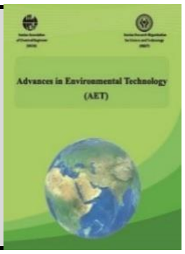
Advances in Environmental Technology 2 (2018) 149-154

Advances in Environmental Technology

journal homepage: http://aet.irost.ir



Statistical physics modeling of equilibrium adsorption of cadmium ions onto activated carbon, chitosan and chitosan/activated carbon composite

Hakimeh Sharififard

Department of Chemical Engineering, Yasouj University, Yasouj, Iran

ARTICLE INFO

Article history:
Received 8 November 2017
Received in revised form
8 January 2019
Accepted 9 January 2019

Keywords:
Cadmium
Adsorption
Statistical physics modeling
Multi-layer model with saturation

ABSTRACT

The adsorption ability of activated carbon, chitosan, and chitosan/activated carbon composite for cadmium separation from aqueous solution was analyzed via statistical physical modeling. The equilibrium data were analyzed by the Langmuir, Hill, double layer model, and multi-layer model with saturation isotherm models. The results showed that the multi-layer model with saturation could well describe the data. The number of adsorbate ions per site, the receiver site density, the number of formed layers, and the energies of adsorption relative to the different layers were estimated by numerical simulation. The results showed that the chitosan/activated carbon had a higher receiver site density and a higher amount of adsorbed ions than the other two adsorbents. The results showed that the cadmium adsorption onto the activated carbon/chitosan composite was a monolayer and exothermic process. With increasing temperature, the amount of cadmium adsorption decreased due to the fact that the number of receiver adsorption sites decreased. Also, the statistical physics modeling indicated that the geometry of the cadmium ions adsorbed onto the adsorbent surface was parallel.

1. Introduction

The presence of heavy metals in water is an environmental concern because of their toxic impact on humans, animals and plants, plus they tend to bioaccumulate. Cadmium is one of the most ubiquitous heavy metals released into the environment via a number of industrials activities such as refineries, printing, production of electric batteries and pigments etc. [1-5]. The existence of cadmium in aquifers threatens human health and the aquatic ecosystem. Cadmium can damage the nervous system, kidneys, and reproductive system [6]. According to global standards, the maximum limit for cadmium in drinking water is 0.005 mg/L [7]. So far, different separation methods have been investigated for removing heavy metals from water [8-14]. The research results have shown that the adsorption separation method is a process with high separation efficiency, low cost, and its simplicity [15,16]. With the increase in global awareness regarding environmental pollution, there is a growing demand for novel adsorbents characterized by high performance and efficiency for removing heavy metals from aqueous systems. Among the various adsorbents reported in the literature, active carbon and chitosan have a high adsorption capacity for the separation of heavy metals [17-18]. There are several important questions concerning the adsorption process. They include the number of adsorbate ions/molecules that are adsorbed onto one adsorption site of the adsorbent, the number of the receiver adsorption sites, and the number of formed adsorption layers. In order to evaluate these parameters, it is necessary to evaluate the microscopic characteristics of the adsorption process. Sellaoui et al. stated that these characteristics can be described using statistical physics modeling [19]. In this work, the microscopic behavior of cadmium adsorption onto activated carbon, chitosan, and chitosan/activated carbon composite was evaluated by means of statistical physics modeling. For this purpose, the adsorption equilibrium data were analyzed via the Langmuir, Hill, Double layer and Multilayer with saturation models.

---

*Corresponding author. Tel.: +98 9171485497
E-mail address: hakimeh.sharifi@gmail.com
DOI: 10.22104/aet.2019.2619.1132

2. Material and methods

2.1. Materials

In this research work, chitosan flakes were purchased from the Fluka Company. The commercial activated carbon was supplied by the Hashemi Nejad gas refinery (Khorasan, Iran). The chitosan/activated carbon composite was synthesized according to a procedure described in our previous paper [6]. The cadmium nitrate was purchased from the Merck Company. The hydrochloric acid and sodium hydroxide solutions were applied to adjust the initial pH of the metal solutions.

2.2. Equilibrium adsorption tests

The dried adsorbent was placed into glass Erlenmeyer flasks which contained the cadmium solution with the initial concentration between 10 - 100 mg/L. The initial pH of the metal solutions was 6. After shaking it for 24 h, filtration was done; the concentration of cadmium ions in the filtrate was detected by using Inductively Coupled Plasma (ICP) and used for analyzing the equilibrium data. These equilibrium tests were conducted at room temperature [6].

2.3. The adsorption isotherms for statistical physical modelling

Different equilibrium isotherms have been proposed to investigate the microscopic analysis of the adsorption process including the Langmuir, Hill, Double layer, and Multilayer model with saturation. The Langmuir isotherm is an empirical model and assumes that one adsorption layer is formed in the adsorption process. The mathematical description of this isotherm is as follows:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_e (mg/g) and C_e (mg/L) are the quantity adsorbed onto the adsorbent surface and the equilibrium concentration of the adsorbate that remained in the solution after adsorption, respectively. K_L (L/g) is the Langmuir constant and q_{max} (mg/g) is the quantity adsorbed when the adsorbent surface is saturated. This model does not describe the other information such as the number of adsorbed ions/molecules onto 1 adsorption site and the number of the receiver adsorption sites of the adsorbent. For this reason, the model was modified and the Hill model was presented. In this model, it is assumed that an adsorption layer is formed onto the adsorbent surface, and the number of molecules or ions adsorbed in each pore is different. It is possible to determine the number of adsorbed ions/molecules onto 1 adsorption site by using this isotherm model. The mathematical relationship of the Hill model is as follows [19]:

$$q_e = \frac{Q_0}{1 + \left(\frac{c_{1/2}}{C_e}\right)^n} \quad (2)$$

This model has three parameters that must be adjusted. These include the amount adsorbed at the monolayer formed at the adsorbent surface (Q_0 mg/g), the concentration of adsorbate at the half-saturation state of the adsorbent surface ($c_{1/2}$ mg/L), and the number of adsorbed ions/molecules onto one adsorption site (n). In this model, it is assumed to be a single-layer adsorption process. So, to investigate the possibility of forming more than one layer, two other models were also used to analyze the data: double layer model with two adsorption energies and Multilayer model with saturation. In the double layer model, it is assumed that the adsorption process takes place at two adsorption layers. Also, it is assumed that the adsorption energies of these two adsorption layers are different: ε_1 for the first layer and ε_2 for the second one. The energy of the first adsorption layer is higher than that for the second layer [19].

$$q_e = nN_m \frac{\left(\frac{C_e}{c_1}\right)^n + 2\left(\frac{C_e}{c_2}\right)^{2n}}{1 + \left(\frac{C_e}{c_1}\right)^n + \left(\frac{C_e}{c_2}\right)^{2n}} \quad (3)$$

In this equation, N_m (number per unit surface) is the number of the receiver adsorption sites onto the adsorbent surface, and n is the number of adsorbed molecules or ions onto 1 adsorption site. The parameters c_1 and c_2 represent the adsorbate concentration at the half-saturation state for the first and second adsorption layers formed onto the adsorbent surface, respectively. Equation (4) presents the multilayer model with saturation

$$\begin{aligned}
q &= nN_m \frac{F_1 + F_2 + F_3 + F_4}{G} \\
F_1 &= -\frac{2\left(\frac{C_e}{c_1}\right)^{2n}}{\left(1 - \left(\frac{C_e}{c_1}\right)^n\right)} + \frac{\left(\frac{C_e}{c_1}\right)^n \left(1 - \left(\frac{C_e}{c_1}\right)^{2n}\right)}{\left(1 - \left(\frac{C_e}{c_1}\right)^n\right)^2} \\
F_2 &= \frac{2\left(\frac{C_e}{c_1}\right)^{2n} \left(\frac{C_e}{c_2}\right)^n \left(1 - \left(\frac{C_e}{c_2}\right)^{nN_m}\right)}{\left(1 - \left(\frac{C_e}{c_2}\right)^n\right)} \\
F_3 &= -\frac{\left(\frac{C_e}{c_1}\right)^n \left(\frac{C_e}{c_2}\right)^{2n} \left(\frac{C_e}{c_2}\right)^{nN} N}{\left(1 - \left(\frac{C_e}{c_2}\right)^n\right)} \qquad (4) \\
F_4 &= \frac{\left(\frac{C_e}{c_1}\right)^n \left(\frac{C_e}{c_2}\right)^{2n} \left(1 - \left(\frac{C_e}{c_2}\right)^{nN}\right)}{\left(1 - \left(\frac{C_e}{c_2}\right)^n\right)^2} \\
G &= \frac{\left(1 - \left(\frac{C_e}{c_1}\right)^{2n}\right)}{\left(1 - \left(\frac{C_e}{c_1}\right)^n\right)} + \frac{\left(\frac{C_e}{c_1}\right)^n \left(\frac{C_e}{c_2}\right)^n \left(1 - \left(\frac{C_e}{c_2}\right)^{nN}\right)}{\left(1 - \left(\frac{C_e}{c_2}\right)^n\right)}
\end{aligned}$$

In the multilayer model with saturation, it is supposed that the adsorbate molecules or ions in the first adsorption layer are adsorbed onto the adsorbent surface by ε_1 (kJ/mol) energy, and the molecules or ions in the other layers are adsorbed by ε_2 (kJ/mol) energy. In this isotherm model, ($N+1$) presents the number of formed adsorption layers onto the adsorbent surface. The c_1 and c_2 parameters can be used to determine the adsorption energy per mol of adsorbate (kJ/mol) for each adsorption layer as follows [19-20]:

$$\varepsilon_1 = -k_B T ln\left(\frac{C_1}{C_s}\right) \tag{5}$$

$$\varepsilon_2 = -k_B T ln\left(\frac{C_2}{C_s}\right) \tag{6}$$

The C_s (mg/g) is the solubility of the adsorbed molecules or ions in the water. The ε_1 (kJ/mol) is the adsorption energy for the first layer and ε_2 (kJ/mol) is the energy related to the second layer of adsorption process. The first adsorption layer is formed through the interaction of the molecules/ions of the adsorbate with the functional groups of an adsorbent surface. But the subsequent adsorption layers are created by the interaction between the molecules/ions of the adsorbate (Figure2 in [19]). The n parameter indicates the geometry of the adsorbate molecules or ions onto the the surface of the adsorbent. Also, n can be used to estimate the degree of aggregation of the adsorbate molecules or ions [19]. When n <1, the one molecule or ion of the adsorbate is shared onto two and/or more adsorption sites. In this case, the geometry of the adsorbate onto the adsorbent surface is parallel and the adsorption process is a multi-adsorption site (anchorage) process. In this case, it can be said that the adsorbate molecules or ions are adsorbed onto both sides of the walls of the pore [21]. When n >1, two or more molecules or ions of adsorbate are adsorbed onto 1 adsorption site, and the geometry of adsorbate onto the adsorbent surface is inclined so that the aggregation of adsorbate molecules or ions occur. In this case, the adsorption process is a multi-adsorbate molecule process.

2.4. Determination of isotherm parameters

All the parameters of these statistical physics models are determined via MATLAB 2011 by minimizing Marquardt's percent standard deviation (MPSD). This parameter is used to test the adequacy and accuracy of the fit of these isotherm models with the experimental data. Based on the obtained results, the regression coefficient, R^2, was calculated for all the equilibrium models. The MPSD equation was calculated as [22]:

$$MPSD = 100 \times \sqrt{\frac{1}{n_m - n_p}} \times \sqrt{\left(\frac{\left(\sum_{i=1}^{N} q_{e,i,exp}\right) - \left(\sum_{i=1}^{N} q_{e,i,cal}\right)}{\sum_{i=1}^{N} q_{e,i,exp}}\right)^2} \tag{7}$$

In this relationship, n_m and n_p are the number of the experimental points and parameters, respectively. Also, the subscript '*exp*' and '*cal*' show the experimental and calculated values of q_e, respectively.

3. Results and discussion

3.1. Comparison between activated carbon, chitosan and chitosan/activated carbon composite

The adsorption equilibrium data for cadmium adsorption onto the activated carbon, chitosan and chitosan/activated carbon composite were analyzed using the Langmuir, Hill, double layer and multilayer with saturation isotherm models. The parameters and R^2 values for these statistical physics models are presented in Table 1. The R^2 values indicate that the equilibrium adsorption of cadmium onto all the adsorbents can be described well with the multilayer with saturation isotherm model. Figure 1 presents the experimental data and the calculated data using the multilayer with saturation model. The data presented in this figure indicate that the multilayer model with saturation can describe well the equilibrium manner for cadmium adsorption onto activated carbon, chitosan and chitosan/activated carbon composite.

The statistical physics modeling result shows that the number of adsorbed ions of cadmium onto these adsorbents (n) is lower than 1; this means that the geometry of cadmium ions adsorbed onto the adsorbent surface is parallel and the cadmium ions are adsorbed onto both sides of the walls of the pore (Figure 2). The result shows that the adsorption ability of the chitosan/activated carbon composite toward the cadmium ions is greater than the other two adsorbents; the number of receiver adsorption sites onto the adsorbent (N_m) is greater for chitosan/activated carbon composite. Also, the number of cadmium ions adsorbed onto one adsorption site is higher for the chitosan/activated carbon composite. In general, n and N_m depend on the physico-chemical properties of the adsorbate ions and adsorbent surface [23]. The physical-chemical properties of these adsorbents are reported in our previous papers [6,15]. The chitosan/activated carbon composite has different kinds of surface functional groups (amine and amide groups of chitosan, carboxylic and carbonyl groups of activated carbon) and therefore, this adsorbent has a high potential for cadmium adsorption via chemical interactions. Hence, the number of receiver adsorption sites for the adsorption of cadmium is high.

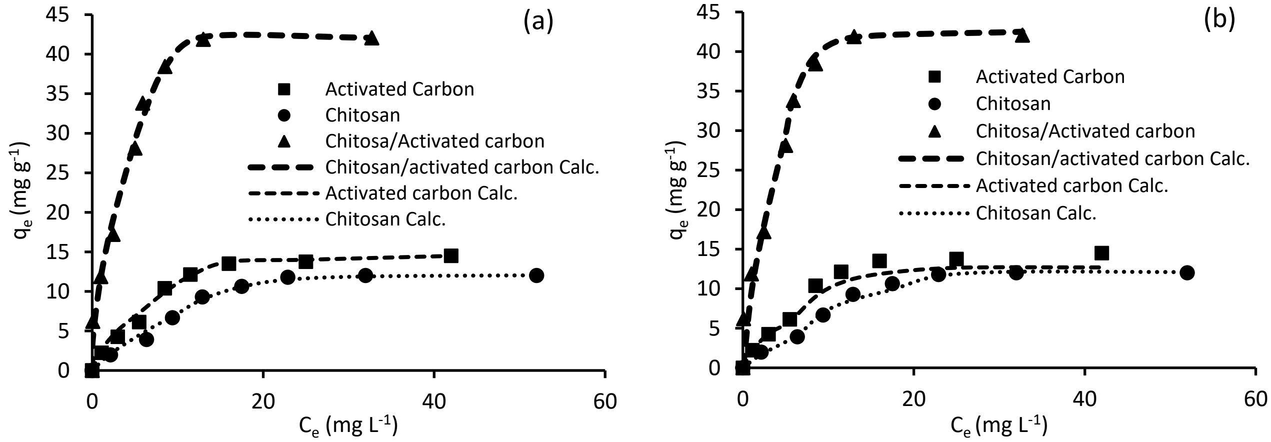


Fig 1. The adsorption isotherms for cadmium adsorption onto Chitosan, Activated carbon, Chitosan/activated carbon chitosan (*Points: Experimental data; Lines: Calculated data from models: a: Multilayer with saturation model*; b: Langmuir)

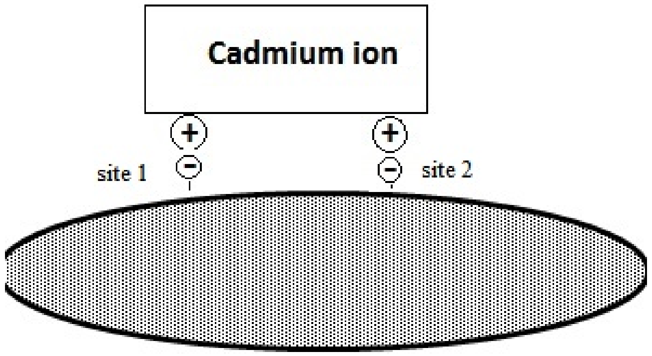


Fig. 2. Anchorage scheme for the Cadmium (II) onto adsorbent surface

Table 1 indicates that the total number of the formed layer is about 1. This means that the cadmium adsorption process is a monolayer adsorption process. Cadmium exists as Cd^{2+} cationic species along the pH <7 and the metal complexes precipitate at a pH ≥ 7. Therefore, due to repulsion between cadmium cationic species, the second layer does not form, and the adsorption process occurs as a monolayer adsorption process. The adsorption energies per mole of cadmium ions adsorbed onto the adsorbents are shown in Table 2. The values of the adsorption energies are negative, meaning that the adsorption process of cadmium onto these adsorbents is exothermic. In this exothermic process, the cadmium ions release energy when adsorbed by the surface functional groups of the adsorbent and give this energy to water (solvent) [24].

Table 1. The constant parameters of Langmuir, Hill, Double Layer, and Multilayer with Saturation model

Multilayer with Saturation model

Parameters	n	N_m	c_1	c_2	N	R^2
Carbon	0.3591	26.99	1.0094	13.3771	0.486	0.999476
Chitosan	0.3341	23.67	1.2594	10.3771	0.5562	0.998304
Chitosan/Activated carbon composite	0.5201	68.6152	0.07	1.06	0.1865	0.999283

Double Layer Model

Parameters	n	N_m	c_1	c_2	R^2
Carbon	1.114	7.035	7.066	5.9032	0.988236
Chitosan	1.5204	4.2156	10.5254	8.7229	0.982805
Chitosan/Activated carbon composite	6.1209	3.332	0.9485	2.2622	0.988876

Hill Model

Parameters	n	q	$c_{1/2}$	R^2
Carbon	0.647	104.622	459.4171	0.972
Chitosan	1.008	1.04E+06	1.53E+06	0.911
Chitosan/Activated carbon composite	0.4998	180.6413	746.2298	0.978

Langmuir Model

Parameters	q_{max}	K_L	R^2
Carbon	10.3	0.24	0.96
Chitosan	10	0.25	0.99
Chitosan/Activated carbon composite	50.5	1.36	0.99

Table 2. The amount of cadmium adsorbed at saturation state and the adsorption energy

Adsorbent	Q_{sat} (mg/g)	-ε (kJ/mol)	-ε(kJ mol/)
Activated carbon	14.40247	-34.7901	-28.3876
Chitosan	12.30666	-34.2419	-29.0168
Chitosan/activated carbon composite	42.34235	-41.4018	-34.6689

The amount of adsorption energy for the cadmium adsorption onto the chitosan/activated carbon is greater than the other two adsorbents, which is due to its high ability to adsorb cadmium. For all the adsorbents, the adsorption energy of the first layer is higher than that of the second adsorption energy. This suggests that the adsorbate ion-surface functional group interaction is stronger than the interaction of the adsorbate ion-adsorbate ion. The magnitude of the adsorption energy is greater than 40 (kJ/mol) for cadmium adsorption onto the composite, which means the predominance of chemical adsorption [19].The total amount of cadmium adsorbed at the saturation state (Q_{sat} mg/g) can be calculated as follows:

$$Q_{sat} = nN_m(1 + N) \tag{8}$$

The calculated Q_{sat} for cadmium adsorbed onto carbon, chitosan, and chitosan/activated carbon composite is presented in Table 2. This data indicates the high potential of chitosan/activated carbon toward cadmium ion removal from aqueous solution.

3.2. The effect of temperature

Figure 3 presents the adsorption isotherms of cadmium adsorption onto chitosan/activated carbon composite at various temperatures. The amount of cadmium adsorbed decreases by increasing temperature, which confirms that the adsorption process is exothermic. The parameters of the multilayer with saturation model at different temperatures are given in Table 3. The data in Table 3 indicate that the number of cadmium ions adsorbed onto 1 adsorption site (*n*) increases with increasing temperature. This behavior could be attributed to an increase in the ions or the molecules colliding with increasing temperature [25]. Results showed that the N_m value decreased with increasing the temperature. It can be said that increasing the solubility of cadmium nitrate with temperature, decreases the amount of cadmium adsorption and thus decreases the number of the receiver adsorption sites. When the solubility increases, the forces of interaction between the cadmium ions and solvent become stronger, and the amount of adsorption is reduce [20]. A comparison of the adsorption energy for the first adsorption layer at different temperatures shows that the amount of released energy decreases by increasing temperature due to a decrease in the amount of cadmium adsorbed.

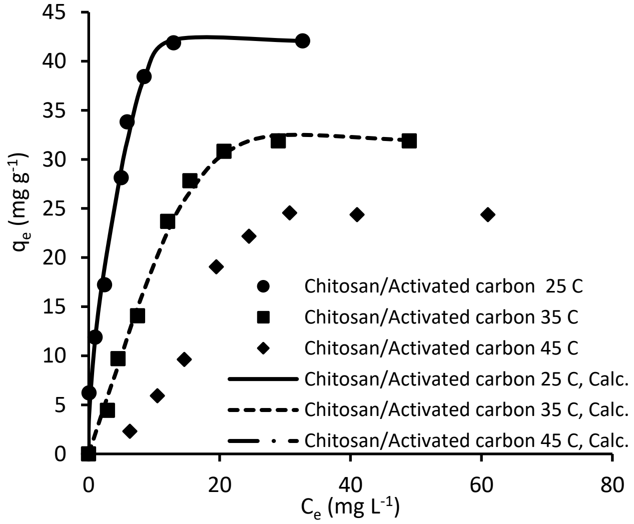


Fig. 3. The adsorption isotherm of cadmium adsorption onto chitosan/activated carbon composite at various temperatures (*Points: Experimental data; Lines: Calculated data from Multilayer with saturation model*)

4. Conclusions

The results of this research indicate that statistical physics modeling is a suitable approach to describe the microscopic characteristics of cadmium adsorption onto chitosan, activated carbon, and chitosan/activated carbon composite. In this method, the physical-chemical parameters included in the adsorption process are determined. The results show that cadmium adsorption onto these adsorbents is a multi-adsorption site (anchorage) process, and the geometry of cadmium ions adsorbed onto the adsorbent surface is parallel. The values of the adsorption energies indicate that the cadmium adsorption is an exothermic process, and the amount of cadmium adsorbed onto adsorbent surface decreases with increasing temperature. Also, the results indicate that cadmium adsorption onto chitosan/activated carbon composite is a monolayer and chemisorption process.

Table 3. Effect of temperature on the cadmium adsorption onto chitosan/activated carbon composite

Temp.	*n*	N_m	c_1	c_2	*N*	R^2	Q_{sat}(mg/g)	$-\varepsilon_1$ (kJ/mol)	$-\varepsilon_2$ (kJ/mol)
25 ºC	0.455	78.615	0.07	1.06	0.186	0.9992	42.450	-41.579	-34.846
35 ºC	0.500	49.009	1.015	7.053	0.304	0.9993	31.998	-34.953	-30.150
45 ºC	0.554	28.910	6.586	18.580	0.533	0.9994	24.561	-30.320	-27.751

References

[1] Wong, K. K., Lee, C. K., Low, K. S., Haron, M. J. (2003). Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere*, *50*(1), 23-28.

[2] Ray, P. Z., Shipley, H. J. (2015). Inorganic nano-adsorbents for the removal of heavy metals and arsenic: a review. *RSC Advances*, *5*(38), 29885-29907.

[3] Amirnia, S., Ray, M. B., Margaritis, A. (2015). Heavy metals removal from aqueous solutions using Saccharomyces cerevisiae in a novel continuous bioreactor–biosorption system. *Chemical engineering journal*, *264*, 863-872.

[4] Sharaf El-Deen, S. E. A., Zhang, F. S. (2016). Immobilisation of TiO_2-nanoparticles on sewage sludge and their adsorption for cadmium removal from aqueous solutions. *Journal of experimental nanoscience*, *11*(4), 239-258.

[5] Colantonio, N., Kim, Y. (2016). Cadmium (II) removal mechanisms in microbial electrolysis cells. *Journal of hazardous materials*, *311*, 134-141.

[6] Hydari, S., Sharififard, H., Nabavinia, M., reza Parvizi, M. (2012). A comparative investigation on removal performances of commercial activated carbon, chitosan biosorbent and chitosan/activated carbon composite for cadmium. *Chemical engineering journal*, *193*, 276-282.

[7] World Health Organization. (2010). *International travel and health: situation as on 1 January 2010*. World Health Organization.

[8] Gonzalez-Munoz, M. J., Rodríguez, M. A., Luque, S., Alvarez, J. R. (2006). Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration. *Desalination*, *200*(1-3), 742-744

[9] Pehlivan, E., Altun, T. (2007). Ion-exchange of Pb2+, Cu2+, Zn2+, Cd2+, and Ni2+ ions from aqueous solution by Lewatit CNP 80. *Journal of hazardous materials*, *140*(1-2), 299-307.

[10] Vasudevan, S., Lakshmi, J., Sozhan, G. (2011). Effects of alternating and direct current in electrocoagulation process on the removal of cadmium from water. *Journal of hazardous materials*, *192*(1), 26-34.

[11] Zhang, S., Xu, F., Wang, Y., Zhang, W., Peng, X., Pepe, F. (2013). Silica modified calcium alginate–xanthan gum hybrid bead composites for the removal and recovery of Pb (II) from aqueous solution. *Chemical engineering journal*, *234*, 33-42.

[12] Hebbar, R. S., Isloor, A. M., Ananda, K., Ismail, A. F. (2016). Fabrication of polydopamine functionalized halloysite nanotube/polyetherimide membranes for heavy metal removal. *Journal of materials chemistry A*, *4*(3), 764-774.

[13] Hao, S., Zhong, Y., Pepe, F., Zhu, W. (2012). Adsorption of Pb^{2+} and Cu^{2+} on anionic surfactant-templated amino-functionalized mesoporous silicas. *Chemical engineering journal*, *189*, 160-167.

[14] Sharififard, H., Zokaee Ashtiani, F., Soleimani, M. (2013). Adsorption of palladium and platinum from aqueous solutions by chitosan and activated carbon coated with chitosan. *Asia-Pacific journal of chemical engineering*, *8*(3), 384-395.

[15] Sharififard, H., Soleimani, M., Ashtiani, F. Z. (2012). Evaluation of activated carbon and bio-polymer modified activated carbon performance for palladium and platinum removal. *Journal of the Taiwan institute of chemical engineers*, *43*(5), 696-703.

[16] Mehrabi, N., Soleimani, M., Yeganeh, M. M., Sharififard, H. (2015). Parameter optimization for nitrate removal from water using activated carbon and composite of activated carbon and Fe_2O_3 nanoparticles. *Rsc Advances*, *5*(64), 51470-51482.

[17] Zhang, L., Zeng, Y., Cheng, Z. (2016). Removal of heavy metal ions using chitosan and modified chitosan: A review. *Journal of molecular liquids*, *214*, 175-191.

[18] Bansal, R. C., Goyal, M. (2005). *Activated carbon adsorption*. CRC press.

[19] Sellaoui, L., Guedidi, H., Knani, S., Reinert, L., Duclaux, L., Lamine, A. B. (2015). Application of statistical physics formalism to the modeling of adsorption isotherms of ibuprofen on activated carbon. *Fluid Phase equilibria*, *387*, 103-110.

[20] Dotto, G. L., Pinto, L. A. A., Hachicha, M. A., Knani, S. (2015). New physicochemical interpretations for the adsorption of food dyes on chitosan films using statistical physics treatment. *Food chemistry*, *171*, 1-7.

[21] Sellaoui, L., Mechi, N., Lima, É. C., Dotto, G. L., Lamine, A. B. (2017). Adsorption of diclofenac and nimesulide on activated carbon: statistical physics modeling and effect of adsorbate size. *Journal of physics and chemistry of solids*, *109*, 117-123.

[22] Marquardt, D. W. (1963). An algorithm for least-squares estimation of nonlinear parameters. *Journal of the society for industrial and applied mathematics*, *11*(2), 431-441.

[23] Knani, S., Aouaini, F., Bahloul, N., Khalfaoui, M., Hachicha, M. A., Lamine, A. B., Kechaou, N. (2014). Modeling of adsorption isotherms of water vapor on Tunisian olive leaves using statistical mechanical formulation. *Physica a: statistical mechanics and its applications*, *400*, 57-70.

[24] Khalfaoui, M., Nakhli, A., Aguir, C., Omri, A., M'henni, M. F., Lamine, A. B. (2014). Statistical thermodynamics of adsorption of dye DR75 onto natural materials and its modifications: double-layer model with two adsorption energies. *Environmental science and pollution research*, *21*(4), 3134-3144.

[25] Khalfaoui, M., Baouab, M. H. V., Gauthier, R., Lamine, A. B. (2006). Acid dye adsorption onto cationized polyamide fibres. Modeling and consequent interpretations of model parameter behaviours. *Journal of colloid and interface science*, *296*(2), 419-427.