CHEMICAL ENGINEERING TRANSACTIONS

VOL. 83, 2021

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Jiří Jaromír Klemeš

ISBN 978-88-95608-81-5; **ISSN** 2283-9216

DOI: 10.3303/CET2183044

Fixed Bed Column Studies for the Adsorption of Cadmium onto Cockle Shell (Anadara Granosa) Powder

Tuan-Anh Nguyen[a,*], Cam-Huy Nhan[a], Minh-Vien Le[a], Phuong-Ha K. Huynh[a], Thanh Khoa Phung[b], Anh Vy Tran[c]

[a]Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT) – Vietnam National University Ho Chi Minh City (VNUHCM), 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, Vietnam
[b]School of Biotechnology, International University, Vietnam National University Ho Chi Minh City (VNUHCM), Quarter 6, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Vietnam
[c]Department of Chemical and Biological Engineering, Gachon University, 1342 Seongnamdaero, Seongnam-si, Korea
anh.nguyen@hcmut.edu.vn

Recently, the pollution of heavy metal ions is getting more attention due to economic development. A number of methods have been proposed for the removal of heavy metal ions in aqueous solutions, and the adsorption technique has been widely utilized due to the effectiveness and flexibility. Cockles are marine bivalve molluscs and their shells are discharged as waste by many restaurants and marine product manufacturers, which causes environmental problems. Cockle shells can be economically reused as an adsorbent for wastewater treatment. In this report, cockle shells were recycled as a material for the removal of cadmium (II) ion by adsorption in a fixed bed column. Experiments were designed according to the Box-Behnken scheme to investigate the effect of the column parameters such as inlet ion concentration, feed flow rate, and mass of adsorbent. The breakthrough curves from experiments were analyzed with Thomas, Bohart–Adams, and Yoon–Nelson models. The results also indicate that the powder derived from cockle shells can be used as a low cost and effective adsorbent for heavy metal removal such as cadmium in a fixed bed column. The observation suggests that the Thomas model and the Yoon-Nelson model are more suitable to predict the adsorption of cadmium (II) ions on onto cockle shell powder in fixed-bed operation mode.

1. Introduction

Recently, the pollution of heavy metal ions is getting more attention in the developing world due to economic development. It was proved that heavy metal ion could cause severe problems to human health and the ecosystem (Khan et al., 2015). Numerous studies and several methods have been reported to treat heavy metal ions in water, such as precipitation, extraction, ion-exchange, coagulation-flocculation, flotation, membrane separation and electrochemical methods (Fu and Wang, 2011). Among them, the adsorption technique has been widely utilized due to its flexibility and cost-efficiency (Kumar et al., 2019). There are many kinds of adsorbents; however, the study of a low-cost and environmental friendly adsorbent is always desirable (Joseph et al., 2019). Food industry wastes such as desiccated coconut wastes (Rahim et al., 2019), oil palm wastes (Lee et al., 2017), coffee husk and spent coffee (Hernández Rodiguez et al., 2018), sugar cane bagasse (Busto et al., 2016), rice husk (Garba et al., 2017) have been utilized in adsorption study for the removal of heavy metals.

Cockles are marine bivalve molluscs and their shells are discharged as waste by many restaurants and marine product manufacturers. Most of them are dumped into landfills, which becomes a potential environmental problem. According to recent research (Zuo et al., 2017), $CaCO_3$ structure in seashells has a strong affinity with heavy metal ions, especially cadmium (II). Using seashells as adsorbent could be an economic and environmental friendly method as the process is highly efficient, low-cost materials for taking advantage of aquaculture's waste product.

For industrial-scale applications, the adsorbents are usually used in the fixed bed column because of the high capacity and continuous operation. The majority of cadmium adsorption studies have been carried out in batch

Paper Received: 10/07/2020; Revised: 06/09/2020; Accepted: 27/09/2020
Please cite this article as: Nguyen T.-A., Nhan C.-H., Le M.-V., Huynh P.-H.K., Phung T.K., Tran A.V., 2021, Fixed Bed Column Studies for the Adsorption of Cadmium onto Cockle Shell (Anadara Granosa) Powder, Chemical Engineering Transactions, 83, 259-264 DOI:10.3303/CET2183044

modes, which are only suitable for the treatment of small quantities of wastewater. There are not many studies that report the adsorption of cadmium ion by food industry waste in a fixed-bed column. In this study, cockle shells were recycled as a material for the removal of cadmium (II) ion by adsorption in a fixed bed column. The operation of the process depends on various parameters, and the effects of inlet cadmium ion concentration, flow rate, and mass of adsorbent on the behavior of the column are investigated. The column experimental data were fit to Thomas, Bohart–Adams, and Yoon–Nelson models to describe the breakthrough curves.

2. Materials and methodology

2.1 Adsorbent and absorbate

Cockle shells (Anadara granosa) grew in the South-East of Vietnam were collected at Ho Chi Minh city's retail store. The organic parts were taken out; after that, the shells were brushed to clean all remaining dirt and organic parts; then wash with deionized water. The shells were dried under the sunlight for three days. After the water had evaporated, the shells were crushed by pestle and sieved to 0.5-1 mm grain size by 0.5 and 1 mm laboratory sieves. Shell powder was preserved in airtight polyethylene bottle at room temperature and used for further column experiments.
Cadmium solutions were prepared from cadmium sulfate octahydrate salt ($3CdSO_4 \cdot 8H_2O$, China) dissolved in deionized water into the desired concentrations.

2.2 Fixed-bed column adsorption

Continuous column adsorption experiments were conducted in a laboratory Pyrex glass tube with an inner diameter of 10 mm and a height of 300 mm. The column was initially packed with a predetermined mass of cockle shell powder. Then the prepared cadmium solution was pumped upward through the column at the desired flow rate by a peristaltic pump. At different time intervals, the samples were collected at the outlet of the column, and the concentration of the samples was determined. An ion selective electrode was used for the quantitative analysis of cadmium (II) ion in the liquid phase. The cadmium ion analytical device is from Hanna Instruments, consists of pH/ISE meter (HI98191), reference electrode (HI5315), and cadmium half-cell ISE electrode (HI4003). The flow to the column was continued until there was no adsorption on the adsorbent, or the cadmium (II) ion concentration of the effluent remained unchanged. The schematic diagram of the experimental set up is shown in Figure 1.

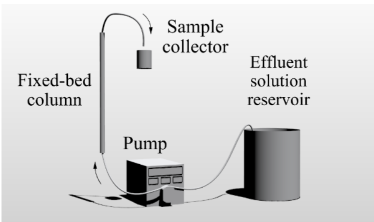

Figure 1: Adsorption column system

In this study, the second-order Box-Behnken design was employed to study the effect of several operating parameters of the column, such as inlet concentration, mass of adsorbent, flow rate on the adsorption performance of the fixed-bed. The detail of variables and levels is shown in Table 1. The full experimental design and results are shown in the next session. pH and temperature of all experiments were maintained in the range of 5.5-7.0 and 25 °C - 27 °C.

Table 1: Levels and values of column parameters

Coded variables	Factors	Levels		
		-1	0	+1
X_1	Inlet concentration (mg/L)	190	200	210
X_2	Mass of shell powder (g)	4.5	5.0	5.5
X_3	Flow rate (mL/min)	7	8	9

2.3 Theory of models for fixed-bed studies

The succeeding operation of a laboratory apparatus towards industrial-scale column can be well analyzed by simple mathematical models (Lakshmipathy and Sarada, 2015). The experimental data of the column from

different operating conditions were examined with well-known and straightforward mathematical models such as the Thomas, Bohart–Adams, and Yoon–Nelson models.
Thomas model (Thomas, 1944) assumes the plug flow behavior and Langmuir adsorption-desorption equilibrium in the bed. The mathematical equation is expressed as Eq(1):

$$\frac{C_t}{C_0} = \frac{1}{1+exp\left(\frac{K_T q_0 m}{Q} - K_T C_0 t\right)} \quad (1)$$

and the simplified linear form is as Eq(2):

$$ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_T q_0 m}{Q} - K_T C_0 t \quad (2)$$

where K_T is the Thomas rate constant (mL min^{-1} mg^{-1}); q_0 is the adsorption capacity (mg g^{-1}); m is the mass of adsorbent in the column (g); Q is the feed flow rate (mL min^{-1})
The adsorption capacity q_0 can be obtained from the experimental breakthrough curve by Eq(3):

$$q_{0\_exp} = \frac{QC_0}{m}\int_0^{\infty}\left(1 - \frac{C_t}{C_0}\right)dt \quad (3)$$

The Bohart–Adams (Bohart and Adams, 1920) assumes that the equilibrium is not instantaneous, and the rate of sorption is proportional to the fraction of sorption capacity. The mathematical form and the linear form are expressed as the following Eq(4) and Eq(5):

$$\frac{C_t}{C_0} = exp\left(K_{BA}C_0 t - \frac{K_{BA}N_0 Z}{U_0}\right) \quad (4)$$

$$ln\left(\frac{C_t}{C_0}\right) = K_{BA}C_0 t - K_{BA}N_0\left(\frac{Z}{U_0}\right) \quad (5)$$

where K_{BA} is the kinetic (mass transfer) constant (L mg^{-1} min^{-1}); U_0 is the superficial velocity (cm min^{-1}); Z is the bed depth of column (cm) and N_0 is the saturation concentration or adsorption capacity (mg L^{-1}).
Yoon–Nelson model (Yoon and Nelson, 1984) assumes that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of sorbate sorption and the probability of sorbate breakthrough on the sorbent. The mathematical equation and the linear form of the model are expressed as Eq(6) and Eq(7):

$$\frac{C_0}{C_t} = 1 + exp(K_{YN}t - t_{0.5}K_{YN}) \quad (6)$$

$$ln\left(\frac{C_t}{C_0 - C_t}\right) = K_{YN}t - t_{0.5}K_{YN} \quad (7)$$

where K_{YN} is the Yoon–Nelson velocity rate constant (min^{-1}); $t_{0.5}$ is the time required for 50 % of adsorbate breakthrough (min).

3. Results and discussion

The mechanism of the uptake of cadmium(II) ions by scallop shell powder are proposed by several studies such as in (Köhler et al., 2007). It can be explained by the surface precipitation of (Cd,Ca)CO_3 solid solutions. The mechanism involves the exchange of calcium ion from the adsorbent and cadmium ions from the solution to form solid-solution nuclei as the following Eq(8).

$$xCd^{2+} + CaCO_{3(s)} = xCa^{2+} + Cd_xCa_{1-x}CO_3 \quad (8)$$

The release of calcium ion also caused an increase in pH of the effluent solution (from 4.5 at the initial to 7).
The dynamic adsorption behavior of the fixed bed column, the breakthrough curve, was simulated using Thomas, Bohart–Adams and Yoon–Nelson models. The coefficient of determination and the values of the models' parameters were obtained using two methods: non-linear fitting (the original equation) and linear regression analysis (the linearized form).

3.1 Thomas model

The Thomas model parameters, the kinetic coefficient K_T and the adsorption capacity of the column q_0, were calculated by non-linear fitting from Eq(1) and linear regression from Eq(2). The values of model parameters obtained by two methods and the coefficients of determination are summarized in Table 2. From Table 2, it can be obtained that the adsorption capacity of the column increased, but the kinetic coefficient decreased with an increase in initial metal ion concentration. The reason was that the driving force for the adsorption is the difference in concentration between the cadmium ion on the adsorbent and the cadmium ion in the solution. The higher driving force due to the higher cadmium ion concentration resulted in better column performance. The higher driving force caused an increase in mass transport resistance and thus reduced the kinetic coefficient k_{TH}. The coefficients of determination (R^2) obtained for all the breakthrough curves are high, which confirms the applicability of the model. The observations suggest that external and internal diffusion were not rate-limiting steps. The results also suggest that it is better to use non-linear regression to fit the experimental data. The value of q_0 was also obtained from the experimental breakthrough curve for comparison and shown in Table 2. The values of q_0 are comparable to the ones obtained from Thomas model by non-linear fitting method. The observation confirmed the advantage of non-linear regression.

Table 2: Parameters of Thomas model obtained by non-linear fitting and linear regression

C_0	M	Q	Z	Linear			Non-Linear			Experime-nts
(mg/L)	(g)	(mL/min)	(cm)	k_{TH} (mL/mg.min)	q_0 (mg/g)	R^2	k_{TH} (mL/mg.min)	q_0 (mg/g)	R^2	q_0 (mg/g)
190	4.5	8	4.32	0.0505	163.51	0.9510	0.0488	152.48	0.9715	157.51
210	4.5	8	4.32	0.0576	243.95	0.9879	0.0549	156.53	0.9952	157.85
190	5.5	8	5.28	0.0743	161.10	0.9568	0.1041	86.58	0.9996	87.72
210	5.5	8	5.28	0.0679	219.59	0.9756	0.0851	124.64	0.9999	122.68
190	5.0	7	4.80	0.0598	197.59	0.8966	0.0767	125.33	0.9963	122.84
210	5.0	7	4.80	0.0547	220.11	0.9094	0.0670	135.75	0.9966	133.75
190	5.0	9	4.80	0.0509	157.75	0.9610	0.0503	133.64	0.9776	134.55
210	5.0	9	4.80	0.0460	167.24	0.9351	0.0462	133.68	0.9827	138.63
200	4.5	7	4.32	0.0508	169.70	0.9497	0.0544	101.55	0.9877	111.66
200	5.5	7	5.28	0.0588	167.02	0.9775	0.0772	95.53	0.9951	97.09
200	4.5	9	4.32	0.0561	173.24	0.9438	0.0484	123.33	0.9849	127.5
200	5.5	9	5.28	0.0645	180.72	0.9602	0.0803	111.23	0.9841	116.73
200	5.0	8	4.80	0.0505	167.36	0.8460	0.0696	129.32	0.9861	132.69
200	5.0	8	4.80	0.0571	182.52	0.8509	0.0828	128.71	0.9961	128.17
200	5.0	8	4.80	0.0621	226.90	0.9767	0.0587	141.06	0.9965	142.33

3.2 Bohart–Adams model

The Bohart–Adam model parameters, the kinetic coefficient (K_{BA}) and the adsorption capacity (N_0), were calculated by non-linear fitting from Eq(4) and linear regression from Eq(5). The values of model parameters obtained by two methods and the coefficients of determination are summarized in Table 3.

Table 3: Parameters of Bohart–Adams model obtained by non-linear fitting and linear regression

C_0	M	Q	Z	Linear			Non-Linear		
(mg/L)	(g)	(mL/min)	(cm)	k_{BA} (mL/mg.min)	N_0 (mg/g)	R^2	k_{BA} (mL/mg.min)	N_0 (mg/g)	R^2
190	4.5	8	4.32	0.0358	282.65	0.9149	0.0187	315.19	0.8783
210	4.5	8	4.32	0.0362	297.36	0.9227	0.0176	329.53	0.9160
190	5.5	8	5.28	0.0378	200.18	0.8500	0.0157	226.13	0.7846
210	5.5	8	5.28	0.0403	236.48	0.9304	0.0195	260.56	0.7060
190	5.0	7	4.80	0.0380	221.20	0.8475	0.0267	227.17	0.9589
210	5.0	7	4.80	0.0352	242.18	0.8571	0.0231	250.81	0.9504
190	5.0	9	4.80	0.0311	288.66	0.8476	0.0146	329.21	0.8727
210	5.0	9	4.80	0.0278	313.28	0.8027	0.0119	361.93	0.8432
200	4.5	7	4.32	0.0300	237.22	0.8334	0.0138	269.68	0.8404
200	5.5	7	5.28	0.0332	200.24	0.9241	0.0174	216.91	0.8698
200	4.5	9	4.32	0.0297	299.54	0.7656	0.0123	341.44	0.8578
200	5.5	9	5.28	0.0379	249.04	0.8457	0.0141	280.09	0.8068
200	5.0	8	4.80	0.0298	261.35	0.7592	0.0203	267.83	0.8952
200	5.0	8	4.80	0.0326	254.46	0.8265	0.0216	260.98	0.9149
200	5.0	8	4.80	0.0390	268.36	0.9004	0.0181	294.12	0.9211

From the results, many of the R^2 values are less than 0.9, which reveals that the data do not fit sufficiently well to the model. The observation suggests a lack-of-fit to the experimental data because the Bohart–Adams model is used to describe the initial period of the adsorption column (Busto et al., 2016). As a result, it can be concluded that the Bohart–Adams model is not applicable to explain the overall adsorption behavior of the column.

3.3 Yoon–Nelson model

The Yoon–Nelson model parameters, the rate constant (K_{YN}) and 50 % breakthrough time ($t_{1/2}$), were calculated by non-linear fitting from Eq(6) and linear regression from Eq(7). The values of model parameters obtained by two methods and the coefficients of determination are summarized in Table 4. From the results, the rate constant, K_{YN}, increased with an increase in inlet cadmium ion concentration. The reason was that the higher concentration offers the higher driving force for the adsorption, which results in a greater uptake rate. The values of $t_{1/2}$ decreased with an increase in flow rate. This happened because the higher flow rate results in faster saturation of cadmium ion in the column. The coefficients of determination obtained for all the breakthrough curves are as high as compared to the Thomas model and closer to 1 than that of the Bohart–Adam model. The observation suggests the goodness of fit of the experimental data to the Thomas model and the Yoon–Nelson model.

Table 4: Parameters of Yoon-Nelson model obtained by non-linear fitting and linear regression

C_0	M	Q	Z	Linear			Non-Linear		
(mg/L)	(g)	(mL/min)	(cm)	k_{YN} (min^{-1})	$t_{1/2}$ (min)	R^2	k_{YN} (min^{-1})	$t_{1/2}$ (min)	R^2
190	4.5	8	4.32	0.0096	484.09	0.9510	0.0093	451.44	0.9715
210	4.5	8	4.32	0.0121	432.39	0.9879	0.0115	419.28	0.9952
190	5.5	8	5.28	0.0141	330.28	0.9568	0.0198	313.29	0.9996
210	5.5	8	5.28	0.0143	403.31	0.9756	0.0179	408.04	0.9999
190	5.0	7	4.80	0.0114	457.73	0.8966	0.0146	471.16	0.9963
210	5.0	7	4.80	0.0115	456.51	0.9094	0.0141	461.74	0.9966
190	5.0	9	4.80	0.0097	429.31	0.9610	0.0096	390.75	0.9776
210	5.0	9	4.80	0.0097	411.79	0.9351	0.0097	353.66	0.9827
200	4.5	7	4.32	0.0102	376.19	0.9497	0.0109	326.42	0.9877
200	5.5	7	5.28	0.0118	390.56	0.9775	0.0154	375.30	0.9951
200	4.5	9	4.32	0.0112	347.71	0.9438	0.0097	308.31	0.9849
200	5.5	9	5.28	0.0129	385.56	0.9602	0.0161	339.88	0.9841
200	5.0	8	4.80	0.0101	414.67	0.8460	0.0139	404.14	0.9861
200	5.0	8	4.80	0.0114	399.56	0.8509	0.0166	402.23	0.9961
200	5.0	8	4.80	0.0124	456.73	0.9767	0.0117	440.80	0.9965

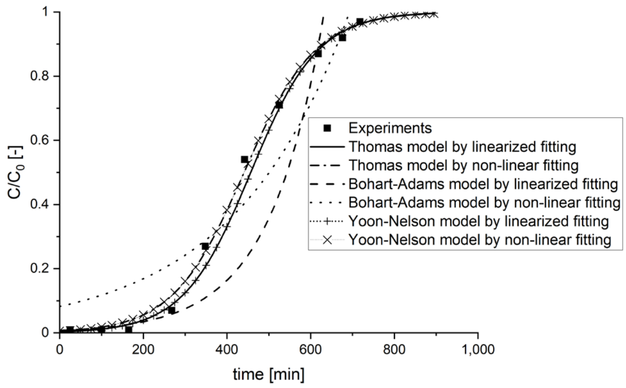

Figure 2: Experimental and predicted breakthrough curves for cadmium adsorption in the fixed-bed column at center point of experimental design (C_0=200 mg/L, M=5.0 g, Q=8 mL/min)

The predicted breakthrough curves were obtained by fitting experimental data to the three models by two methods for cadmium adsorption in the fixed-bed column at the center point of experimental design (C_0=200 mg/L, *M*=5.0 g, *Q*=8 mL/min) are presented in Figure 2. From the comparison between the predicted value and experimental data in the figure and the coefficients of determination, it can be concluded that the Thomas model and the Yoon-Nelson model are suitable for predicting the adsorption behavior of cadmium ion onto cockle shell powder in a fixed-bed column. The observation also suggests that the non-linear fitting method provides better prediction compare to the linear regression method.

4. Conclusions

This study explores the efficiency of the adsorbent derived from cockle shells in removing the heavy metal ion cadmium (II) from aqueous solution in a fixed-bed column. The effect of various operating parameters such as inlet concentration, mass of adsorbent and flow rate was investigated. The experimental breakthrough curves were analyzed by several models and two fitting methods. The observation suggests that the Thomas model and the Yoon-Nelson model are more suitable to predict the adsorption of cadmium(II) ions onto cockle shell powder in fixed-bed operation mode. The results also indicated the potential application of this method in the treatment of heavy metal ions in wastewater. The fixed bed adsorption of cadmium(II) ion with the presence of other ions has not been carried out, this is recommended for future studies.

Acknowledgments

This research is funded by Vietnam National University Ho Chi Minh City (VNU-HCM) under grant number C2018-20-15.

References

Bohart G.S., Adams E.Q., 1920, Some aspects of the behavior of charcoal with respect to chlorine, Journal of the American Chemical Society, 42(3), 523-544.

Busto Y., Palacios E., Aloma I., Rios L., Cortez M., Calero M., Yera M., 2016, Removal continuous studies of chromium (VI) using sugar cane bagasse, Chemical Engineering Transactions, 52, 901-906.

Fu F., Wang Q., 2011, Removal of heavy metal ions from wastewaters: A review, Journal of Environmental Management, 92(3), 407-418.

Garba A., Nasri N., Basri H., Zain H., Hayatu U., Abdulrasheed A., Mohsin R., Majid Z., Rashid N., 2017, Modelling of cadmium(II) uptake from aqueous solutions using treated rice husk: Fixed-bed studies Chemical Engineering Transactions, 56, 229-234.

Rodiguez M.H., Yperman J., Carleer R., Maggen J., Dadi D., Gryglewicz G., Bruggen V.B., Hernández J.F., Calvis A.O., 2018, Adsorption of Ni(II) on spent coffee and coffee husk based activated carbon, Journal of Environmental Chemical Engineering, 6(1), 1161-1170.

Joseph L., Jun B.-M., Flora J.R.V., Park C.M., Yoon Y., 2019, Removal of heavy metals from water sources in the developing world using low-cost materials: A Review, Chemosphere, 229, 142-159.

Khan A., Khan S., Khan M.A., Qamar Z., Waqas M., 2015, The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: A review, Environmental Science and Pollution Research, 22(18), 13772-13799.

Köhler S.J., Cubillas P., Rodríguez-Blanco J.D., Bauer C., Prieto M., 2007, Removal of cadmium from wastewaters by aragonite shells and the influence of other divalent cations, Environmental Science & Technology, 41(1), 112-118.

Kumar R., Laskar M.A., Hewaidy I.F., Barakat M.A., 2019, Modified adsorbents for removal of heavy metals from aqueous environment: A review, Earth Systems and Environment, 3(1), 83-93.

Lakshmipathy R., Sarada N.C., 2015, A fixed bed column study for the removal of Pb^{2+} ions by watermelon rind, Environmental Science: Water Research & Technology, 1(2), 244-250.

Lee X., Lee L., Hiew B., Gan S., Thangalazhy-Gopakumar S., 2017, Evaluation of the effectiveness of low cost adsorbents from oil palm wastes for wastewater treatment, Chemical Engineering Transactions, 56, 937-942.

Rahim A.R.A., Rabat N.E., Johari K., Saman N., Mat H., 2019, Removal of lead (II) Ions from aqueous solution using desiccated coconut waste as low-cost adsorbent, Chemical Engineering Transactions, 72, 169-174.

Thomas H.C., 1944, Heterogeneous ion exchange in a flowing system, Journal of the American Chemical Society, 66(10), 1664-1666.

Yoon Y.H., Nelson J.H., 1984, Application of gas adsorption kinetics I. A theoretical model for respirator cartridge service life, American Industrial Hygiene Association Journal, 45(8), 509-516.

Zuo W.-Q., Chen C., Cui H.-J., Fu M.-L., 2017, Enhanced removal of Cd(II) from aqueous solution using $CaCO_3$ nanoparticle modified sewage sludge biochar, RSC Advances, 7(26), 16238-16243.