CrossMark

RESEARCH ARTICLE

Interpretation of single and competitive adsorption of cadmium and zinc on activated carbon using monolayer and exclusive extended monolayer models

Lotfi Sellaoui[1] · Guilherme L. Dotto[2] · Abdelmottaleb Ben Lamine[1] · Alessandro Erto[3]

Abstract In this work, a modeling analysis based on experimental tests of cadmium/zinc adsorption, in both single-compound and binary systems, was carried out. All the experimental tests were conducted at constant pH (around neutrality) and temperature (20 °C). The experimental results showed that the zinc adsorption capacity was higher than that of cadmium and it does not depend on cadmium presence in binary system. Conversely, cadmium adsorption is affected by zinc presence. In order to provide good understanding of the adsorption process, two statistical physics models were proposed. A monolayer and exclusive extended monolayer models were applied to interpret the single-compound and binary adsorption isotherms of zinc and cadmium on activated carbon. Based on these models, the modeling analysis demonstrated that zinc is dominant in solution and more favorably adsorbed on activated carbon surface. For instance, in single-compound systems, the number of ions bound per each receptor site was n (Zn^{2+}) = 2.12 > n (Cd^{2+}) = 0.98. Thus, the receptor sites of activated carbon are more selective for Zn^{2+} than for Cd^{2+}. Moreover, the determination of adsorption energy through the adopted models confirmed that zinc is more favored for adsorption in single-compound system (adsorption energies equal to 12.12 and 7.12 kJ/mol for Zn and Cd, respectively) and its adsorption energy does not depend on the cadmium presence in binary system. Finally, the adsorption energy values suggested that single-compound and binary adsorption of zinc and cadmium is a physisorption.

Keywords Single and competitive adsorption · Statistical physics models · Zinc · Cadmium · Activated carbon

Introduction

The presence of heavy metals in natural and industrial water and subsurface aquifers represents a serious threat for environment and, in particular, for human health (Nordberg et al. 2015; Imran 2012, 2014). The chronic exposure to heavy metals has been frequently linked with several severe pathologies and with the development of various cancers. They are persistent throughout the environment to the point that they can undergo to a series of long-range transport mechanisms that enhance their diffusion through the environmental phases.

Water contamination mainly derives from industrial activities, such as production and processing of metals, mineral industry, chemical industry, waste and water management, and energy-related sources associated with fuel combustion. However, in some cases, the contribution of natural sources, such as rock leaching or volcanic activities, is not negligible and can determine the contamination of groundwater as well. Hence, the development of reliable and efficient depuration technologies has become a pressing need, in particular when a multiple contamination occurs, which represents the most frequent case. To this aim, the adsorption of toxic heavy metals both in single-compound and multi-component systems on different adsorbents is attracting much attention due to its good efficiencies and

✉ Lotfi Sellaoui
sellaouilotfi@yahoo.fr

1 Unité de Recherche de Physique Quantique, UR 11 ES 54, Faculté des Sciences de Monastir, Université de Monastir, 5000 Monastir, Tunisia

2 Chemical Engineering Department, Federal University of Santa Maria–UFSM, 1000, Roraima Avenue, Santa Maria, RS 97105-900, Brazil

3 Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, P.le Tecchio, 80, 80125 Naples, Italy

general applicability. Several researches have been reported in the pertinent literature (Di Natale et al. 2017; Rybicka et al. 1995; Imran and Aboul-Enein 2002; Imran 2006), and even if many different and low-cost adsorbents have been proposed (Babel and Kurniawan 2003; Erto et al. 2013; Imran et al. 2012; Imran 2010, 2012), activated carbons are by far the most adopted to remove these pollutants (Leyva et al. 2001; Pardo et al. 2004; Gonzalez and Pliego-Cuervo 2014). Many experimental and theoretic studies were carried out to understand the behavior of single-compound and binary adsorption systems of important heavy metals, such as cadmium, zinc, lead, and nickel (Vocciante et al. 2014; Gabaldon et al. 1996; Srivastava et al. 2006; Imran 2006, 2010). However, the modeling description of single-compound and, more interestingly, multi-component systems is a still open issue in the literature. Indeed, a reliable model able to predict or describe an adsorption system in a wide range of operating conditions (i.e., in terms of different combinations of pollutant concentrations) is an invaluable tool, in order to support a thorough design of adsorption devices.

The present work is an experimental and modeling study on cadmium and zinc adsorption on activated carbon in both single-compound and binary systems. Dedicated experimental tests were carried out in order to highlight the difference in adsorption capacity due to the copresence of two ions, adopting same operating conditions in terms of pH and temperature of the single-compound tests. The same adsorption system was studied in a previous published work by Erto et al. (2015), in which the differences in adsorption capacity were explained by classical observations mainly based on the different affinity of activated carbon toward each single ion and on the ion dimensions (Erto et al. 2015). However, a phenomenological approach was adopted for the description of the competitive effects and, even if the adopted model succeeded, a deeper insight at molecular level could result of great help in order to define the mechanisms and the dynamics of competition.

The present work aims to propose further interesting interpretations of zinc and cadmium adsorption on activated carbon in both single-compound and binary systems by using the monolayer and exclusive extended monolayer model, respectively. The development of these models, which were successfully applied to different adsorption systems (Sellaoui et al. 2016a, b), consists in carefully writing the partition function containing statistical properties of the treated systems. The two models are characterized by some steric and energetic parameters controlling the adsorption process, and their determination provided useful information about the adsorption mechanism in both single-compound and binary systems.

Materials and method

Adsorption tests were carried out at $T = 20$ °C and neutral pH, in batch stirred glass reactors, kept in a PID-controlled thermostatic oven. All the tests were conducted in model aqueous solutions; stock solutions of cadmium and zinc were prepared by dissolving a given quantity of $Cd(NO_3)_2 \cdot 4H_2O$ and/or $Zn(NO_3)2 \cdot 6H_2O$ (Sigma-Aldrich, 99.9%), respectively, in distilled water. A commercial granular activated carbon (GAC, Aquacarb 207EA^{TM} by Sutcliffe Carbon) was used for all the experimental runs, using a 1.2-mm average particle diameter. This material has a BET surface area of 950 m^2 g^{-1} and a micropore volume of 0.249 cm^3 g^{-1}, mainly centered in the pore size region of 8–18 Å(measured by Carlo Erba SORPTOMATIC 1900). The chemical composition of the sorbent revealed a high ash content (9.58%), evaluated by elemental analysis (Perkin Elmer 2400 series, CHNS Analyzer). A complete list of chemical and physical characteristics can be found in Erto et al. (2010).

The adsorption tests were conducted as follows. A constant mass of adsorbent (1 g) was added to 0.1 L of metal (either Zn or Cd) solution, at different initial concentrations. Similarly, for the binary tests, 0.1 L of Zn/Cd solution was used with same activated carbon dosage (0.5 g) and initial concentration ratio of the two analytes ($C_{Zn}^0:C_{Cd}^0$), but each experimental point corresponded to different zinc and cadmium initial concentrations, in order to describe two complete adsorption isotherms in the range of concentrations typically found in polluted waters.

Preliminary kinetic tests carried out in the same working conditions, for both cadmium and zinc single-compound systems, showed that contact times of 60 and 72 h, respectively, for cadmium and zinc, were sufficient to reach the equilibrium condition without any additional stirring. On the contrary, for binary tests, 7 days were necessary to achieve equilibrium conditions for both the investigated metals.

At equilibrium, the reactors were sampled and the metal concentration in the solution and on the GAC surface was measured. To this purpose, the solution was filtered and analyzed for pH and metal concentration while the GAC was leached with 0.1 L of nitric acid (1 M) to extract all the adsorbed metals. Finally, the extractive solution was analyzed to measure the metal uptake on the solid surface and was compared with the same quantity calculated through a metal mass balance, allowing for a maximum error of 6%. To assure the accuracy, reliability, and reproducibility of the data collected, all the isotherm tests were repeated in triplicate and only average values were reported. In each replica of test, the standard deviation in zinc/cadmium concentration was below 7% and that in adsorption capacity was around 6%. All the labware used in the study was previously soaked in nitric acid (1 M), triply rinsed with distilled water, and oven dried.

Analytical concentrations of both zinc and cadmium were measured by air/acetylene flame atomic absorption spectrophotometry (AAS-F) by using a Varian SpectrAA-220 spectrophotometer.

Models for single and competitive adsorption

Before to select the adsorption models, a preliminary analysis of the adsorption isotherm profiles is essential in order to understand the physical phenomenon. The adsorption isotherm profiles of zinc and cadmium in single-compound systems (Fig. 1a) are characterized by the same shape. Adsorption capacity increases with equilibrium concentration, and an asymptote is not reached in the investigated range. Hence, a solid saturation phenomenon can occur at far higher concentrations and, from isotherm shapes, it is likely to be coincident for both the analytes. At our knowledge, a unique predicted saturation phenomenon gives a clear idea of the adsorption energy of the receptor site of activated carbon, suggesting that the two ions adsorb on one type of receptor site. Concerning the binary adsorption isotherm profiles (Fig. 1b), it is clear that a physical interaction occurred between the two ions. Despite that the two ions are positively charged, this phenomenon describes a strong reduction of the adsorbed quantity of cadmium with respect to the corresponding single-compound system, whereas this quantity remains practically constant for zinc. The electrostatic repulsion effect in this situation can be considered as negligible as the interaction with the solid surface is greater. Hence, it confirms that these ions are adsorbed on the same type of receptor site and a competitive effect arises for the adsorption on the same receptor site. The phenomenological analysis of the adsorption isotherms allowed selecting the appropriate statistical physics models for the interpretation of experimental data in both single-compound and binary systems.

Monolayer model for single-compound adsorption

For this model, we supposed that the ions adsorb with one energy $(-\varepsilon)$ which describes the interactions with the adsorbent surface of activated carbon. It represents the general case of the Langmuir model. Indeed, it is known that the Langmuir model assumes that each adsorption site accommodates one

ion whatever the studied system; differently, our model supposes that a receptor site (S) can accept n ions. The adsorption of zinc and cadmium can be represented by this chemical pseudo-reaction:

$$nX^{2+} + S \rightleftarrows X^{2+}{}_nS \tag{1}$$

in which X^{2+} represents the adsorbed ion., $X^{2+}{}_nS$ is the formed complex, and S is the receptor site.

Based on our previous works, the partition function of one receptor site is given by this simple expression (Sellaoui et al. 2016a, b, c, d, e):

$$z_{gc} = 1 + e^{\beta(\varepsilon+\mu)} \tag{2}$$

In this expression, ε represents the adsorption energy of the receptor site, μ is the chemical potential of the adsorbed ion, and β is the Boltzmann factor.

The adsorption model can be expressed by Sellaoui et al. (2016a, b, c, d, e):

$$Q = \frac{nN_M}{1 + \left(\frac{c_{1/2}}{c}\right)^n} \tag{3}$$

in which Q is the adsorption capacity. The model expression contains three adjustable parameters: the number of ions per site (n), the adsorbed quantity obtained at saturation $(Q_0 = nN_M)$, and the concentration at half saturation $(c_{1/2})$.

Exclusive extended monolayer model for competitive adsorption

The described model for single-compound adsorption was extended for the interpretation of binary adsorption. In this model, it was assumed that zinc and cadmium are present as Zn^{2+} and Cd^{2+} ions (Erto et al. 2015), respectively, and they adsorb on the same type of receptor site, symbolized by S. Moreover, this site accepts exclusively

Fig. 1 Fitting of Zn^{2+} and Cd^{2+} adsorption isotherms in single-compound (**a**) and binary (**b**) systems ($T = 20\ °C$). Comparison with monolayer and extended monolayer models
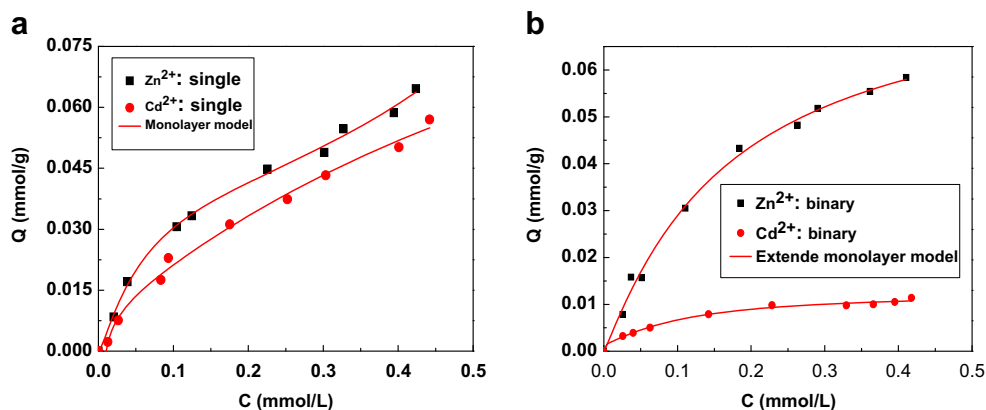
Zn^{2+} or Cd^{2+} ions with two different $(-\varepsilon_1)$ and $(-\varepsilon_2)$ energies, respectively. It was supposed also that the receptor site accepts n_1 and n_2 ions of Zn^{2+} and Cd^{2+}, respectively. We can summarize these assumptions by two adsorption pseudo-reactions:

$$n_1 A^{2+} + S \rightleftarrows A^{2+}{}_{n_1} S \tag{4}$$

$$n_2 B^{2+} + S \rightleftarrows B^{2+}{}_{n_2} S \tag{5}$$

in which A^{2+} and B^{2+} represent the Zn^{2+} and Cd^{2+} ions.

The partition function under the hypotheses of one receptor site which contains the statistical properties of the equilibrium binary adsorption is given by the following expression (Sellaoui et al. 2016a, b):

$$z_{gc} = 1 + e^{\beta(\varepsilon_1 + \mu_1)} + e^{\beta(\varepsilon_2 + \mu_2)} \tag{6}$$

This expression is characterized by three coupled terms: the first term (1) showed that the receptor site is initially empty, and the two other terms $\left(e^{\beta(\varepsilon_1 + \mu_1)} + e^{\beta(\varepsilon_2 + \mu_2)}\right)$ explain that the receptor site is occupied by Zn^{2+} and Cd^{2+} ions, respectively. In the last expression, μ_1 and μ_2 represent the chemical potentials of Cd^{2+} and Zn^2 ions on the receptor site, respectively. Important details in terms of the model development were provided in previously published works (Sellaoui et al. 2016a, b). The model expressions describing the evolution of the adsorbed quantity (Q_{a1}, Q_{a2}) as a function of metal equilibrium concentrations are written as follows:

$$Q_{a1} = \frac{n_1 N_M \left(\frac{c_1}{c_{01}}\right)^{n_1}}{1 + \left(\frac{c_1}{c_{01}}\right)^{n_1} + \left(\frac{c_2}{c_{02}}\right)^{n_2}} \tag{7}$$

$$Q_{a2} = \frac{n_2 N_M \left(\frac{c_2}{c_{02}}\right)^{n_2}}{1 + \left(\frac{c_1}{c_{01}}\right)^{n_1} + \left(\frac{c_2}{c_{02}}\right)^{n_2}} \tag{8}$$

in which $Q_{asat1} = n_1 N_M$ and $Q_{asat2} = n_2 N_M$ are the adsorbed quantities of Zn^{2+} and Cd^{2+} ions, respectively, at saturation. The adsorption isotherms in single and binary systems were interpreted by the two model parameters described in this section. The fitting of the adsorption isotherms is reported in Fig. 1.

A good correlation between models and the experimental adsorption isotherms in both single-compound and binary systems was established. Indeed, the R^2 values controlling the fitting quality varied between 0.974–0.991 and 0.970–0.997 in single and binary systems, respectively. Table 1 sums the adjustable parameter values of the two models.

Table 1 Values of adjustable parameters in single and binary systems

	Zn^{2+}	Cd^{2+}	Zn^{2+} (Zn^{2+}/Cd^{2+})	Cd^{2+} (Zn^{2+}/Cd^{2+})
n	2.12	0.98		
n_1			2.05	
n_2				0.50
N_M	0.041	0.070	0.042	0.022
Q_{ast}	0.088	0.069		
Q_{ast1}			0.087	
Q_{ast2}				0.011

Single-compound and binary adsorption isotherm interpretation

Number of ions per site: n, n_1, and n_2

The removal of metal ions from aqueous solution may be attributed mainly to specific interactions with oxygen-containing functional groups, through metal complex formation on the surface of the carbon and/or donor–acceptor electron interactions (Gao et al. 2009). In general, the determination of the number of ions bonded per receptor site offers many interesting indications to understand the single-compound and binary adsorption phenomena, according to their values deduced by the fitting of appropriate models (Sellaoui et al. 2015, 2016a, b). If n or n_i ($i = 1,2$) > 1, we can measure the aggregation number in solution of the adsorbed ions, indicating that the adsorption is a multi-ion process. If n or $n_i = 1$, i.e., one ion is bonded per site, it means that lateral interactions are established between the ions and the adsorption surface reflecting that adsorption is a mono-ion process. Finally, if n or $n_i < 1$, it means that the Zn^{2+} and Cd^{2+} ions are arranged horizontally on activated carbon, thus suggesting that the adsorption is a multi-anchorage phenomenon. Based on the fitting results reported in Table 1, the parameter values in single-compound systems resulted as follows: n (Zn^{2+}) = 2.12 > n (Cd^{2+}) = 0.98. Thus, the receptor site of activated carbon is more selective for Zn^{2+} than for Cd^{2+}. The result could be explained by a higher interaction potential of Zn^{2+} due to the small size of activated carbon pores. Moreover, it is possible observing that Zn^{2+} and Cd^{2+} ions form a dimer ($n = 2.12$) and monomer ($n = 0.98$) in solution, respectively. This difference is likely ascribable to a different activation energy of the adsorption phenomenon of Zn^{2+} and Cd^{2+}, for which temperature also plays a role. This activation energy is responsible for this aggregation number that is superior for Zn^{2+} than for Cd^{2+}. Hence, Zn^{2+} adsorption is more thermally activated than that of Cd^{2+}.

Concerning the binary adsorption, the number of ions per site varies as follows: n_1 (Zn^{2+} (Zn^{2+}/Cd^{2+})) = 2.05 > n_2 (Cd^{2+} (Zn^{2+}/Cd^{2+})) = 0.50. It is clear that the value of Zn^{2+} ions

bonded per site in binary system practically remains the same compared with single-compound system, but the number of Cd^{2+} ions is reduced practically to half, hence confirming the results observed in Fig. 1b. This result confirms that the Zn^{2+} ion is dominant in solution and exerts a competitive effect, which results in an inhibition effect for Cd^{2+} ions to be adsorbed on the same receptor site of activated carbon.

About the adsorbate position on activated carbon, in single - compound system, it was noticed that the n number of Cd^{2+} per site is 0.98. The value indicated that the 98% of Cd^{2+} ions interact by an inclined position on adsorbent surface. Differently, in binary system $n = 0.5$, then these ions are arranged on two receptor sites. An equal arrangement indicates that each 50% of Cd^{2+} interacts with a receptor site. In many works, single and binary adsorption of Cd^{2+} and Zn^{2+} on different activated carbons were interpreted by Langmuir and extended Langmuir models (Gonzalez and Pliego-Cuervo 2014; Mohan and Singh 2002). It is known that these models assume that the adsorbent pore accepts one molecule whatever the treated system. Differently, in this work, all the adsorption isotherms were studied by statistical physics models assuming that the adsorbent site can accept n, n_1, and n_2 molecules (n, n_1, and n_2 are variables). In conclusion, the number of ions bonded per site during the adsorption process offers supplementary information and a deeper understanding of the single and binary adsorption process.

Adsorbed quantity at saturation

The adsorbed quantity at saturation represents a basic parameter, which gives useful indications about the adsorption process and the competitive effects between the two ions. The values of this parameter in single-compound systems are 0.088 and 0.069 mmol/g for Zn^{2+} and Cd^{2+}, respectively, but for the binary system are 0.087 and 0.011 mmol/g for Zn^{2+} and Cd^{2+}, respectively. This difference is due to the higher affinity of activated carbon for Zn^{2+} ions, which produces a stronger interaction between Zn^{2+} ions and the activated carbon active sites. To describe the effect of the second ion in the binary system, it is possible to present three different cases with respect to the value of the ratio of adsorbed quantity at saturation of the ion in binary (Q_c) and single (Q_s) system. If $Q_c/Q_s = 1$, then no interaction between the Zn^{2+} and Cd^{2+} ions occurs. In other words, the mixture has no effect on the adsorption of each of the adsorbates. If $Q_c/Q_s > 1$, the ions promote the adsorption of each other as a synergistic adsorption. Finally, if $Q_c/Q_s < 1$, the presence of a second ion in the binary system reduces the adsorption of the ion; hence, it is an antagonistic adsorption. In our study, the ratio (Q_c/Q_s) was found to be 1 and 0.15 for Zn^{2+} and Cd^{2+}, respectively. This confirmed that Zn^{2+} ion adsorption was not influenced by the presence of Cd^{2+} and that Cd^{2+} adsorption is significantly reduced by the presence of Zn^{2+} ion in solution. As a conclusion, Zn^{2+} adsorption in binary system does not depend on the presence of Cd^{2+}. In terms of comparison, it is useful to remember that the literature indicated different possible behaviors for the same system (Leyva-Ramos et al. 2001; Mohan and Singh 2002; Fagundes-Klen et al. 2007; Srivastava et al. 2008; Cazon et al. 2013). We envisage that these behaviors mirror the different structure and active site distribution on the investigated adsorbents and might not depend on steric hindrance of zinc ion and carbon pore size distribution.

General discussion and adsorption energy

According to many published documents, the difference between the adsorbed quantities in single-compound and binary systems was ascribed to different reasons. For example, McBride (1989) explained that the specific adsorption of heavy metals is mostly related to the ionic potential and electronegativity. In the same context, Erto et al. (2015) declared that this difference is in relation with the affinity of adsorbent surface and ion dimensions, due to steric hindrance. On another side, thermodynamically, Minceva et al. (2008) claimed that the enthalpy of ions represents an important factor to explain the adsorption magnitude of metal ions onto a same adsorbent surface. In a recent published work based on single-compound and binary systems of Pb^{2+} and Zn^{2+} on activated carbon, Depci et al. (2012) showed that the adsorption capacity of Pb^{2+} is greater than that of Zn^{2+} and have attributed the highest adsorption capacity to the higher electronegativity of Pb^{2+}. In this work, based on statistical physics models, we tried to explain the differences between the adsorbed quantity in single-compound and binary systems by using model parameters. Based on our model expressions, in general, two factors are able to control the single-compound and binary adsorption process, whatever the studied system. As described in the previous section, the single-compound and binary adsorption was sterically governed by the number of ions bonded per site and by the adsorbed quantity at saturation. For Cd^{2+}, the reduction in the adsorbed quantity is mainly due to the reduction in the number of ions bonded per site. A very good correlation between the two parameters also explains that the Zn^{2+} ion is more adsorbed than Cd^{2+} in single-compound systems, and in binary system, as its adsorption does not depend on the presence of Cd^{2+}. Moreover, the model parameter of Zn^{2+} adsorption remained constant in both single-compound and binary systems (same values), while a strong reduction for the corresponding values of Cd^{2+} in binary adsorption was observed. Concerning this point, the statistical physics models offer other interesting options to

analyze the phenomenon and to derive important information. This option concerns the calculation of the adsorption energy in order to energetically characterize and compare the single-compound and the binary systems.

A simple evaluation of the adsorption energy values by using this mathematical formula: $-\Delta E_1 = -RT ln(c_s/c_1)$ showed that the interactions between Zn^{2+} ions and activated carbon surface in single-compound system (12.12 kJ/mol) are stronger than the corresponding interactions of Cd^{2+} (7.12 kJ/mol). The same parameters calculated by the classical Langmuir model resulted to be 3.76 and 3.21 kJ/mol for Zn^{2+} and Cd^{2+}, respectively (Erto et al. 2015). The differences can be ascribed to the different mechanisms hypothesized. Moreover, the adsorption energies of Zn^{2+} in single-compound and binary systems resulted to be the same as well as the number of ions bonded per site and the adsorbed quantity at saturation. In particular, the adsorption energy of Zn^{2+} in binary system has practically the same value as in single-compound system (11.92 kJ/mol), whereas a notable reduction of the corresponding value for Cd^{2+} is present (2.19 kJ/mol). This explains that the difference between the adsorbed quantities is mainly due to the difference between the interactions of the studied ions and the activated carbon. Finally, we can understand that the single-compound and binary systems were well controlled by the adsorption energies and, based on the estimated values, it is clear that for all the investigated systems, adsorption is a physisorption.

Conclusion

The adsorption of zinc and cadmium from aqueous solution onto activated carbon, in both single-compound and binary systems, was studied. Experimental results showed that zinc is more adsorbed than cadmium both in single-compound and binary systems and, in the latter case, its adsorption capacity is not affected by cadmium presence. Differently, cadmium adsorption capacity is significantly reduced by the presence of zinc. Two models constructed by using the statistical physics were applied to attribute new interpretations at molecular level to zinc and cadmium adsorption on activated carbon in single-compound system and to understand the competitive effect between the ions. The model application sterically explained that the zinc is dominant in solution and more attracted by the activated carbon, due to higher affinity. Indeed, the study and estimation of number of ions per site and adsorbed quantity at saturation elucidated that the zinc is more favored for adsorption in single-compound system and its adsorption does not vary on the presence of cadmium. Finally, the adsorption energy analysis completed and confirmed the description of the observed phenomena suggesting that this difference is mainly due to the highest interaction between zinc and activated carbon with respect to cadmium.

References

Babel S, Kurniawan TA (2003) Low-cost adsorbent for heavy metals uptake from contaminated water: a review. J Hazard Mater 97: 219–243

Cazon JP, Viera M, Donati E, Guibal E (2013) Zinc and cadmium removal by biosorption on Undaria pinnatifida in batch and continuous processes. J Environ Manag 129:423–434

Depci T, RızaKul A, Onal Y (2012) Competitive adsorption of lead and zinc from aqueous solution on activated carbon prepared from Van apple pulp: study in single- and multi-solute systems. Chem Eng J 200–202:224–236

Di Natale F, Orefice M, La Motta F, Erto A, Lancia A (2017) Unveiling the potentialities of activated carbon in recovering palladium from model leaching solutions. Sep Purif Technol 174:183–193

Erto A, Andreozzi R, Di Natale F, Lancia A, Musmarra D (2010) Experimental and statistical analysis of trichloroethylene adsorption onto activated carbon. Chem Eng J 156:353–359

Erto A, Giraldo L, Lancia A, Moreno-Piraján JC (2013) A comparison between a low-cost sorbent and an activated carbon for the adsorption of heavy metals from water. Water Air Soil Pollut 224:1531–1541

Erto A, Di Natale F, Musmarra D, Lancia A (2015) Modeling of single and competitive adsorption of cadmium and zinc onto activated carbon. Adsorption 21:611–621

Fagundes-Klen MR, Ferri P, Martins TD, Tavares CRG, Silva EA (2007) Equilibrium study of the binary mixture of cadmium–zinc ions biosorption by the *Sargassum filipendula* species using adsorption isotherms models and neural network. Biochem Eng J 34:136–146

Gabaldon C, Marzal P, Ferrer J, Seco A (1996) Single and competitive adsorption of Cd and Zn onto a granular activated carbon. Water Res 30:3050–3060

Gao Z, Bandosz TJ, Zhao Z, Hand M, Qiua J (2009) Investigation of factors affecting adsorption of transition metals on oxidized carbon nanotubes. J Hazard Mater 167:357–365

Gonzalez PG, Pliego-Cuervo YB (2014) Adsorption of Cd(II), Hg(II) and Zn(II) from aqueous solution using mesoporous activated carbon produced from *Bambusa vulgaris* striata. Chem Eng Res Des 92: 2715–2724

Imran A (2006) Instrumental methods in metal ions speciation: chromatography, Capillary Electrophoresis and Electrochemistry. Taylor & Francis Ltd., New York ISBN: 0-8493-3736-4

Imran A (2010) The quest for active carbon adsorbent substitutes: inexpensive adsorbents for toxic metal ions removal from wastewater. Sep Purif Rev 39:95–171

Imran A (2012) New generation adsorbents for water treatment. Chem Rev 112:5073–5091

Imran A (2014) Water treatment by adsorption columns: evaluation at ground level. Sep Purif Rev 43:175–205

Imran A, Aboul-Enein HY (2002) Speciation of arsenic and chromium metal ions by reversed phase high performance liquid chromatography. Chemosphere 48:275–278

Imran A, Asim M, Khan TA (2012) Low cost adsorbents for removal of organic pollutants from wastewater. J Environ Manag 113:170–183

Leyva R, Bernal LA, Guerrero RM, Fuentes L (2001) Competitive adsorption of Cd(II) and Zn(II) from aqueous solution onto activated carbon. Sep Sci Technol 36:3673–3687

Leyva-Ramos R, Bernal-Jacome LA, Guerrero-Coronado RM, Fuentes-Rubio L (2001) Competitive adsorption of Cd(II) and Zn(II) from aqueous solution onto activated carbon. Sep Sci Technol 36:3673–3687

McBride MB (1989) Reactions controlling heavy metal solubility in soils. Adv Soil Sci 10:1–56

Minceva M, Fajgar R, Markovska L, Meshko V (2008) Comparative study of Zn^{2+}, Cd^{2+} and Pb^{2+} removal from water solution using

natural clinoptilolitic zeolite and commercial granulated activated carbon. Equilibrium of adsorption. Sep Sci Technol 43:2117–2143

Mohan D, Singh KP (2002) Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste. Water Res 36:2304–2318

Nordberg GF, Fowler BA, Nordberg M (2015) Chapter 1: toxicology of metals: overview, definitions, concepts, and trends. In: Nordberg GF, Fowler BA (eds) Handbook on the toxicology of metals, 4th edn. Academic Press, San Diego, pp 1–12

Pardo BR, Fernández-González C, Pinilla-Gil E, Cuerda-Correa EM, Gomez-Serrano V (2004) Adsorption kinetics of zinc in multicomponent ionic systems. J Colloid Interface Sci 277:292–298

Rybicka EH, Calmano W, Breeger A (1995) Heavy metals sorption/desorption on competing clay minerals; an experimental study. Appl Clay Sci 9:369–381

Sellaoui L, Guedidi H, Knani S, Reinert L, Duclaux L, Ben Lamine A (2015) Application of statistical physics formalism to the modeling of adsorption isotherms of ibuprofen on activated carbon. Fluid Phase Equilib 387:103–110

Sellaoui L, Bouzid M, Duclaux L, Reinert L, Knani S, Ben Lamine A (2016a) Binary adsorption isotherms of two ionic liquids and ibuprofen on an activated carbon cloth: simulation and interpretations using statistical and COSMO-RS models. R Soc Chem Adv 6:67701–67714

Sellaoui L, Depci T, Kul AR, Knani S, Ben Lamine A (2016b) A new statistical physics model to interpret the binary adsorption isotherms of lead and zinc on activated carbon. J Mol Liq 214:220–230

Sellaoui L, Dotto GL, Gonçalves JO, Pinto LAA, Knani S, Ben Lamine A (2016c) Equilibrium modeling of single and binary adsorption of Food Yellow 4 and Food Blue 2 on modified chitosan using a statistical physics theory: new microscopic interpretations. J Mol Liq 222:151–158

Sellaoui L, Guedidi H, Masson S, Reinert L, Levêque JM, Knani S, Ben Lamine A, Khalfaoui M, Duclaux L (2016d) Steric and energetic interpretations of the equilibrium adsorption of two new pyridinium ionic liquids and ibuprofen on a microporous activated carbon cloth: statistical and COSMO-RS models. Fluid Phase Equilib 414:156–163

Sellaoui L, Knani S, Erto A, Abdennaceur Hachicha M, Ben Lamine A (2016e) Equilibrium isotherm simulation of tetrachlorethylene on activated carbon using the double layer model with two energies: steric and energetic interpretations. Fluid Phase Equilib 408:259–264

Srivastava VC, Mall ID, Mishra IM (2006) Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash. Chem Eng J 117:79–91

Srivastava VC, Mall ID, Mishra IM (2008) Removal of cadmium(II) and zinc(II) metal ions from binary aqueous solution by rice husk ash. Colloids Surf A 312:172–184

Vocciante M, Trofa M, Auria TD, Giraldo L, Rodriguez-Estupiñan P, Moreno Pirajan JC, Erto A (2014) A rigorous procedure for the design of adsorption units for the removal of cadmium and nickel from process wastewaters. J Clean Prod 77:35–46