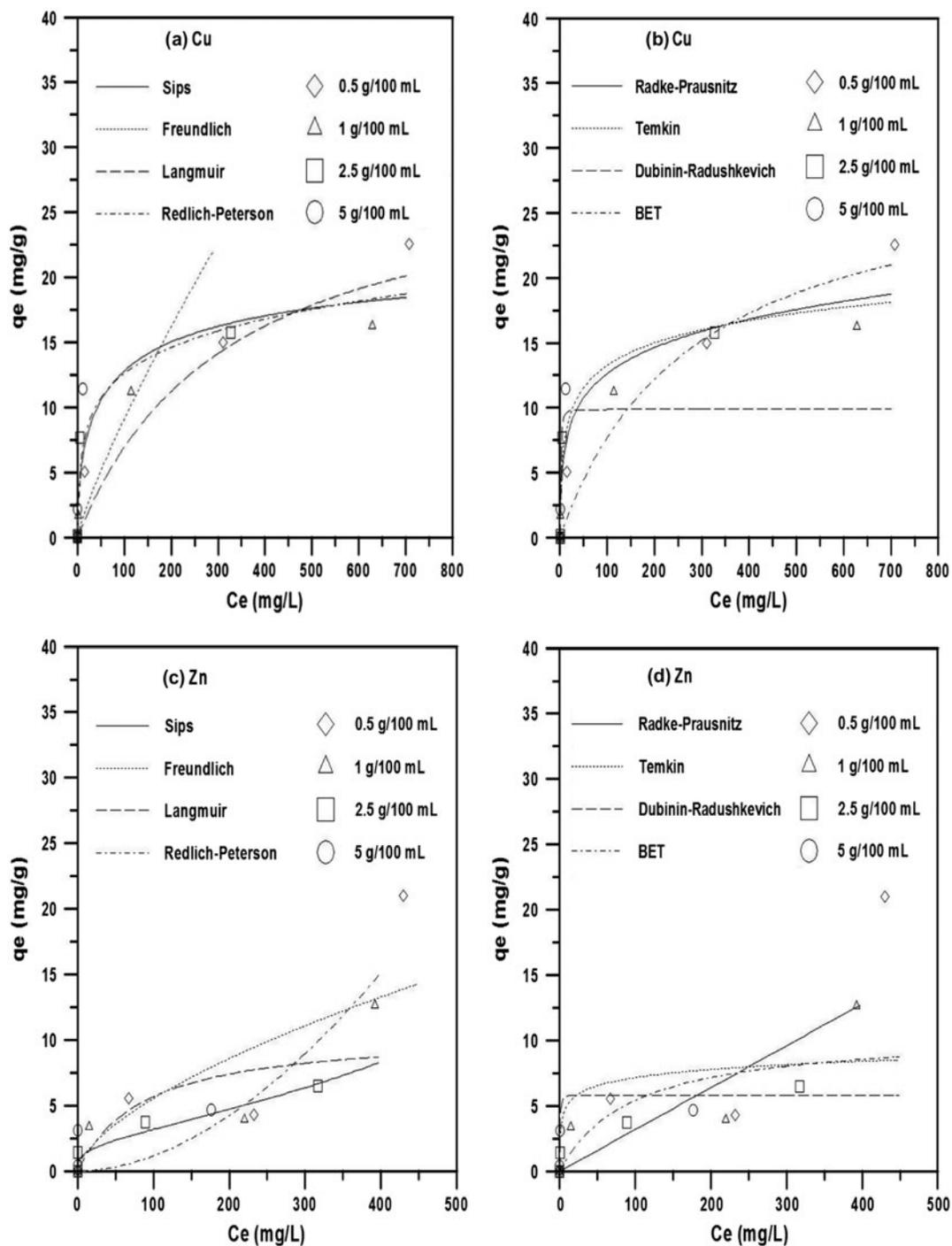


Fig. 3. Pure adsorption isotherms for (a & b) Cu and (c & d) Zn onto CKD particles.

Cu and Zn were selected as representatives of heavy metal contaminants. To simulate the water's Cu or Zn contamination, a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (manufactured by SD Fine-Chem Limited, India) was prepared and added to the specimen to obtain a representative concentration.

4.2. Total (apparent) adsorption–precipitation

Batch equilibrium experiments are conducted to specify the best values of contact time, initial pH, and agitation speed (data not shown); these values were found to be 30 min, 3, and 250 rpm, respectively. A

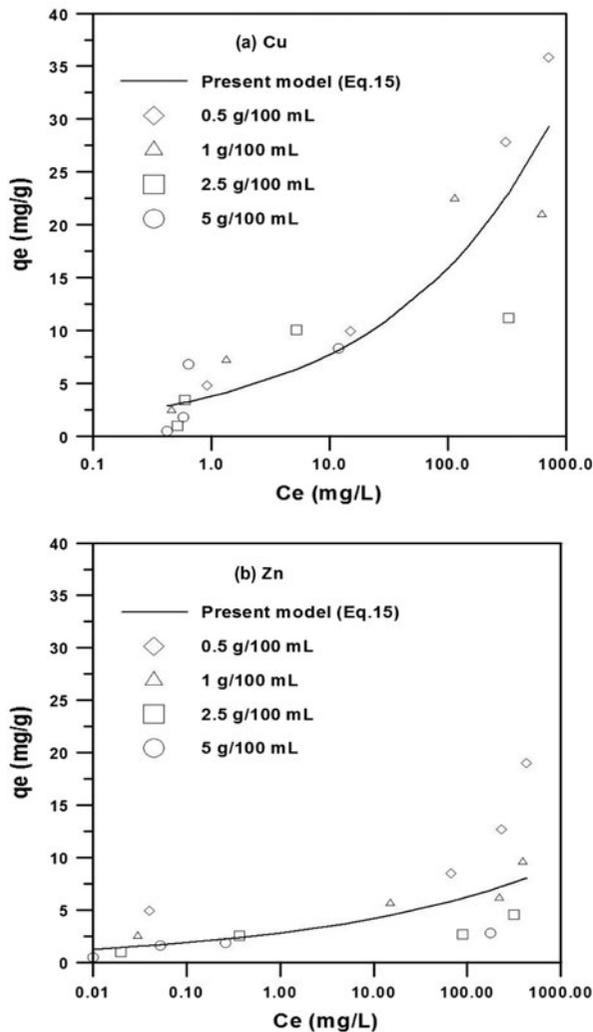


Fig. 4. Experimental results fitted with the developed model (Eq. (15)) for (a) Cu and (b) Zn precipitation.

Table 3

Constants of the developed isotherm model (Eq. (16)) for Cu and Zn adsorption–precipitation onto CKD particles

Constants	k_s	β_s	a_s	$1/(Q_0b)$	$1/Q_0$
Cu	11.168	2.003	0.709	4.656	-0.069
Zn	0.026	0.067	-0.665	-1.449	0.952

series of 250 mL flasks were employed, and each one was filled with 100 mL of Cu or Zn solution. A specific dosage of adsorbent was added into different flasks, and the solution in each flask was continuously stirred at high speed using an orbital shaker. A fixed volume (20 mL) of the solution was withdrawn from each flask and filtered to separate the adsorbent; 10 mL of the clear solution was pipetted out for the

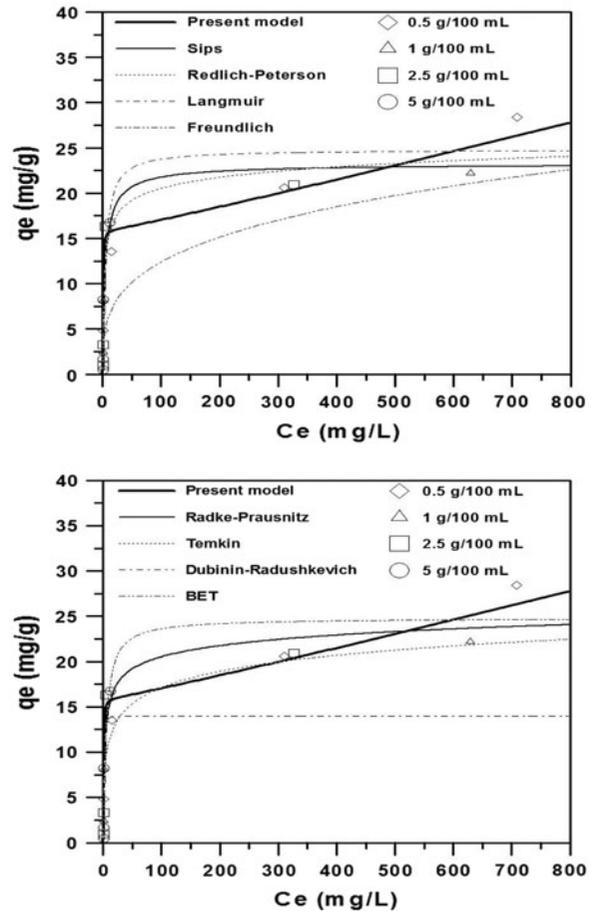


Fig. 5. Total adsorption–precipitation isotherm model for Cu onto CKD particles as described by the developed model (Eq. (16)) in comparison with the conventional models.

determination of the residual metal concentration in the solution using the Shimadzu AA-6300 flame atomic absorption spectrophotometer. The adsorbed concentration of metal ion onto the CKD was obtained by a mass balance.

All experiments were achieved under the optimal values of contact time, initial pH of solution, and agitation speed. These experiments were conducted with initial metal concentrations of 25, 100, 500, and 1,000 mg/L, and CKD dosages of 0.5, 1, 2.5, and 5 g/100 mL.

4.3. Pure precipitation

A specific quantity of adsorbent was added into 100 mL of acidic uncontaminated water (pH 3), and the solution was continuously stirred at high speed by using an orbital shaker for 30 min. Then, the solution was filtered to separate out the adsorbent using a similar procedure to the “tea-bag” experiment described

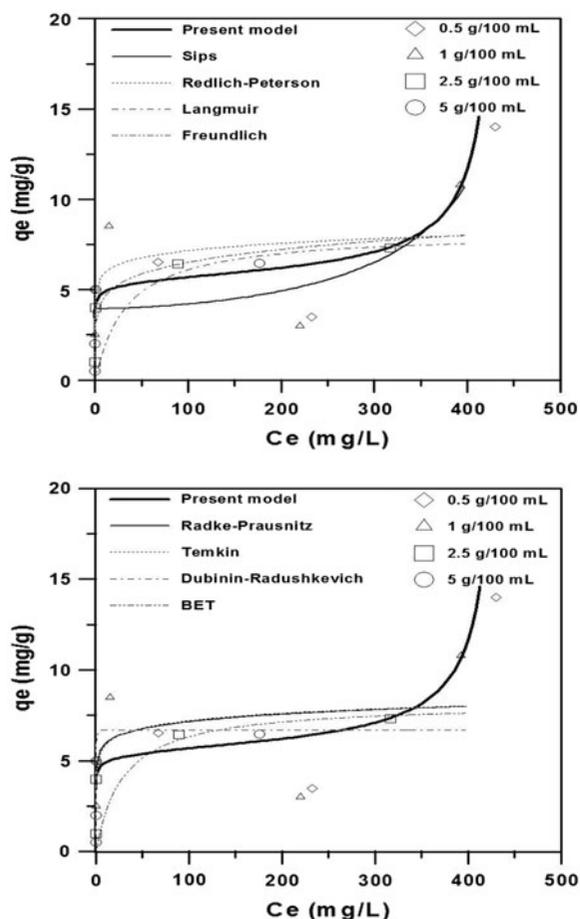


Fig. 6. The total adsorption–precipitation isotherm model for Zn onto CKD particles as described by the developed model (Eq. (16)) in comparison with the conventional models.

elsewhere [17]. The clear solution was mixed with the Cu or Zn solution, and the resultant solution was filtered after the required equilibrium time. The residual metal concentration in the filtered solution was quantified by the Shimadzu AA-6300 flame atomic absorption spectrophotometer, and the precipitated concentration was obtained by a mass balance. The pH of the solution was measured at each stage of this process using the WTW pH 330i meter, and these experiments were conducted under the same conditions adopted in the determination of the total adsorption–precipitation.

5. Results and discussion

The experimental results revealed a lag in metal removal by pure precipitation in comparison with that by total adsorption–precipitation. This can be attributed to direct contact between CKD and metal ions in the total adsorption–precipitation case, which

increases the probability of attachment of the metal ions onto the CKD adsorbent.

Figs. 1 and 2 show that pure adsorption of metal ions onto CKD can be specified as a complementary portion of total adsorption–precipitation (Eq. (14)). It is clear that the total adsorption–precipitation increased with increasing CKD dosage. The adsorption portion increased (i.e. the precipitation portion decreased) when the mass of reactive material was increased in high concentrations. These results show that pure precipitation overcomes the total adsorption–precipitation in the low concentrations. This can be attributed to the formation of hydroxide ions as a result of chemical reactivity of CKD. This process may be faster than the adsorption process that needs a relatively longer time to achieve the maximum adsorption capacity.

Fig. 3 shows the pure adsorption isotherm models of Cu and Zn onto CKD. There is a poor agreement between the predicted values and experimental results for two-parameter isotherms, which may be due to a high heterogeneity of reactive materials [18]. However, three-parameter isotherms, especially Sips isotherm model presents a reasonable agreement with the experimental results. The pure precipitation results were plotted using various isotherm models (data not shown), of which the Langmuir model fitted well. Globalization of this behavior can be performed by transforming the Langmuir model through a relation $\ln(C_e/q_e)$ versus $\ln(C_e)$ instead of the direct relation of the Langmuir model, which presents the following relationship relating the adsorbed value due to precipitation with the residual concentration (Fig. 4):

$$q_{e,p} = \frac{C_e}{\exp\left(\frac{1}{Q_0 b}\right) C_e^{1/Q_0}} \quad (15)$$

Table 4
Coefficient of determination (R^2) for all isotherm models used in the present study for fitting the experimental results

Isotherm	R^2	
	Cu	Zn
Freundlich	0.543	0.444
Langmuir	0.892	0.565
Temkin	0.794	0.479
Dubinin–Radushkevich	0.551	0.439
BET	0.889	0.457
Redlich–Peterson	0.924	0.366
Radke–Prausnitz	0.922	0.366
Sips	0.912	0.631
Present study	0.956	0.753

where Q_0 and b are the Langmuir isotherm constants. Consequently, total adsorption–precipitation isotherm can be rewritten as follows:

$$q_{e,t} = (q_{e,ad})_{\text{Sips}} + (q_{e,p}) \quad (15)$$

$$q_{e,t} = \frac{k_s C_e^{\beta_s}}{1 + \alpha_s C_e^{\beta_s}} + \frac{C_e}{\exp\left(\frac{1}{Q_0 b}\right) C_e^{1/Q_0}} \quad (16)$$

where $q_{e,t}$ is the total mass of metal removed by simultaneous adsorption–precipitation, $q_{e,ad}$ is the mass of metal removed by pure adsorption, $q_{e,p}$ is the mass of metal removed by pure precipitation, and constants k_s , β_s , α_s are the Sips isotherm coefficients. These constants were estimated for Cu and Zn by nonlinear regression analysis using the IBM SPSS Statistics version 20 (Table 3). Figs. 5 and 6 in combination with Table 4 show that the present model was a better representative than the conventional models for characterization of the relationship between the total adsorption–precipitation and the residual concentration for contaminants treated with CKD.

6. Conclusions

An analytical isotherm expression based on mass conservation principle for simulating the total simultaneous adsorption–precipitation, pure adsorption, and pure precipitation was developed in the present study. The proposed isotherm-based simulation is an efficient alternative to a more conventional models that can be integrated with several contaminant transport codes such as COMSOL Multiphysics 3.5a (2008) in description the solute transport through field applications. This approach employs the three parameters of the Sips isotherm expression as the base model for the characterization of pure adsorption. This expression was subsequently modified by allowing the introduction effect of pure precipitation by the transformation of the Langmuir model through relating $\ln(C_e/q_e)$ to $\ln(C_e)$ instead of the direct relation of C_e/q_e to C_e . Thus, the developed isotherm model could successfully represent the relationship between the total adsorption–precipitation and the residual concentration for Cu or Zn treated with CKD.

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