Adsorption-Precipitation Mechanisms for Cadmium Removal from Polluted water

Prof.Dr. Ayad Abd Al-Hamza Faisal
Department of Environmental Engineering
College of Engineering, University of Baghdad.
ayadabedalhamzafaisal@yahoo.com

Hadeel Kareem Jasim
Department of Environmental Engineering
College of Engineering, University of Baghdad.
hadeel.k_alrubaiey@yahoo.com

Abstract

The subject of using inexpensive by-product material (cement kiln dust (CKD)) is considered attractive in terms of sustainable green development and eliminating cost of disposal. In the present study an extension for analytical sorption model derived by Sulaymon et al. (2016) was achieved for distinguishing between adsorption and/or precipitation mechanisms in the presence of CKD. This model was validated with the batch experimental measurements obtained for simulated water with pH of 3, agitation speed not less than 200 rpm and contact time either of 40 min for cadmium under different values of adsorbent dosage and contaminant concentrations. The developed model successfully described the isotherm relationship for total sorption (adsorption + precipitation) of cadmium with coefficient of determination equal to 0.90 where the precipitation has highest proportion (≥ 70%).

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

Introduction

Contaminated sites represent a major challenge for the long-term sustainability of the environment. In addition to their potential adverse impacts on human health, surface and groundwater quality, and ecological processes, they also represent a lost economic opportunity.Sources of contaminants include those arising from anthropogenic activities such as industrial and agricultural practices, mining activities, accidental spillages, and so on, and natural geogenic processes, with the latter largely associated with metals such as arsenic, lead and cadmium [11].

Adsorption/desorption and precipitation/dissolution are the major mass transfer mechanisms that control the treatment processes of heavy metals with using cement kiln dust (CKD). Many theoretical and experimental studies in the past two decades have investigated these mechanisms. Unfortunately, none of these studies could clearly distinguish between these two mechanisms. The studies can be classified into three groups; where the first one dealing with CKD as an adsorbent material and pure adsorption is the predominant mechanism [1], [21]. The second group signified that the precipitation is the common mechanism in the removal of heavy metals because the pH of the aqueous solution can be raised due to presence of lime in the composition of CKD [9], [10], [23]. The last group of studies explained that the removal of contaminants can be achieved due to CKD-contaminants interaction without specifying the type and contribution of adsorption/precipitation mechanisms [8], [14].

Hence, there is a need to specify the predominant mechanisms and the efficacy of CKD in the treatment of aqueous solutions contaminated with the cadmium ions. This can be achieved by a set of batch experiments in combination with using an analytical isotherm model that derived by Sulaymon [18] and developed in the present study.

Accordingly, the objective of this study was to find the predominant mechanism for removal of cadmium contaminant by CKD and this can be achieved by experimental methodology that adopted for the characterization of the precipitation mechanism in combination with developing an analytical isotherm model.

2. Derivation of the simultaneous adsorption–precipitation equation

Sulaymon [18] derived an analytical isotherm expression that recognized between the adsorption and precipitation when occurred together.

This expression is evaluated the quantity of contaminant removed by total sorption and precipitation where the difference between them will be the portion removed by adsorption. This model can be summarized as follows:

Precipitation by metal (M) hydrolysis

$$X_2O + H_2O \rightarrow 2X(OH) \qquad (1)$$

$$MSO_4 + 2X(OH) \rightarrow M(OH)_2 \downarrow + X_2SO_4 \qquad (2)$$

Where $X: K, Na$

The metal can be adsorbed onto CKD particle:

$$M(OH)_2 + CKD \rightarrow CKD - \{-M(OH)_2\} \qquad (3)$$

The quantity of sorbate remaining in the aqueous solution at equilibrium state is ($V\,C_{eq}$) and the complementary quantity adsorbed onto CKD particle is ($m\,q_{eeq}\big|_{C_{eq}}$) where the total quantity can be calculated as follows:

$$VC_o = m\,q_{eeq}\big|_{C_{eq}} + VC_{eq} \qquad (4)$$

The total quantity of sorbate can be removed by apparent adsorption (q_{eapp}) (i.e. adsorption and precipitation) is calculated by the difference between initial and equilibrium concentrations of dissolved metal as follows:

$$q_{eapp} = \frac{V(C_{10} - C_{1f})}{m} \qquad (5)$$

C_{10} & C_{1f} are the intial (t =0) and the final equilibrium (t=∞) concentration of metal in the solution (mg/L), the adsorption-precipitation processes can be described in the equilibrium condition as follows:

$$Total\ mass\ of\ M = \{mass\ remains\ as\ dissolved\ ions\ \{adsorbed\ mass\} + \{precipitated\ mass\} \qquad (6)$$

Or;

$$VC_{10} = VC_{1f} + \{adsorbed\ mass\} + \{precipitated\ mass\} \qquad (7)$$

From Eq.7, adsorbed mass will be:

$$\{adsorbed\ mass\} = VC_{10} - VC_{1f} - \{precipitated\ mass\} \qquad (8)$$

Also, this mass is quantified by adsorption as:

$$\{adsorbed\ mass\} = m\ q_e|_{C'_{1f}} \qquad (9)$$

Where $q_e|_{C'_{1f}}$ is the quantity of adsorption after return the portion of metal that released from precipitation to the aqueous solution as follows:

$$C'_{1f} = C_{1f} + C_{1f_p} \qquad (10)$$

Where C'_{1f} is concentration of dissolved contaminant at equilibrium state where no precipitation occurred and C_{1f_p} is the portion of metal can be precipitated where it is value as follows:

$$C_{1f_p} = C_{10} - C'_{1f_p} \qquad (11)$$

Where C'_{1f_p} is the equilibrium concentration when no adsorption process occured. Hence, Eq.11 can be rewritten as:

$$C'_{1f} = C_{1f} + C_{10} - C'_{1f_p} \qquad (12)$$

Consequently,

$$q_e = \frac{\mathrm{V}(C_{10} - C'_{1f})}{\mathrm{m}} \text{ or } q_e|_{C'_{1f}} = \frac{V\left(C_{10} - C_{1f} - C_{10} + C'_{1f_p}\right)}{m} \text{ or } q_e|_{C'_{1f}} = \frac{V\left(C'_{1f_p} - C_{1f}\right)}{m} \qquad (13)$$

This model was used in the present study for distinguishing between adsorbed and precipitated fractions of cadmium in the aqueous solution treated by CKD.

3. Sorption isotherms

The sorption isotherm model cannot provide evidence picture about the kind of the predominant reaction which may be adsorption, precipitation or others [15]. This argument leads to use the ‘‘sorption’’ word as the more general term to characterize any type of retention [16].

The plotting of the isotherm data and describing the adsorption experiments with finding the best fitting is of great importance. In the present study, a set of sorption models are used to simulate the performance of CKD in removing of dissolved pollutants. These models can classified according to the number of constants into two types; two and three constant models. Freundlich (1906), Langmuir (1916), Temkin (1934), BET (1938) and Dubinin-Radushkevich (1960) are examples on the first type and they can be used for description of pure adsorption and precipitation. While Redlich-Peterson (1959), Radk and Prausnitz (1972) and Sips (1984) are represented the second type and they more suitable for description of total sorption (i.e., adsorption-precipitation). These isotherms are listed in **Table 1**.[5], [17], [6], [7].

4. Materials and methods

4.1. Mediums and contaminants

The reactive material used was cement kiln dust (CKD) which is produced as by-product from the new Al-Kufa cement factory, Kufa, Al-Najaf city, Iraq. This material is considered as nonhomogeneous [3]. Its chemical composition is explained in **Table. 2**.

Table. 1 Two and three-parameter single-component isotherm models

Isotherm	**Form**
Freundlich	$q_e = a_F C_e^{b_F}$
Langmuir	$q_e = \dfrac{Q_o b C_e}{1 + b C_e}$
Temkin	$q_e = \dfrac{RT}{b_{Te}} \ln(a_{Te} C_e)$
Dubinin–Radushkevich	$q_e = q_D \exp\left[-B_D \left(RT\, ln\left\{1 + \dfrac{1}{C_e}\right\}\right)^2\right]$

BET	$q_e = \dfrac{q_m b C_e}{(C_s - C_e)\left[1 + (b-1)^{C_e/C_s}\right]}$
Redlich–Peterson	$q_e = \dfrac{K_R C_e}{1 + a_R C_e^{\beta_R}}$
Radke–Prausnitz	$q_e = \dfrac{q_{mRP} \cdot K_{RP} C_e^{mRP}}{K_{RP} + q_{mRP} C_e^{mRP-1}}$
Sips	$q_e = \dfrac{K_s C_e^{\beta_s}}{a_s C_e^{\beta_s} + 1}$

Table. 2 The chemical composition of CKD

Constituents	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	L.O.I*	K_2O	Na_2O eq.**
Mean (wt. %)	11.72	3.82	2.76	46.25	2.49	11.05	19.60	1.378	0.661

* Loss on ignition; **= Na_2O+ 0.658 K_2O

Cd was selected as representatives of heavy metal contaminants. To simulate the water's Cd contamination and a solution of Cd $(NO_3)_2.4H_2O$ (SD Fine-Chem Limited, India) was prepared and added to the specimen to obtain a representative concentration.

4.2. Total (apparent) adsorption–precipitation

Batch experiments were conducted to specify the effect of many conditions such as contact time, initial concentration of contaminant, and agitation speed on the treatment process for acidic contaminated water (initial pH= 3) (dosage=0.1, 0.2, 0.3, 0.5 g/100ml).

In addition, these experiments are very important in the specifying the total sorption in the removal process.

Flasks of 250 mL were prepared and 100 mL of cadmium aqueous solution was added into each flask. Certain quantity of CKD was employed in the prepared flasks and the solutions in the flasks were continuously agitated on the shaker at specified speed. The aqueous solution from each flask was filtered to separate the CKD sorbent and the supernatant was analyzed for measuring the remained cadmium concentration using the atomic absorption spectrophotometer (Sens AA, Austeria). The sorbed concentration of contaminant onto CKD sorbent was calculated by a mass balance. The experimental conditions are listed below:

1. Initial concentrations of cadmium used in the present experiments were 100, 250, 500 and 1000 mg/L.
2. The weight of CKD was changed according to the order; 0.1, 0.2 and 0.3 g/ 100 mL for aqueous solution contaminated with cadmium.
3. The time required for agitating of CKD with contaminated water was changed in the range from 10 to 180 min. This was to investigate the effect of agitation time on the percentage removal of contaminant.
4. Agitation speed used in this set of tests has the values ranged from 0 to 250.
5. The temperature at which agitation took place was 25°C.
6. The volume pipetted out at the end of each test after filtration process was changed from 5 to 10 mL.
7. The CKD material must be separated from the aqueous solution at the end of each experiment by filtration.
8. The final concentration of contaminant (C_f) was measured in the filtered liquid.
9. Sorption isotherm relationship can be plotted between q_e and C_f.

4.3. Pure precipitation

Certain amount of CKD was mixed with 100 mL of acidic water where the initial pH of 3 and the resultant mixture agitated at specified speed for duration of 40 min for cadmium. Then, the CKD sorbent was separated from the aqueous solution by using an experimental procedure similar to "tea-bag" experiment [20]. The pollutant (cadmium) was added to the supernatant and the mixture was agitated until achieving the equilibrium at the time described previously. The aqueous solution was filtered to remove the chemical precipitates and the concentration of dissolved contaminant was measured by the Atomic absorption spectrophotometer (AAS) (Sens AA, Austeria). Mass balance was used to calculate the concentration of contaminant removed by precipitation. The experimental procedure of pure precipitation was implemented under the best conditions specified through the total sorption experiments.

5. Results and discussion

Fig. 1 plotted the results of total (apparent) sorption for cadmium with respect to isotherm models described previously. The figures signified that the initial concentrations of contaminant are varied for each adopted value of sorbent dosage and they have values of 100, 250, 500 and 1000 mg/L for cadmium to satisfy the range required to build the sorption isotherm model. In spite of presence a reasonable matching between batch results and these models, still the need for acceptable agreement is required and this clear from the values of determination coefficients (R^2). Accordingly, the representative of the experimental total sorption results by more adequate model is represented a unique task. Step-wise procedure with mass balance principle was used in the present study to develop the sorption model which is an extension to one derived by Sulaymon [18].

This model can be used for distinguishing between adsorption and precipitation mechanisms when occurred simultaneously. It can be applied for cadmium (i.e. heavy metal) removal from aqueous solutions using CKD material.

Pure precipitation was measured experimentally for cadmium using the procedure described and the values are plotted in the **Fig. 2 and Fig. 3**. It is clear that the removal of cadmium by pure precipitation is lagged than that removed by total sorption (adsorption-precipitation) mechanism, the increased probability of cadmium ions removal may be resulted from direct contact between these ions and CKD for total sorption.

The values of pure adsorption due to CKD can be predicted as a complementary portion of the total sorption as illustrated in the **Fig. 2** and **Fig.3**. These figures signified that the total removal (=precipitation + adsorption) was related directly with the dosage of CKD.

It seems that the portion of contaminant removed by adsorption is increased in the high concentrations due to increase of CKD mass. However, the opposite behavior was recognized for low concentrations where the pure precipitation was high compared to the total sorption as shown in **Fig. 2**. This may be attributed to form of cadmium hydroxide due to reactivity of CKD. It is clear that the adsorption process may be slower than the precipitation process and this means that the achieving of maximum adsorption capacity is required approximately longer time. However, the precipitation process represents the predominant mechanism for removing of cadmium from aqueous solution using CKD for conditions under consideration.

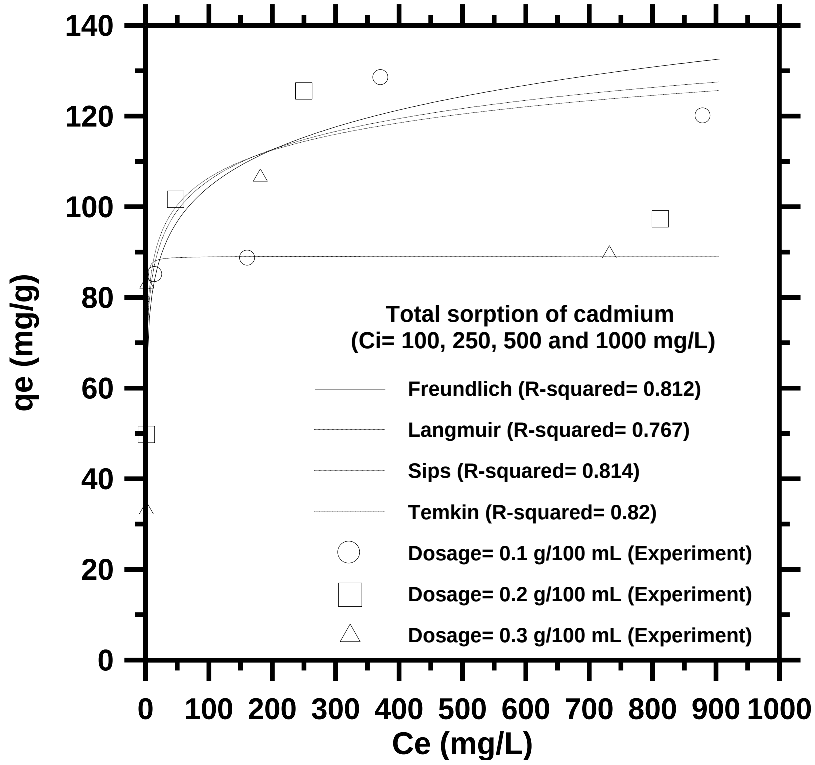


Fig. 1 (a) Total (apparent) sorption isotherm models for cadmium ions onto the CKD particles.

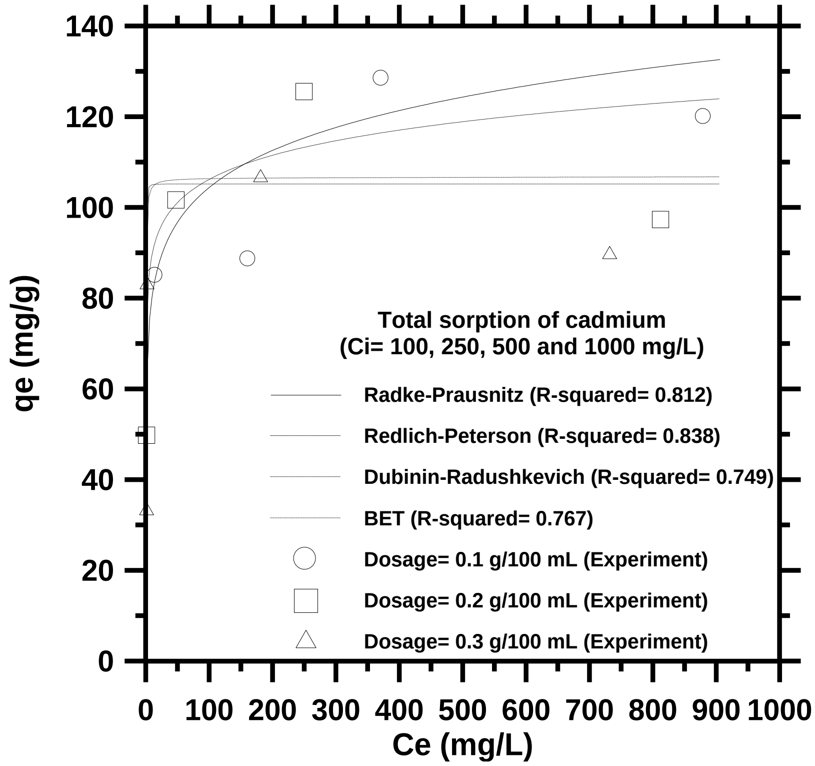


Fig. 1 (b) Total (apparent) sorption isotherm models for cadmium ions onto the CKD particles.

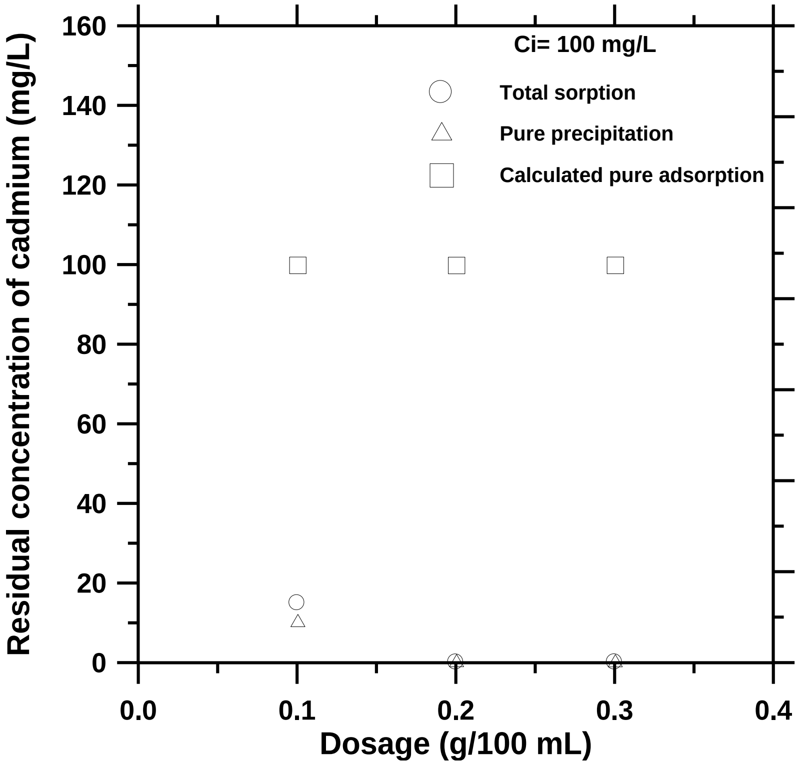


Fig. 2 (a) The shares of mechanisms that participated in the removal of cadmium ions from aqueous solutions using CKD as sorbent.

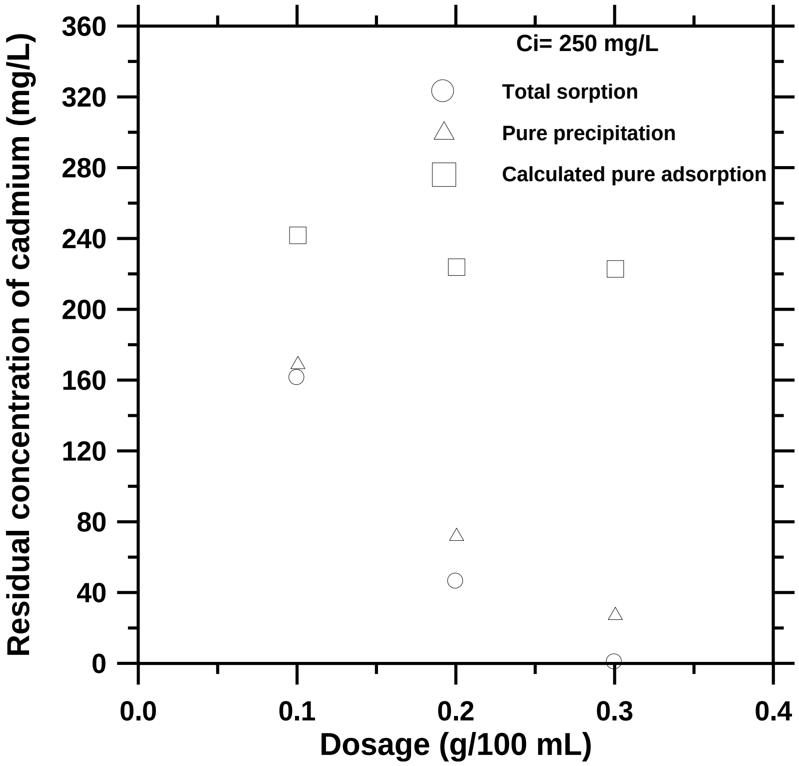


Fig. 2 (b) The shares of mechanisms that participated in the removal of cadmium ions from aqueous solutions using CKD as sorbent.

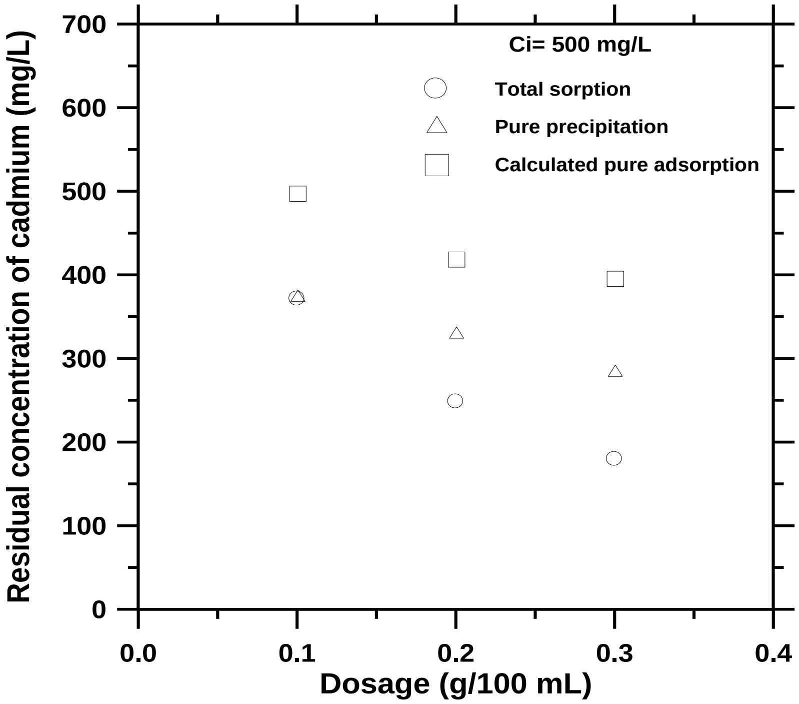


Fig. 2 (c) The shares of mechanisms that participated in the removal of cadmium ions from aqueous solutions using CKD as sorbent.

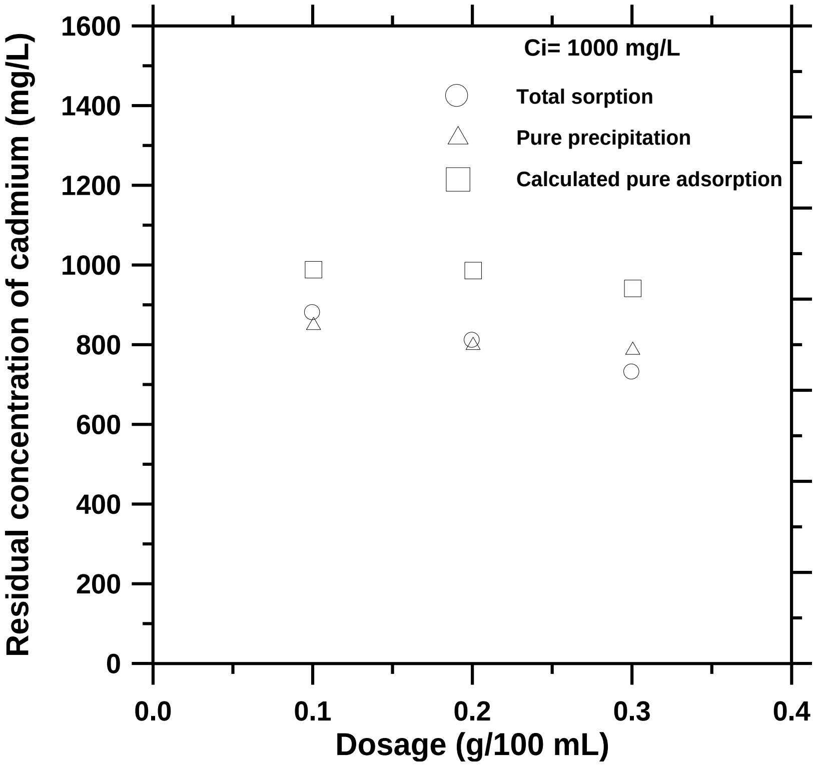
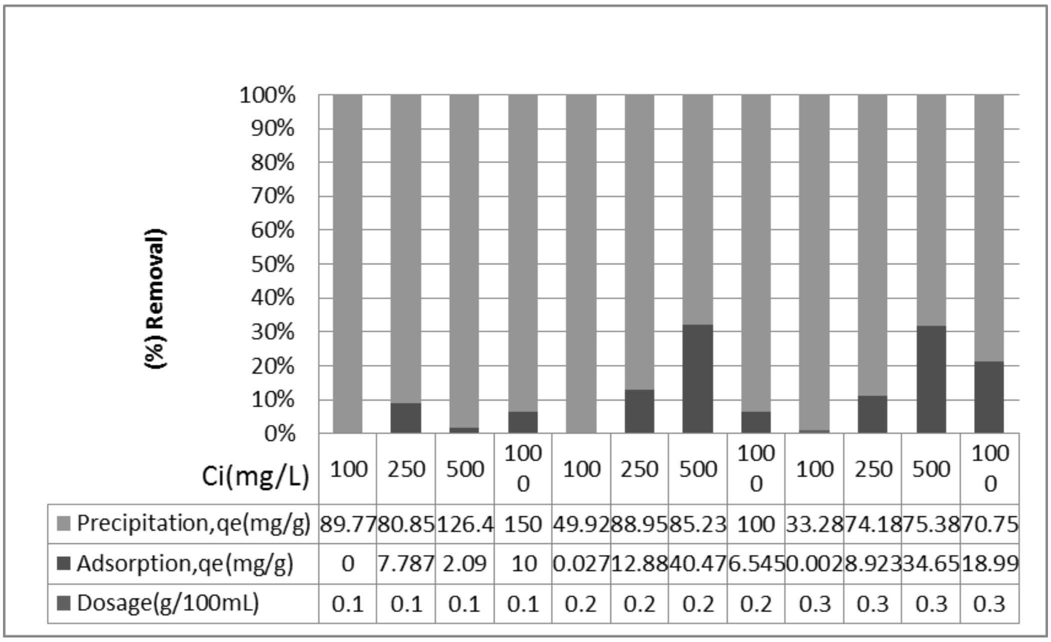


Fig. 2 (d) The shares of mechanisms that participated in the removal of cadmium ions from aqueous solutions using CKD as sorbent.



Ci(mg/L)	100	250	500	1000	100	250	500	1000	100	250	500	1000
▨ Precipitation,qe(mg/g)	89.77	80.85	126.4	150	49.92	88.95	85.23	100	33.28	74.18	75.38	70.75
■ Adsorption,qe(mg/g)	0	7.787	2.09	10	0.027	12.88	40.47	6.545	0.002	8.923	34.65	18.99
■ Dosage(g/100mL)	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3

Fig. 3 Percentage removal shares of precipitation and adsorption mechanisms that participated in the removal of cadmium ions from aqueous solutions using CKD as sorbent.

The adsorption isotherm models of cadmium onto CKD reactive material for calculating pure adsorption were plotted in **Fig. 4**. These models are drawn in global coordinates [20] for all batch tests with initial pH of aqueous solution equal to 3. It is clear that there is a low matching between predicted values of adsorption and adopted adsorption models and this may be due to a high heterogeneity of CKD material [3]. However, Dubinin-Radushkevich isotherm model has the highest value of R^2 and, accordingly, this model can be used to represent the pure adsorption portion in the equation of total sorption as in the following equation:

$$q_{e,t} = q_{e,ad} + q_{e,p} \qquad (14)$$

Where $q_{e,t}$, $q_{e,ad}$, and $q_{e,p}$ are the mass of contaminant sorbed by total sorption, pure adsorption, and pure precipitation respectively .

The measurements of pure precipitation are represented by different sorption models and these results were tended to coincide with Radke-Prausnitz model. This means that the precipitation portion ($q_{e,p}$) in equ. (14) can be represented by Radke-Prausnitz model. Consequently, the total sorption isotherm can be rewritten as:

$$q_{e,t} = q_D \exp\left[-B_D \left(RT \ln\left\{1 + \frac{1}{C_e}\right\}\right)^2\right] + \frac{q_{mRP} \cdot K_{RP} C_e^{mRP}}{K_{RP} + q_{mRP} C_e^{mRP-1}} \qquad (15)$$

The constants of all used models were evaluated for cadmium by non-linear regression using IBM SPSS Statistics version 20. **Fig. 5** shows that the present model equ. (15) can be successfully describing the adsorption-precipitation as a function of equilibrium concentration for water contaminated with cadmium and the treatment achieved by CKD sorbent.

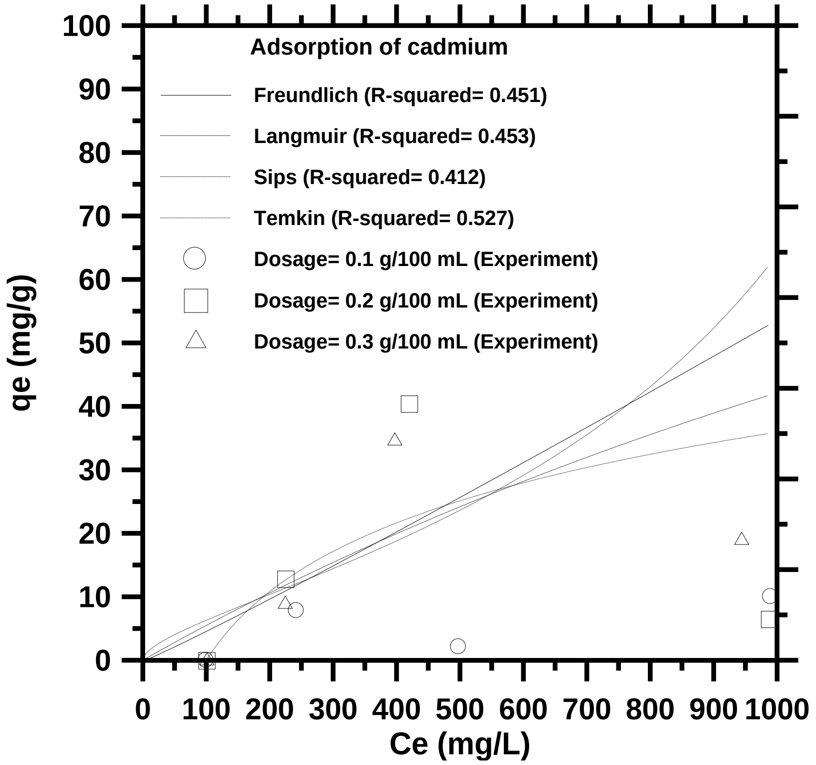


Fig. 4 (a) Isotherm models for adsorption of cadmium onto CKD particles.

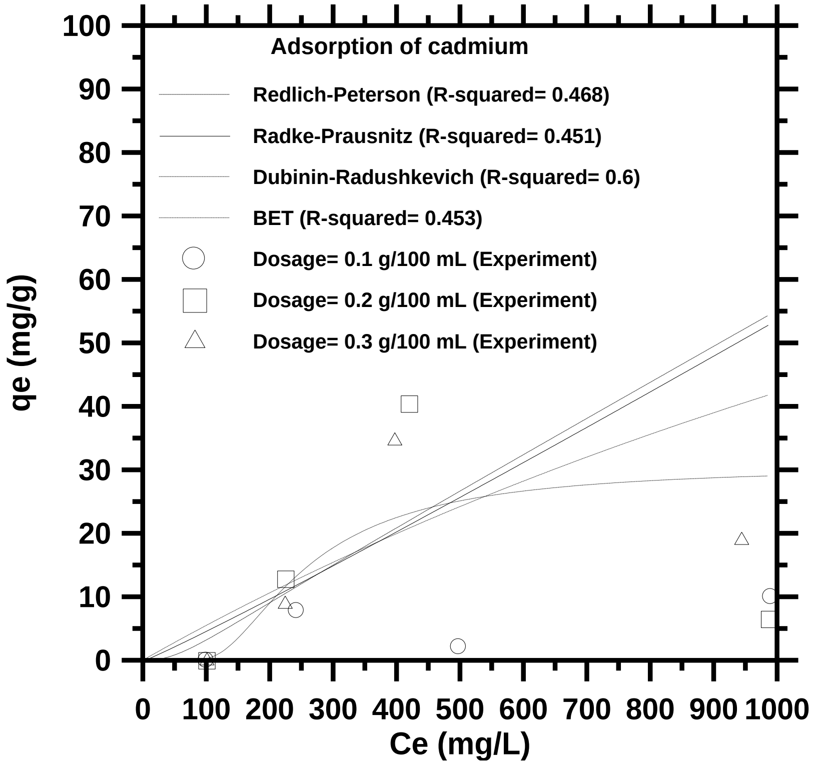


Fig. 4(b) Isotherm models for adsorption of cadmium onto CKD particles.

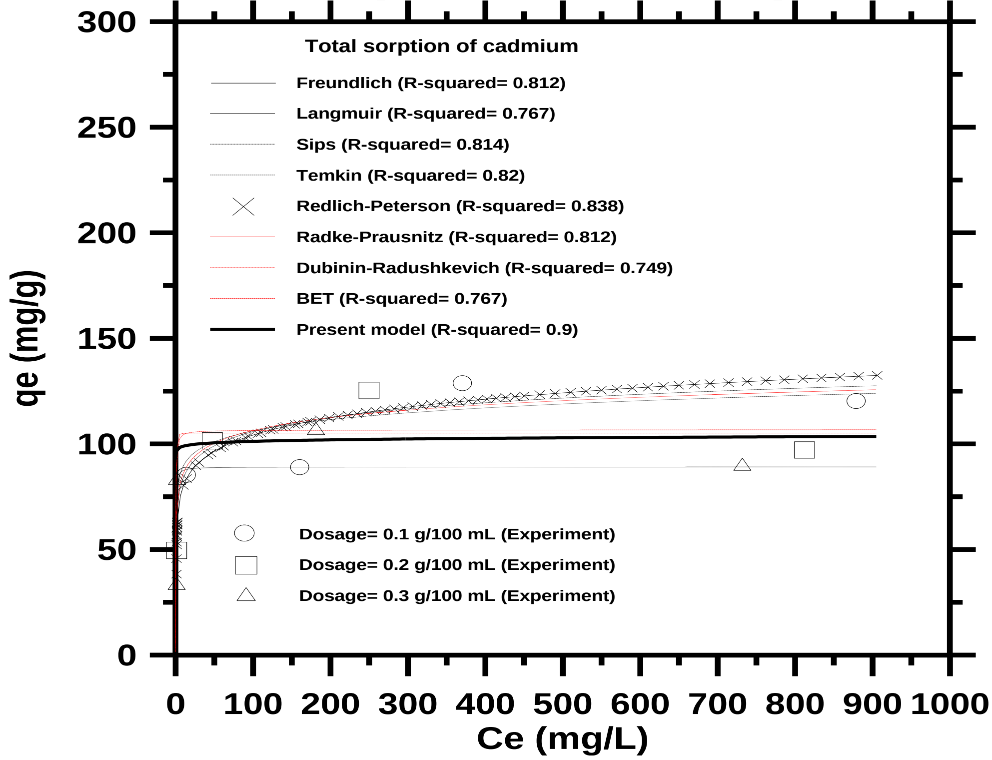


Fig. 5 Total sorption isotherm for cadmium onto CKD particles; comparison of present model (Eq.15) with the conventional models.

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 batch results proved that the cadmium is removed from contaminated water by two mechanisms namely; adsorption and precipitation where the second mechanism is the predominant with proportion not less than 70% and, consequently, the proportion of adsorption is not exceeded 30% for all conditions under consideration.

The results proved that the Dubnin-Radushkevich isotherm can be used as the base expression in the developed analytical sorption model for description of pure adsorption, while the Radke-Prausnitz expression can be represented the pure precipitation for complementing of this model. Thus, the developed model could be successfully represented the relationship between the total adsorption-precipitation and the residual concentration of cadmium treated with CKD.

References

[1] Al-Meshragi M., Ibrahim H.G. and Aboabboud M.M., 2008. Equilibrium and kinetics of chromium adsorption on cement kiln dust. Proceedings of the World Congress on Engineering and

Computer Science, WCECS, San Francisco, CA, October 22–24, 2008.

[2] Bear J. and Cheng A. H.D., 2010, Modeling groundwater flow and contaminant transport (theory and applications of transport in porous media), Springer, ISBN: 978-1-4020-6681-8.

[3] Colangelo F. And Cioffi R., 2013, Use of cement kiln dust, blast furnace slag and marble sludge in the manufacture of sustainable artificial aggregates by means of cold bonding pelletization, Materials 6, 3139–3159.

[4] El-Awady M.H. and Sami T.M., 1997. Removal of heavy metals by cement kiln dust. Bull. Environ. Contam. Toxicol. 59, 603-610, Springer-Verlag, New York Inc.

[5] Foo K.Y., Hameed B.H.,2010, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J. 156, 2–10.

[6] Hamdaoui O., Naffrechoux E., 2007, Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon part I. Two-parameter models and equations allowing determination of thermodynamic parameters, J. Hazard. Mater. 147, 381–394.

[7] Ho Y.S., Porter J.F., McKay G., 2002, Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems, Water Air Soil Pollut. 141, 1–33.

[8] Klimantavièiûtë, M.G., Virbalytë D., Pakðtas V., Juðkënas R. and Pigaga A., 2005. Interaction of heavy metal ions with cement kiln dust. Ekologija., 1, 31–36.

[9] Mackie A.L. and Walsh M.E., 2012 Bench-scale study of active mine water treatment using cement kiln dust (CKD) as a neutralization agent, Water Res. 46 327–334.

[10] Mackie A.L., Walsh M.E. and C.B. Lake, 2010, Investigation into the use of cement kiln dust (CKD) for wastewater treatment, PCA R&D Serial No. SN3038, Portland Cement Association.

[11] Naidu R., Smith E., Owens G., Bhattacharya P. and Nadebaum P. editors.2006, Managing Arsenic in the Environment, CSIRO.

[12] Naidu R, Birke V, Permeable Reactive Barrier: Sustainable Groundwater Remediation, 2014. Volume 1 of Advances in Trace Elements in the Environment, CRC Press. P 4

[13] Qusey, M. K., Reactive barrier treatment wall technology for remediation of inorganic contaminated groundwater, ph.D. thesis ,college of engineering-university of basrah, Iraq, 2014.

[14] Saraya M.E., Aboul-Fetouh M.E. , Nassar H.S. and Abd-El-Rahman A.M., 2011. Removal of direct dyes with cement kiln dust. Journal of Materials Science and Engineering, B 1, 97-105.

[15] Scheidegger A.M. and Sparks D.L. 1996. A critical assessment of sorption-desorption mechanisms at

the soil mineral/water interface. Soil Sci. 161:813-831

[16] Sposito G. (1984) The Surface Chemistry of Soils. Oxford University Press, New York, 234 p.

[17] Sulaymon, A.H., Abbood D.W. and Ali A.H., 2011. Competitive adsorption of phenol and lead from synthetic wastewater onto granular activated carbon. Journal of Environmental Science and Engineering, 5, 1389-1399.

[18] Sulaymon, A.H., Faisal , A. A.H, and Khaliefa , Q. M. ,(2016), Simultaneous Adsorption – Precipitation Characterization as Mechanisms for Metals Removal from Aqueous Solutions by Cement Kiln Dust (CKD), Desalination and Water Treatment , 57, 819-826.

[19] Townshend A. and Jackwerth E.,1989, Precipitation of major constituents for trace pre-concentration: Potential and problems, Pure Appl. Chem. 61, 1643–1656.

[20] Volesky B., 2004, Sorption and Bio-sorption, BV-Sorbex Inc., Montreal, Canada.

[21] Waly, T.A., Dakroury A.M., El-Sayed G.O. and El-Salam S.A., 2010. Assessment removal of heavy metals ions from wastewater by cement kiln dust (CKD). Journal of American Science, 6(12), 910-917.

[22] Wang S., Nan Z., Li Y., Zhao Z., 2009, The chemical bonding of copper ions on kaolin from Suzhou, China, Desalination 249, 991–995.

[23] Zaki, N. G., Khattab I. A. and Abd El-Monem N.M., 2007. Removal of some heavy metals by CKD leachate. Journal of Hazardous Materials, 147, 21–27.

[24] Zhu C., Martin S., Ford R. and Nuhfer N., 2003, Experimental and modeling studies of co-precipitation as an attenuation mechanism for radionuclides, metals, and metalloid mobility, Geophys. Res. Abstr. 5, 06552.

اليتي الامتزاز والترسيب للمياه الملوثة بالكادميوم

أ.د. اياد عبد الحمزة فيصل،
هديل كريم جاسم
قسم الهندسة البيئية
كلية الهندسة، جامعة بغداد

الخلاصة

ان موضوع استخدام مواد ثانوية غير مكلفة يعتبر ملفت للانتباه في مفهوم التنمية الخضراء المستدامة والقضاء غلى تكلفة التخلص من تلك المواد. في هذه الدراسة تم عمل امتداد/ تطوير لنموذج الامتزاز التحليلي المستمدة من سليمون وآخرون(2016) وذلك للتمييز بين آليات الامتزاز و/ او الترسيب مع وجود مادة غبار افران الاسمنت. و كان هذا النموذج متوافق مع القياسات المختبرية التجريبية التي تم الحصول عليها وذلك من أجل محاكاة المياه الجوفية ذات الرقم الهيدروجيني 3، سرعة التحريض لا تقل عن 200 دورة في الدقيقة ووقت تماس 40 دقيقة للكادميوم تحت قيم مختلفة من الجرعات للممتزات والتركيز الملوثات. وقد وصف النموذج المطور بنجاح العلاقة لإجمالي الامتزاز (الامتصاص + الترسيب) في الكادميوم مع معامل تحديد يساوي 0.90 حيث كان الترسيب لديه أعلى نسبة (≤ 70٪). عكسيا، فإن عملية الامتزاز تكون هي المسؤولة فقط عن إزالة البنزين.

الكلمات الافتتاحية: المعادن الثقيلة، الترسيب، الامتزاز، التلوث، غبار افران الاسمنت.