



Synergic adsorption in the simultaneous removal of acid blue 25 and heavy metals from water using a $\text{Ca}(\text{PO}_3)_2$ -modified carbon

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ABSTRACT

We report the simultaneous adsorption of acid blue 25 dye (AB25) and heavy metals (Zn^{2+} , Ni^{2+} and Cd^{2+}) on a low-cost activated carbon, whose adsorption properties have been improved via a surface chemistry modification using a calcium solution extracted from egg shell wastes. Specifically, we have studied the removal performance of this adsorbent using the binary aqueous systems: AB25– Cd^{2+} , AB25– Ni^{2+} and AB25– Zn^{2+} . Multi-component kinetic and equilibrium experiments have been performed and used to identify and characterize the synergic adsorption in the simultaneous removal of these pollutants. Our results show that the presence of AB25 significantly favors the removal of heavy metals and may increase the adsorption capacities up to six times with respect to the results obtained using the mono-cationic metallic systems, while the adsorption capacities of AB25 are not affected by the presence of metallic ions. It appears that this anionic dye favors the electrostatic interactions with heavy metals or may create new specific sites for adsorption process. In particular, heavy metals may interact with the $-\text{SO}_3^-$ group of AB25 and to the hydroxyl and phosphoric groups of this adsorbent. A response surface methodology model has been successfully used for fitting multi-component adsorption data.

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1. Introduction

Dyes and heavy metals are hazardous pollutants often found together in wastewaters of several industries [1]. These pollutants have a significant ecological impact on ecosystem and can modify the physical and chemical properties of water affecting the aquatic flora and fauna [1–3]. For example, the dyes contained in wastewaters reduce the light penetration and may prevent the photosynthesis [4]. In addition, some dyes may degrade to generate carcinogens and toxic compounds for human beings and other living organisms. On the other hand, the presence of heavy metal ions in industrial effluents and drinking water resources is also relevant due to its toxicological profile and potential impacts on the human health and environment [5]. Therefore, the removal of both pollutants from wastewaters is currently one of the most important environmental tasks for research and technology development on water management [6].

The treatment of wastewaters polluted by dyes and heavy metals can be performed via chemical precipitation, ion exchange, electrolysis, membrane separation and adsorption [1,5–17].

However, the management of these pollutants in multi-component mixtures (i.e., dyes–heavy metals) is difficult and ineffective using some traditional purification processes [1]. Adsorption process is considered as an economical and robust method for improving water quality and can be used to remove a great variety of pollutants. Until now, various adsorbents have been used to remove dyes and heavy metals in mono-component solutions, and they include activated carbons, natural and synthetic polymers, clays, zeolites, biomasses, agricultural and industrial by-products [10–20]. In particular, the adsorption on activated carbon appears to be the most competitive technology, in terms of costs and removal performance, to reduce the concentrations of these pollutants in wastewaters [12,20].

In the majority of adsorption studies performed for the removal of heavy metals and water decolorization, mono-component systems have been analyzed and a limited emphasis has been given to the study of multi-component systems. However, multi-component adsorption studies are useful to identify the competitive effects of several pollutants on adsorbent performance and play an important role for the proper design and operation of water purification processes [21]. When two or more pollutants are present in solution, they may increase or decrease or may not change the adsorption capacity of the adsorbent [22–24]. Under these conditions, the adsorbent performance may

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depend on the number of pollutants present in solution and its concentration.

To date, the amount of literature on adsorption processes for simultaneous dye and heavy metal removal from water in multi-component systems is rather limited [25,26]. For example, Shukla and Pai [25] reported the adsorption of copper, nickel and zinc on dye loaded groundnut shells and sawdust from aqueous solutions. These authors showed that application of the dye to these materials resulted in an enhancement of adsorption capacities for heavy metals. Visa et al. [26] studied the simultaneous removal of methylene blue and cadmium, copper and nickel in multi-component systems using fly ash modified with NaOH. This study indicated that high removal efficiencies were obtained at low heavy metal concentration while the uptake of these metals was affected by competitive adsorption processes as their concentrations increased. However, further studies are necessary to improve the knowledge of adsorption process for the simultaneous removal of these hazardous pollutants (i.e., dye and heavy metals) from wastewaters using activated carbons and other adsorbents. This type of studies is useful and fundamental for designing effective and low-cost wastewater treatment methods.

In this paper, we report the simultaneous adsorption of acid blue 25 dye (AB25) and heavy metals (Zn^{2+} , Ni^{2+} and Cd^{2+}) on a low-cost activated carbon, which has been modified for improving its adsorption properties using a solution obtained from egg shell wastes and acetic acid [27]. Specifically, we have studied the multi-component removal performance of this adsorbent using the binary systems: AB25– Cd^{2+} , AB25– Ni^{2+} and AB25– Zn^{2+} . Note that these pollutants can be found together in wastewaters. For example, zinc and AB25 are used in the paper manufacturing and, as a consequence, they can be present simultaneously in the effluents discharged by this industry. Additionally, the management and disposal of industrial effluents is usually improper in developing countries. Therefore, polluted effluents of different industries can be mixed, before its proper treatment, causing the simultaneous presence of both heavy metals and AB25 in wastewaters. To the best of our knowledge, adsorption studies involving these pollutants in binary solutions have not been reported. These experiments have been used to identify and characterize the synergic adsorption effects in the simultaneous removal of these pollutants using this adsorbent. In addition, the adsorbent characterization by several techniques has helped in understanding the multi-component adsorption data and we have proposed a possible mechanism for the simultaneous removal of both pollutants using this carbon. The extended Langmuir, non-modified Langmuir and Sips multi-component isotherms and a response surface methodology model have been used to fit the adsorption data obtained from the simultaneous removal of these pollutants. In summary, our results show that the presence of AB25 significantly favors the removal of heavy metal ions and may increase the adsorption capacities up to six times with respect to the results obtained using the mono-cationic metallic systems. These results are significant from a practical point of view because of the presence of this dye may significantly improve the removal of heavy metals and, as a consequence, the application of specific treatment methods to reduce the content of metallic species in wastewaters can be avoided if AB25 is present.

2. Methodology

2.1. Adsorbent preparation and characterization

A commercial bituminous carbon from Clarimex Company (Mexico) was used as adsorbent. This carbon was milled and sieved to retain the 18–20 mesh fractions. Later, adsorbent particles were washed with deionized water until pH was constant and, finally,

Table 1

Elemental composition and textural parameters of raw bituminous carbon and $Ca(PO_3)_2$ -modified carbon.^a

Elemental composition, %	Adsorbent ^b		Textural parameters	Adsorbent ^b	
	RC	MC		RC	MC
Carbon	87.3	75.56	S_{BET} , m ² /g	961	931
Hydrogen	0.84	1.53	V_{total} , cm ³ /g	0.529	0.522
Nitrogen	0.56	1.75	V_{mic} , cm ³ /g	0.369	0.355
Sulfur	0.29	0.20	D_p , nm	2.203	2.243
Oxygen	3.48	18.60			

^a Parameters taken from Guijarro-Aldaco et al. [27].

^b RC is the raw bituminous carbon and MC is the $Ca(PO_3)_2$ -modified carbon.

they were dried at 110 °C for 24 h. This commercial carbon was modified using a solution obtained from hen egg shell wastes and acetic acid (HES) according to the procedure reported by Guijarro-Aldaco et al. [27]. In summary, HES wastes were washed with deionized water and dried. HES particles were milled and sieved to retain the 35–40 mesh fractions. The calcium solution was obtained from these particles using a ratio of 0.05 g of HES per 1 mL of acetic acid (25% v) under constant agitation for 5 h. This calcium-solution was filtered to separate the membrane of HES and diluted with deionized water to obtain a calcium concentration of 3276 mg/L. This diluted solution was used for the impregnation of bituminous carbon employed in this study. Note that this solution has a significant content of calcium because the egg shell contains up to 95% of $CaCO_3$. Chemistry surface modification of bituminous carbon was performed via the following stages [27]: (1) adsorbent pre-treatment using an H_3PO_4 solution at 30 °C for 2 h, (2) calcium impregnation of carbon at 30 °C for 4 h using a ratio of 0.2 g of adsorbent per mL of calcium solution extracted from HES, and (3) thermal treatment of calcium-impregnated carbon at 400 °C for 3 h. This $Ca(PO_3)_2$ -modified carbon was washed with deionized water at 50 °C until pH was constant and finally dried at 110 °C for 24 h. Details of the procedure for carbon modification are provided by [27]. This adsorbent was used in the simultaneous adsorption experiments of both AB25 dye and heavy metals. Elemental composition and textural parameters of both raw and modified bituminous carbons have been determined in [27] and are reported in Table 1. According to [27], all the chemical and physical properties of raw bituminous carbon are not significantly affected when it is treated with this impregnation process and only its surface chemistry is modified. It is important to remark that the calcium content of HES can be used as activation agent for improving carbon adsorption properties because this cation is thought to play an important role in the removal of heavy metals through ion exchange and other mechanisms [27]. As a consequence, the maximum adsorption capacities for heavy metal removal can be significantly enhanced after the chemical modification of bituminous carbon. In general, the adsorption capacities of $Ca(PO_3)_2$ -modified carbon are an order of magnitude higher than those obtained using raw commercial bituminous carbon [27].

Samples of raw adsorbent and adsorbent loaded with both AB25 and heavy metals were characterized using Scanning Electron Microscopy/Energy-dispersive X-ray spectroscopy (SEM/EDX), X-ray photoelectron spectroscopy (XPS) and FT-IR spectroscopy. XPS analyses were performed with an Alpha X-ray spectrometer, operated in the Constant Analyzer Energy (CAE) mode, with a pass energy of 20 eV and using a non-monochromatic radiation from AlK anode (main $h\nu = 1486.68$ eV). The curve fitting of component peaks was performed via non-linear least-squares algorithm using a mixture of Gaussian and Lorentzian peak shapes (Voigt). FT-IR spectra were registered from a disc, which was prepared by mixing 0.8 mg of adsorbent with 400 mg of KBr, and then pressing the resulting mixture successively at 5 and 10 tonnes/cm² for 5 min

under vacuum. FT-IR spectra were recorded between 4000 and 400 cm^{-1} using a MIDAC spectrometer. From the spectrum of each sample, the reference spectrum of a similar thickness pure KBr disc was subtracted. Finally, carbon samples were observed under a SEM (QuantaFEG 650, FEI) equipped with an EDX detector.

2.2. Multi-component adsorption studies of AB25 and heavy metals on $\text{Ca}(\text{PO}_3)_2$ -modified carbon

Binary systems of AB25– Cd^{2+} , AB25– Ni^{2+} and AB25– Zn^{2+} were used in the adsorption experiments. These solutions were prepared from AB25 dye (Sigma–Aldrich), nitrate salts of Zn^{2+} , Ni^{2+} and Cd^{2+} (J.T. Baker) and deionized water. In particular, the chemical properties of AB25 dye are: (a) colour index number: 62055, (b) molecular weight: 416.38 g/mol, (c) empirical formula: $\text{C}_{20}\text{H}_{13}\text{N}_2\text{NaO}_5\text{S}$ and (d) λ_{max} : 600 nm.

Batch adsorption experiments were performed using initial concentrations ranging from 20 to 500 mg/L for AB25 and from 25 to 100 mg/L for heavy metals. Specifically, multi-component adsorption studies were performed by shaking a fixed mass of adsorbent (0.02 g) with fixed volumes of binary solutions (10 mL) at 30 °C. Based on the fact that kinetic studies are important to identify the equilibrium time and that the calculation of adsorption rates are useful for process design and for understanding the possible adsorption mechanisms, the kinetic adsorption parameters were determined using binary solutions (i.e., dye–metal ion) with different initial concentrations.

On other hand, equilibrium adsorption experiments were performed to study the competitive effects of both pollutants on multi-component removal performance of $\text{Ca}(\text{PO}_3)_2$ -modified carbon. In these experiments, we used a full factorial design (see Table 2) where the main factors of the adsorption process were the initial concentrations of both AB25 and heavy metal ion (i.e., Cd^{2+} , Ni^{2+} or Zn^{2+}) in the binary solution. For equilibrium adsorption experiments, suspensions (binary solution-adsorbent) were maintained at 30 °C, for 24 h, using a temperature-controlled shaker, operating at 200 rpm. pH of adsorption kinetic and equilibrium experiments was the natural value of the multi-component solutions, which ranged from 5.2 to 5.7. Note that these conditions are below the onset for hydrolysis of Zn^{2+} , Cd^{2+} and Ni^{2+} in order to prevent metal precipitation. Response variable of this factorial design was the adsorbed amount of AB25, Zn^{2+} , Ni^{2+} and Cd^{2+} on modified carbon. For comparison purposes, the adsorbent performance using mono-component solutions of dye and each metal ion has been also considered in our experiments at the same operating conditions (i.e., pH, temperature and adsorbent dosage). Statistica® software was used to perform the statistical analysis of results obtained from the experimental designs.

Dye concentration was determined by UV–Vis spectrometry at the maximum absorbance of AB25 (i.e., 600 nm) using a UV–Vis HACH DR 5000 spectrophotometer. Concentrations of Zn^{2+} , Ni^{2+} and Cd^{2+} were determined with a Perkin Elmer AAnalyst 100 atomic absorption spectrophotometer equipped with an air–acetylene burner. All the experiments were conducted in triplicate, and the average results are reported in this study. Reproducibility of the experiments was in general within 6%.

Adsorption capacities for heavy metal ions and dye (q_i , mg/g) on adsorbent were calculated by a mass balance

$$q_i = \frac{(C_{0,i} - C_{f,i})V}{m} \quad (1)$$

where $C_{0,i}$ and $C_{f,i}$ is the initial and final concentration (mg/L) of pollutant i (i.e., dye or heavy metal) in the binary solution, V is the volume (L) of dye–metal ion solution used for adsorption experiments and m is the adsorbent amount (g).

2.3. Modeling of simultaneous adsorption of heavy metals and AB25 using $\text{Ca}(\text{PO}_3)_2$ -modified carbon

The modeling of multi-component adsorption has been a research topic during many years [28] and, until now, several models have been proposed and can be applied to fit multi-component adsorption data for heavy metal and dye removal. These models are useful for the optimal design of water treatment processes. Usually, the classical isotherm equations for mono-component adsorption (e.g., Langmuir and Freundlich) have been extended and modified to represent multi-component adsorption equilibrium [22,24,28–31]. In this study, we have used the extended Langmuir, non-modified Langmuir and Sips multi-component isotherms for modeling the simultaneous adsorption of heavy metals and AB25. In particular, extended Langmuir model considers that the active sites are uniform and that all the sorbate molecules in solution compete for the same surface sites [23]. This model is given by

$$q_{e,i} = \frac{q_{\text{max}}K_iC_{e,i}}{1 + \sum_{j=1}^c K_jC_{e,j}} \quad (2)$$

where q_{max} is the maximum multi-component adsorption capacity and shows an unique value for the different species in competition, and K_i is an adjustable parameter for each pollutant. Non-modified Langmuir is an extension of the conventional Langmuir isotherm where the adsorption takes place at specific homogeneous sites within the adsorbent [23,24]. This model considers specific adjustable parameters ($q_{m,i}$ and $K_{L,i}$) for each species in competition and is defined as

$$q_{e,i} = \frac{q_{m,i}K_{L,i}C_{e,i}}{1 + \sum_{j=1}^c K_{L,j}C_{e,j}} \quad (3)$$

Non-modified Sips is also an extension of the basic Sips isotherm and is characterized by specific adjustable parameters (a_{si} , b_{si} and n_{si}) for each pollutant in competition, where

$$q_{e,i} = \frac{a_{si}C_{e,i}^{1/n_{si}}}{1 + \sum_{j=1}^c b_{sj}C_{e,i}^{1/n_{si}}} \quad (4)$$

This equation corresponds to a special case of surface energetic heterogeneity [32]. Details of these models and their application for modeling multi-component adsorption data can be found in Reynel-Avila et al. [24].

Herein, it is convenient to remark that several authors have suggested that the prediction of multi-component adsorption data can be performed using model parameters obtained from mono-component adsorption isotherms [33]. Unfortunately, this approach may fail to describe the interaction between different pollutants in multi-component systems and usually provides poor predictions for multi-component adsorption equilibrium [22,28]. Therefore, we have determined the parameters of multi-component models that provide the best fit to measured data using a proper data correlation procedure. The parameter determination of these isotherm models is based on the minimization of the following objective function

$$F_{\text{obj}} = \sum_{j=1}^{\text{ndat}} \left[\left(\frac{q_{e,\text{dye}}^{\text{exp}} - q_{e,\text{dye}}^{\text{calc}}}{q_{e,\text{dye}}^{\text{exp}}} \right)^2 + \left(\frac{q_{e,\text{metal}}^{\text{exp}} - q_{e,\text{metal}}^{\text{calc}}}{q_{e,\text{metal}}^{\text{exp}}} \right)^2 \right] \quad (5)$$

where $q_{e,\text{dye}}^{\text{exp}}$ and $q_{e,\text{metal}}^{\text{calc}}$ are the experimental and predicted adsorption capacities for dye and heavy metal in binary system, and ndat is the overall number of experimental data. In this study, a non-linear regression approach employing a stochastic global optimization method was used to determine the model parameters of Eqs. (2)–(4). Even though these models have a simple mathematical

Table 2Experimental design used for the simultaneous adsorption of AB25 and heavy metals on Ca(PO₃)₂-modified carbon.

	Levels	Factor A: initial concentration of AB25, mg/L				
		0	20	125	250	500
Factor B: initial concentration of heavy metal ion, mg/L	0		$q_{e,[20,0]}$	$q_{e,[125,0]}$	$q_{e,[250,0]}$	$q_{e,[500,0]}$
	25	$q_{e,[0,25]}$	$q_{e,[20,25]}$	$q_{e,[125,25]}$	$q_{e,[250,25]}$	$q_{e,[500,25]}$
	50	$q_{e,[0,50]}$	$q_{e,[20,50]}$	$q_{e,[125,50]}$	$q_{e,[250,50]}$	$q_{e,[500,50]}$
	75	$q_{e,[0,75]}$	$q_{e,[20,75]}$	$q_{e,[125,75]}$	$q_{e,[250,75]}$	$q_{e,[500,75]}$
	100	$q_{e,[0,100]}$	$q_{e,[20,100]}$	$q_{e,[125,100]}$	$q_{e,[250,100]}$	$q_{e,[500,100]}$

structure and relatively few adjustable parameters, the parameter estimation problems for modeling adsorption data have usually non-linear and non-convex solution spaces [19,34]. Therefore, the use of traditional local optimization methods (e.g., quasi-newton or simplex method) for solving this optimization problem is not reliable. Specifically, in this study the stochastic optimization method Simulated Annealing was used because our results show that this meta-heuristic is reliable and suitable for adsorption data modeling [19,27,34].

Statistical criteria were used to compare the performance of models tested. Specifically, the criteria used to measure the goodness of the fittings of models were the objective function value (F_{obj}) and the mean absolute percentage deviation (E) between calculated and experimental adsorption capacities, where

$$E_i = \frac{100}{\text{ndat}} \sum_{j=1}^{\text{ndat}} \left| \frac{q_{e,i}^{\text{exp}} - q_{e,i}^{\text{calc}}}{q_{e,i}^{\text{calc}}} \right|_j \quad (6)$$

These statistics were accompanied by a study of the behavior of the relative residuals $e_{ij} = (q_{ij}^{\text{exp}} - q_{ij}^{\text{calc}})/q_{ij}^{\text{exp}}$ to identify obvious patterns and to perform comparison of tested models.

3. Results

3.1. Kinetic studies

Adsorption kinetics of AB25 and Cd²⁺, Ni²⁺ and Zn²⁺ on Ca(PO₃)₂-modified carbon using single and binary solutions are reported in Figs. 1 and 2. Our results show that the dye adsorption kinetic is not significantly affected by the presence of these metal ions. Practically, the equilibrium adsorbed amount of AB25 on adsorbent is the same in both single and binary solutions. For example, the dye adsorption capacity is around 110 mg/g using a binary solution with an initial dye concentration of 500 mg/L. This adsorption capacity is independent of both the type of heavy metal and its initial concentration in binary system (see Fig. 1). However, adsorption kinetics of all heavy metals are affected by the dye content in binary systems. In fact, the presence of AB25 favors the adsorption of all heavy metals and the adsorption capacities increase with dye concentration in binary solutions. Note that these adsorption capacities are higher than those obtained in mono-cationic metallic solutions. For example, using binary solutions with an initial dye concentration of 500 mg/L and a metal concentration of 100 mg/L, the adsorbed amounts of Zn²⁺, Ni²⁺ and Cd²⁺ increased from 4 to 16 mg/g, from 5 to 15 mg/g and from 8 to 23 mg/g, respectively. It is convenient to remark that, although Figs. 1 and 2 contain data for selected concentrations of heavy metals and AB25, this pattern of adsorbent performance is typical for others concentrations of both pollutants.

Adsorption kinetic rates of dye and heavy metals on modified carbon were calculated using the pseudo second order kinetic model [35]. Ho et al. [36] have showed that this kinetic expression

is useful to describe multi-component systems. This kinetic model is defined as

$$q_{t,i} = \frac{q_{te,i}^2 k_i t}{1 + q_{te,i} k_i t} \quad (7)$$

and the initial adsorption rate h is given by

$$h = 2kq_{te}^2 \quad (8)$$

where $q_{t,i}$ is the adsorption capacity of tested pollutant i (mg/g) at time t (min), $q_{te,i}$ is the theoretical adsorption capacity of pollutant i (mg/g) at equilibrium, and k is the rate constant of pseudo-second order adsorption (g/mg min).

Adsorption rate parameters are reported in Tables 3 and 4. Results of data fitting indicate that pseudo second order model provides a proper description of simultaneous adsorption of both AB25 and heavy metals in binary systems. In fact, all determination coefficients (R^2) were better than 0.95 indicating that the pseudo second order model properly fitted to the experimental data.

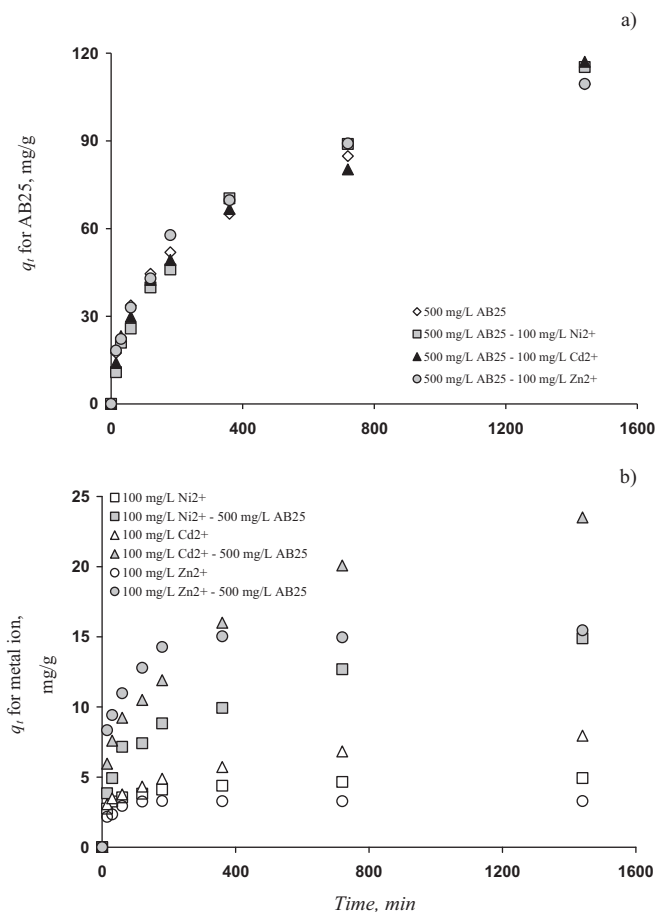


Fig. 1. Adsorption kinetics of (a) AB25 and (b) heavy metals on Ca(PO₃)₂-modified carbon using binary solutions.

Table 3
Kinetic parameters of pseudo-second order model for the simultaneous adsorption of AB25 and heavy metals on $\text{Ca}(\text{PO}_3)_2$ -modified carbon.

Solution	Concentration, mg/L	Pollutant	q_{te} , mg/g	k , g/(mg min)	h	R^2
AB25 alone	500	AB25	117.65	2.31E-05	0.64	0.9763
AB25-Ni ²⁺	500–100	AB25	129.87	1.56E-05	0.52	0.9788
		Ni ²⁺	15.48	3.00E-04	0.14	0.9870
Ni ²⁺ alone	100	Ni ²⁺	4.98	3.34E-03	0.17	0.9990
		AB25	125.00	1.80E-05	0.56	0.9552
AB25-Cd ²⁺	500–100	Cd ²⁺	24.88	1.56E-04	0.19	0.9852
		AB25	117.65	2.50E-05	0.69	0.9853
Cd ²⁺ alone	100	Cd ²⁺	8.18	6.99E-04	0.09	0.9898
		AB25	117.65	2.50E-05	0.69	0.9853
AB25-Zn ²⁺	500–100	AB25	117.65	2.50E-05	0.69	0.9853
		Zn ²⁺	15.63	1.55E-03	0.76	0.9998
Zn ²⁺ alone	100	Zn ²⁺	3.31	2.67E-02	0.58	0.9999

Table 4
Kinetic parameters of pseudo-second order model for the simultaneous adsorption of AB25 and Zn²⁺ on $\text{Ca}(\text{PO}_3)_2$ -modified carbon.

Solution	Concentration, mg/L	Pollutant	q_{te} , mg/g	k , g/(mg min)	h	R^2
AB25 alone	20	AB25	10.54	1.33E-03	0.29	0.9992
	500	AB25	117.65	2.31E-05	0.64	0.9763
	1000	AB25	156.25	2.12E-05	1.04	0.9833
Zn ²⁺ alone	100	Zn ²⁺	3.31	2.67E-02	0.58	0.9999
		AB25	9.78	2.32E-03	0.44	0.9996
AB25-Zn ²⁺	20–100	Zn ²⁺	3.83	2.74E-02	0.80	0.9999
		AB25	117.65	2.50E-05	0.69	0.9853
	500–100	Zn ²⁺	15.63	1.55E-03	0.76	0.9998
		AB25	158.73	1.40E-05	0.71	0.9727
	1000–100	Zn ²⁺	17.95	2.16E-04	0.14	0.9986
		AB25	156.25	2.12E-05	1.04	0.9833

Overall, our calculations confirm that the dye adsorption rate (k_{AB25}) is not significantly affected by the presence of heavy metal ions in multi-component solutions. However, the kinetic adsorption parameters of heavy metals are clearly affected by the presence

of AB25 in binary systems. In general, the rate constants of heavy metals decrease with dye concentration due to the simultaneous presence of both pollutants in adsorption system. It is convenient to remark that the adsorption rate constants (k) of all heavy metal ions are an order of magnitude higher than those values observed for AB25 in both mono-component and multi-component systems. In particular, the adsorption rate of Zn²⁺ is higher than those reported for both Ni²⁺ and Cd²⁺ ions. Our results indicate that adsorption process of metal ions is faster in the initial stage than that obtained for AB25 adsorption in both mono- and multi-component solutions. This is because the dye has a higher molecular weight than those of heavy metal ions. Note that this pollutant characteristic affects the mass transfer mechanisms involved in adsorption process. In general, it appears that initial rate constants h depend on the initial concentrations of both pollutants. At tested conditions, the adsorption equilibrium was obtained at 1440 min for all binary systems.

3.2. Equilibrium studies

Figs. 3 and 4 show the results of experimental designs used to study the simultaneous adsorption of both AB25 and heavy metals. To perform data analysis, the effect of both dye and heavy metals in multi-component removal performance of $\text{Ca}(\text{PO}_3)_2$ -modified carbon has been studied and determined using the ratio of adsorption capacities (R_q)

$$R_{q,i} = \frac{q_{e,i}}{q_{0,i}} \quad (9)$$

where $q_{e,i}$ is the adsorption capacity for pollutant i in the binary solution and $q_{0,i}$ is the adsorption capacity of that pollutant with the same initial concentration in a mono-component solution. Literature indicates that: (a) if $R_{q,i} > 1$, the adsorption of pollutant i is promoted by the presence of other pollutants, (b) if $R_{q,i} = 1$, there is no effect on adsorption capacity of pollutant i , and (c) if $R_{q,i} < 1$, the presence of other pollutants suppresses the adsorption of pollutant i [24,37–39]. This analysis has been used to study and characterize the performance of modified carbon in the removal of AB25 and heavy metal ions under competitive conditions.

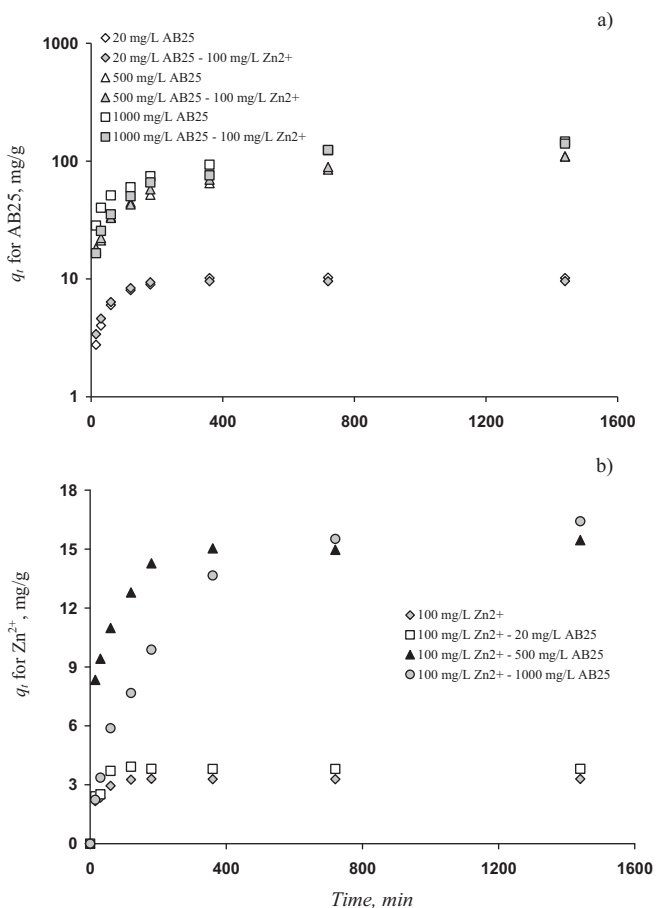


Fig. 2. Adsorption kinetics of (a) AB25 and (b) Zn²⁺ on $\text{Ca}(\text{PO}_3)_2$ -modified carbon using binary solutions.

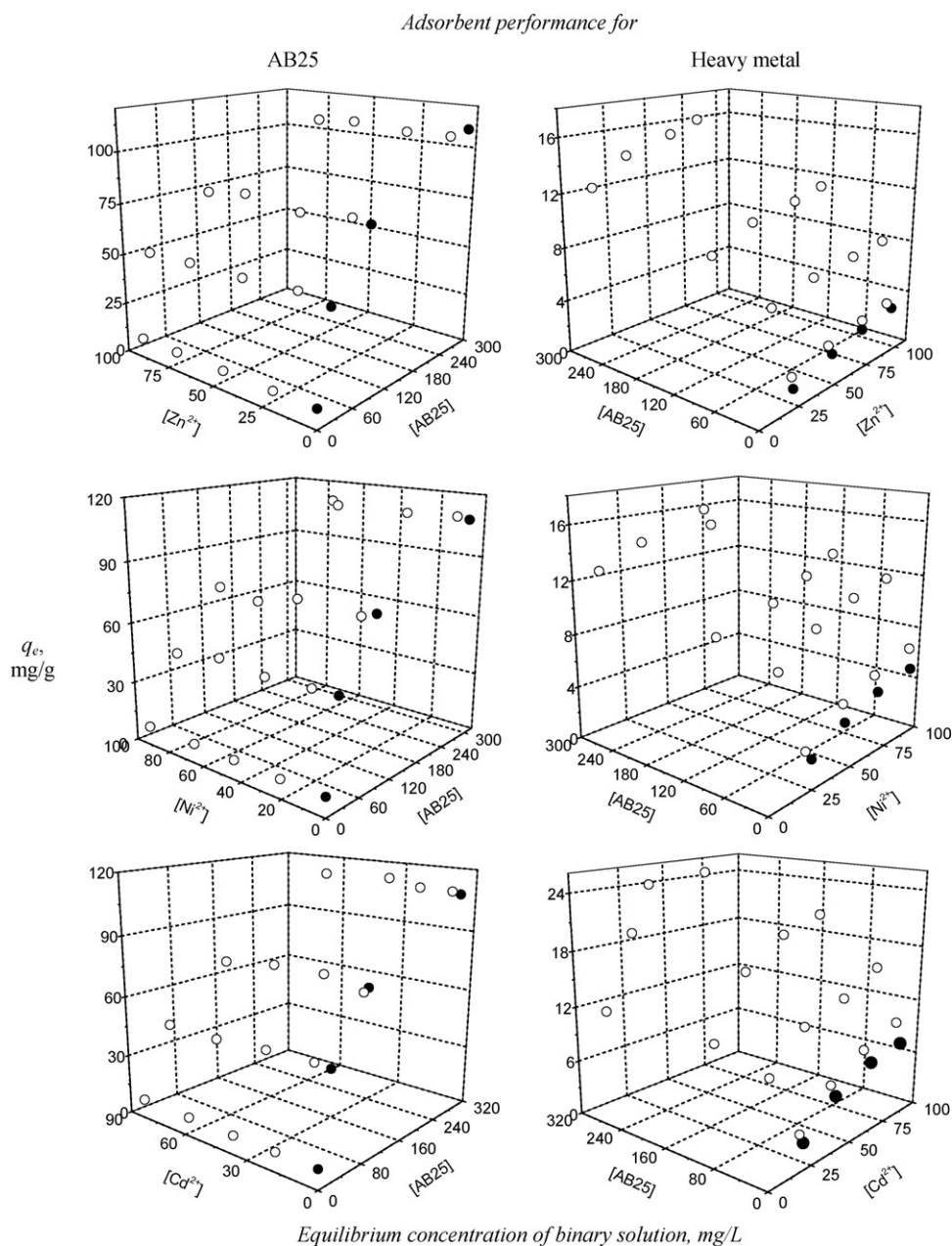


Fig. 3. Multi-component adsorption equilibrium of AB25, Zn^{2+} , Ni^{2+} and Cd^{2+} on $Ca(PO_3)_2$ -modified carbon using binary solutions of dye–heavy metal. (●) Mono-component and (○) multi-component system.

In particular, Fig. 3 shows the results for multi-component adsorption of dye and heavy metals on $Ca(PO_3)_2$ -modified carbon, while the results for $R_{q,i}$ are plotted in Fig. 4 as a function of the initial concentration (dye–heavy metal) of tested binary systems. For comparison purposes, the mono-component isotherms of each pollutant are also included in Fig. 3. Our results show that the increment of dye concentrations significantly affects the uptake of all heavy metal ions in the bi-pollutant system. Note that the adsorption capacities for Zn^{2+} , Cd^{2+} and Ni^{2+} can be significantly improved (i.e., $R_{q,i} > 1.0$) by the presence of AB25 in binary solutions. Specifically, the maximum adsorption capacities for Zn^{2+} , Cd^{2+} and Ni^{2+} are, respectively, 3.4, 8.0 and 5.0 mg/g in mono-cationic metallic systems, and 16.3, 25.3 and 16.0 mg/g for binary systems; i.e., the adsorption capacities in binary solutions are an order of magnitude higher than those values observed for mono-component systems. However, the effect of AB25 concentration is less significant at higher metal concentrations especially

for Zn^{2+} ions. Statistical analysis of our experimental designs, using R_q as dependent variable, confirmed this interactive effect between dye and metal ion concentrations. In summary, this synergic adsorption depends on both the metal ion and dye concentrations and its magnitude is also different for tested heavy metals. Herein, it is convenient to remark that similar findings have been reported by Shukla and Pai [25]. These authors determined that the adsorption of copper, nickel and zinc may increase up to 100% using dye loaded groundnut shells and sawdust.

On other hand, the adsorption capacities of AB25 are not affected by the presence of heavy metal ions in binary solutions (i.e., $R_{q,AB25} \cong 1.0$ for all binary systems at tested conditions). The maximum adsorbed amount of AB25 is $\cong 110$ mg/g in all binary systems, see Fig. 3. Therefore, these results are useful to discard the competitive adsorption between AB25 and Zn^{2+} , Cd^{2+} and Ni^{2+} on $Ca(PO_3)_2$ -modified carbon.

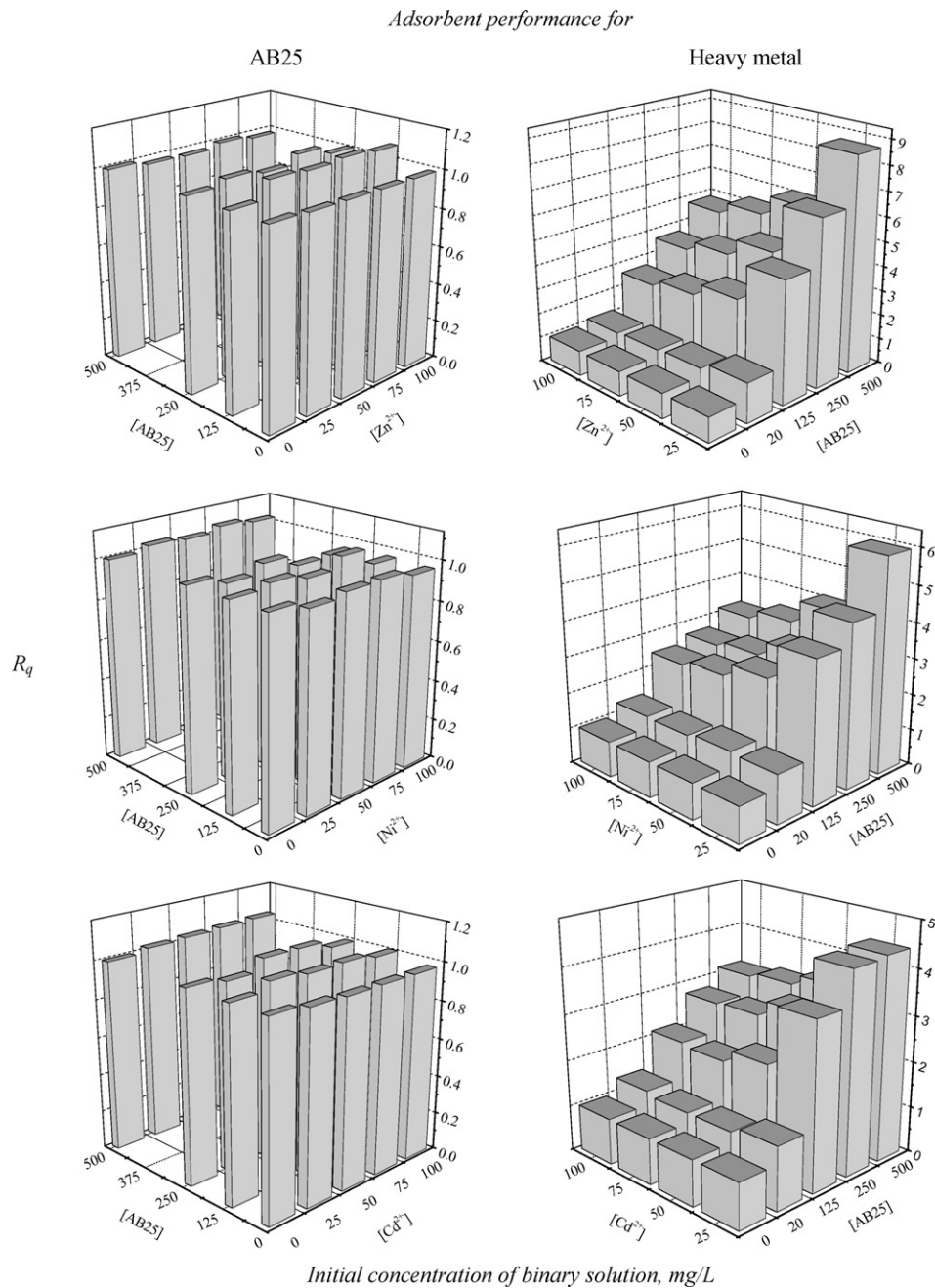


Fig. 4. Ratio of adsorption capacities (R_q) versus the initial concentration of binary solution for the simultaneous removal of AB25, Zn^{2+} , Ni^{2+} and Cd^{2+} using $Ca(PO_3)_2$ -modified carbon.

Results of data modeling of multi-component adsorption experiments are given in Table 5. It is clear that tested multi-component isotherm models failed to fit our binary adsorption data. These models showed a mean absolute percentage deviation (E) from 3 to 66%. In general, the performance of the models used for fitting the simultaneous removal of both AB25 and heavy metals is poor and is given by: non-modified Sips > non-modified Langmuir > extended Langmuir. In particular, non-modified Sips model gave better data correlations but its accuracy is not proper and suitable for process design. Considering this fact, we have used an empirical model based on the response surface methodology RSM [40] for fitting the simultaneous adsorption data of AB25 and heavy metals. Specifically, the responses (i.e., equilibrium adsorption capacities $q_{e,i}$) of our experimental design can be related to the independent factors (i.e., equilibrium concentrations of pollutants $C_{e,i}$) by linear or

quadratic models. Then, we have considered a quadratic RSM model for modeling multi-component adsorption data, which is defined as

$$q_{e,i} = \beta_0 + \sum_{i=1}^k \beta_i C_{e,i} + \sum_{i=1}^k \beta_{ii} C_{e,i}^2 + \sum_{i=1}^k \sum_{j=i+1}^k \beta_{ij} C_{e,i} C_{e,j} \quad (10)$$

where k is the number of factors in the experimental design, β_0 is the constant coefficient, β_i , β_{ij} and β_{ii} are the coefficients of linear, interaction, and quadratic terms of RSM model. Parameters of this RSM model were determined using a multiple linear regression analysis according to classical statistical procedures [40]. Table 6 reports the RSM models obtained for all correlations performed and our results show that the experimental data are best described by RSM models. Specifically, these models showed a mean

Table 5Parameters of multi-component adsorption models used for data fitting of the simultaneous adsorption of AB25 and heavy metals on Ca(PO₃)₂-modified carbon.

System	Extended Langmuir					E, %			
	q_{\max}	K_1	K_2	F_{obj}	AB25	Metal			
AB25–Cd ²⁺	218.520	7.15E–03	2.55E–03	6.650	33.50 ± 29.79	65.57 ± 31.68			
AB25–Ni ²⁺	197.052	9.11E–03	1.71E–03	5.375	31.03 ± 27.65	52.50 ± 32.12			
AB25–Zn ²⁺	310.387	2.99E–03	8.07E–04	7.080	44.92 ± 30.12	52.23 ± 30.87			
System	Non-modified Langmuir					E, %			
	$q_{m,1}$	$K_{L,1}$	$q_{m,2}$	$K_{L,2}$	F_{obj}	AB25	Metal		
AB25–Cd ²⁺	193.890	2.18E–02	30.236	9.33E–02	5.407	41.73 ± 28.70	51.80 ± 29.73		
AB25–Ni ²⁺	182.189	3.71E–02	20.712	8.58E–02	4.439	35.56 ± 28.97	41.53 ± 29.53		
AB25–Zn ²⁺	207.156	1.51E–02	17.445	5.70E–02	6.453	44.58 ± 31.26	47.07 ± 29.19		
System	Non-modified Sips							E, %	
	a_{s1}	b_{s1}	n_{s1}	a_{s2}	b_{s2}	n_{s2}	F_{obj}	AB25	Metal
AB25–Cd ²⁺	31.374	4.402	0.001	10.841	6.619	0.001	0.482	3.36 ± 2.90	26.46 ± 21.08
AB25–Ni ²⁺	27.434	4.041	0.001	6.717	6.064	0.001	0.215	5.18 ± 3.66	16.86 ± 24.65
AB25–Zn ²⁺	44.702	6.715	0.001	8.647	18.022	0.001	0.777	7.12 ± 5.57	22.60 ± 11.34

Table 6Response surface methodology models used for data fitting of the simultaneous adsorption of AB25 and heavy metals on Ca(PO₃)₂-modified carbon.

System	RSM models	R ²	E, %
AB25–Zn ²⁺	$q_{\text{AB25}} = 49.10871 + 0.472605C_{e,\text{AB25}} + 0.173207C_{e,\text{Zn}^{2+}} - 0.000206C_{e,\text{AB25}}C_{e,\text{Zn}^{2+}} - 0.000972C_{e,\text{AB25}}^2 - 0.001527C_{e,\text{Zn}^{2+}}^2$	0.996	1.45
	$q_{\text{Zn}^{2+}} = 5.69485 + 0.058552C_{e,\text{AB25}} + 0.085935C_{e,\text{Zn}^{2+}} - 0.000046C_{e,\text{AB25}}C_{e,\text{Zn}^{2+}} - 0.000124C_{e,\text{AB25}}^2 - 0.00064C_{e,\text{Zn}^{2+}}^2$	0.999	0.51
AB25–Ni ²⁺	$q_{\text{AB25}} = 40.50745 + 0.452578C_{e,\text{AB25}} + 0.418539C_{e,\text{Ni}^{2+}} + 0.000213C_{e,\text{AB25}}C_{e,\text{Ni}^{2+}} - 0.000798C_{e,\text{AB25}}^2 - 0.005147C_{e,\text{Ni}^{2+}}^2$	0.992	2.74
	$q_{\text{Ni}^{2+}} = 7.103656 + 0.023883C_{e,\text{AB25}} + 0.127031C_{e,\text{Ni}^{2+}} - 0.000078C_{e,\text{AB25}}C_{e,\text{Ni}^{2+}} - 0.00001C_{e,\text{AB25}}^2 - 0.000814C_{e,\text{Ni}^{2+}}^2$	0.987	1.31
AB25–Cd ²⁺	$q_{\text{AB25}} = 45.29104 + 0.518318C_{e,\text{AB25}} + 0.235232C_{e,\text{Cd}^{2+}} - 0.000006C_{e,\text{AB25}}C_{e,\text{Cd}^{2+}} - 0.001028C_{e,\text{AB25}}^2 - 0.002974C_{e,\text{Cd}^{2+}}^2$	0.996	1.88
	$q_{\text{Cd}^{2+}} = 7.017207 + 0.091198C_{e,\text{AB25}} + 0.367684C_{e,\text{Cd}^{2+}} - 0.000123C_{e,\text{AB25}}C_{e,\text{Cd}^{2+}} - 0.0002C_{e,\text{AB25}}^2 - 0.00336C_{e,\text{Cd}^{2+}}^2$	0.979	3.76

absolute percentage deviation (E) from 0.51 to 3.76% and correlation coefficients (R^2) higher than 0.99 in all binary systems. Therefore, these empirical models can be used for design and optimization of multi-component adsorption process involving AB25 and heavy metals.

3.3. Adsorbent characterization

Textural characteristics and chemical functionality of the Ca(PO₃)₂-modified carbon for heavy metal removal has been discussed in [27]. Based on this fact, characterization results presented in this study are mainly focused on the modification that occurs in

this adsorbent when both dye and heavy metals are simultaneously adsorbed. Fig. 5 shows the SEM images of carbon with and without adsorbed dye and heavy metals. In general, the adsorbent particles are globular and no change was observed in its morphology after the simultaneous adsorption of tested pollutants. However, EDX results show interesting differences in the adsorbent at 100 μm, see Table 7. EDX spectroscopy confirms our previous conclusion and shows that there is an increment of the amount of heavy metals in the samples of adsorbent loaded with AB25. Overall, EDX analysis indicate that the relative content of Zn²⁺, Cd²⁺ and Ni²⁺ are, respectively, 0.27, 0.55 and 0.7% for adsorbent samples from mono-component solutions, and 2.38, 3.31 and 2.30% for adsorbent

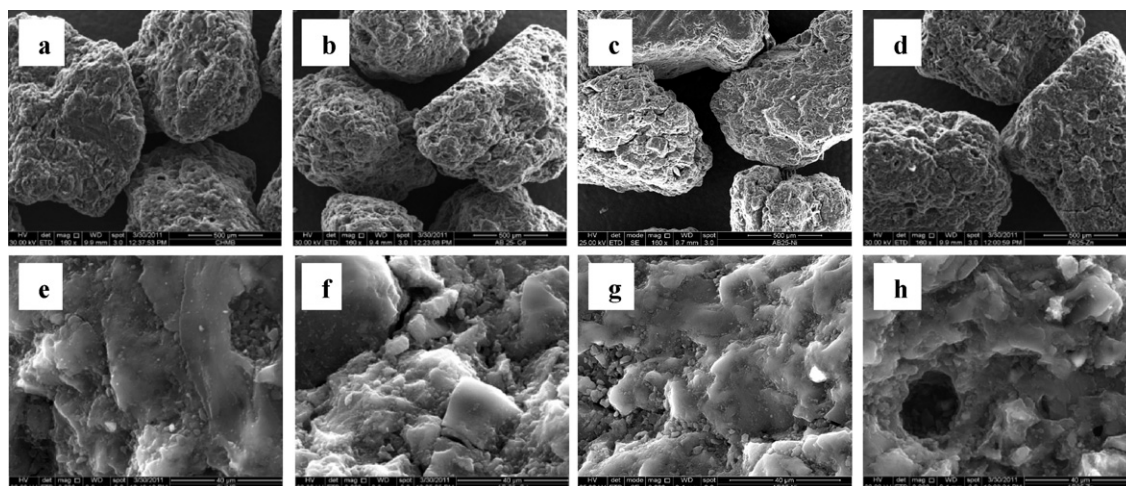


Fig. 5. SEM images at two magnifications (500 and 40 μm) of Ca(PO₃)₂-modified carbon used for the simultaneous adsorption of AB25 and heavy metals in binary systems. Samples: (a and e) raw carbon, (b and f) modified carbon after adsorption of AB25–Cd²⁺, (c and g) AB25–Ni²⁺ and (d and h) AB25–Zn²⁺.

Table 7
Results of EDX and XPS analysis of $\text{Ca}(\text{PO}_3)_2$ -modified carbon with and without adsorbed dye and heavy metals.

EDX Element	w% in adsorbent sample ^a							
	Raw	AB25	Cd ²⁺	Ni ²⁺	Zn ²⁺	AB25–Cd ²⁺	AB25–Ni ²⁺	AB25–Zn ²⁺
C	84.76	82.61	85.81	83.98	84.38	78.04	79.64	81.82
O	10.04	11.43	9.54	11.07	11.53	15.19	14.21	10.89
Al	0.74	1.19	0.80	0.81	0.65	0.50	0.58	0.71
Na	–	1.09	–	–	–	–	–	–
Si	0.97	0.82	1.13	1.05	0.89	0.61	0.68	0.96
P	0.64	0.21	0.28	0.28	0.28	0.10	0.07	0.21
S	2.35	2.59	1.89	1.63	1.56	2.18	2.53	3.03
Ca	0.04	0.05	–	–	0.02	0.07	–	–
Fe	0.47	–	–	0.48	0.42	–	–	–
Cl	–	0.02	–	–	–	–	–	–
Cd	–	–	0.55	–	–	3.31	–	–
Ni	–	–	–	0.70	–	–	2.30	–
Zn	–	–	–	–	0.27	–	–	2.38

XPS Element	w% in adsorbent sample ^a							
	Raw	AB25	Cd ²⁺	Ni ²⁺	Zn ²⁺	AB25–Cd ²⁺	AB25–Ni ²⁺	AB25–Zn ²⁺
C	94.24	92.56	94.85	93.44	94.23	92.85	92.01	92.14
O	5.34	5.47	5.15	5.44	5.27	5.89	6.03	5.58
P	0.41	–	–	–	–	–	–	–
N	–	0.91	–	–	–	–	1	1.02
S	–	0.46	–	–	<0.15	0.59	0.5	0.5
Si	–	0.6	–	1.11	0.5	0.5	0.46	0.53
Cd	–	–	–	–	–	0.16	–	–
Zn	–	–	–	–	–	–	–	0.23

^a Undetected.

samples obtained from binary solutions. On the other hand, Table 7 also shows results from XPS analysis. In this case, low percentages of Cd²⁺ (0.16%) and Zn²⁺ (0.23%) were observed only in the carbon samples loaded with the mixture AB25–Cd²⁺ and AB25–Zn²⁺. XPS analysis corresponding to C 1s, N 1s, O 1s and S 2p were performed (the spectra are not reported in this paper). In general, no changes were observed in the XPS electronic spectra of C 1s and N 1s for adsorbent loaded with both pollutants. The analysis for C 1s and O 1s showed that the ether and hydroxyl groups are predominant in the adsorbent surface besides the phosphate groups [27]. Note that some interesting changes in the bands for the spectra of O 1s and S 2p were observed. For example, for O 1s, a proportional increase was evident in the band at 531.5 eV in the carbon sample loaded with both dye and heavy metals in comparison with the raw adsorbent and the adsorbent loaded with only one pollutant (i.e., dye or heavy metal). Also, in the S 2p spectra, in particular for the peak corresponding to oxidized sulfur of –SO₃[–] groups of AB25, two bands were observed (167.5 and 168.5 eV). The band at 168.5 eV is more intense when this dye has been adsorbed on carbon. However, when the dye and heavy metals are simultaneously adsorbed, these two bands (i.e., 167.5 and 168.5 eV) have the same intensity. Finally, FT-IR spectra of $\text{Ca}(\text{PO}_3)_2$ -modified carbon with and without adsorbed dye and heavy metals are shown in Fig. 6. In general, no significant differences were observed between the raw carbon (Fig. 6a) and the carbon loaded with both pollutants (Fig. 6b–h). Four principal bands were identified in these spectra, the first at 3434 cm^{–1} corresponding to stretching vibration O–H of phenolic groups, the second at 1711 cm^{–1} which is characteristic of carbonyl groups, the third at 1570 cm^{–1} corresponding to stretching vibration C=C of aromatic compounds and, finally the band at 1080 cm^{–1} characteristic of stretching vibrations C–O [41].

Based on these characterization results and adsorption experiments, an adsorption mechanism for removal of heavy metals in the presence of AB25 is proposed and described in Fig. 7. It appears that adsorption performance of $\text{Ca}(\text{PO}_3)_2$ -modified carbon in the simultaneous removal of AB25 and heavy metals is probably caused by the fact that the anionic dye favors the electrostatic interactions with metal ions or may create new specific sites for adsorption

process, thus improving the adsorption capacities of this novel adsorbent. In particular, the metallic species may interact with the –SO₃[–] group of AB25 and with the hydroxyl and phosphoric groups of $\text{Ca}(\text{PO}_3)_2$ -modified carbon. It is important to remark that similar trends have been reported by Visa et al. [26] for the simultaneous adsorption of methylene blue and copper using fly ash. Specifically, they concluded that the increase in the copper adsorption efficiency can be explained considering the largest methylene blue affinity for the substrate. According to these authors, it appears that the

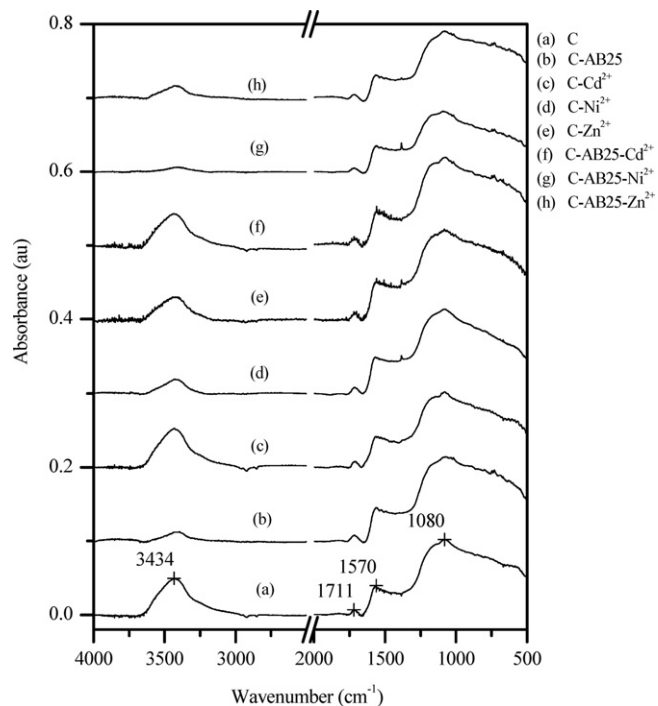


Fig. 6. FT-IR spectra of $\text{Ca}(\text{PO}_3)_2$ -modified carbon with and without loaded dye and heavy metals.

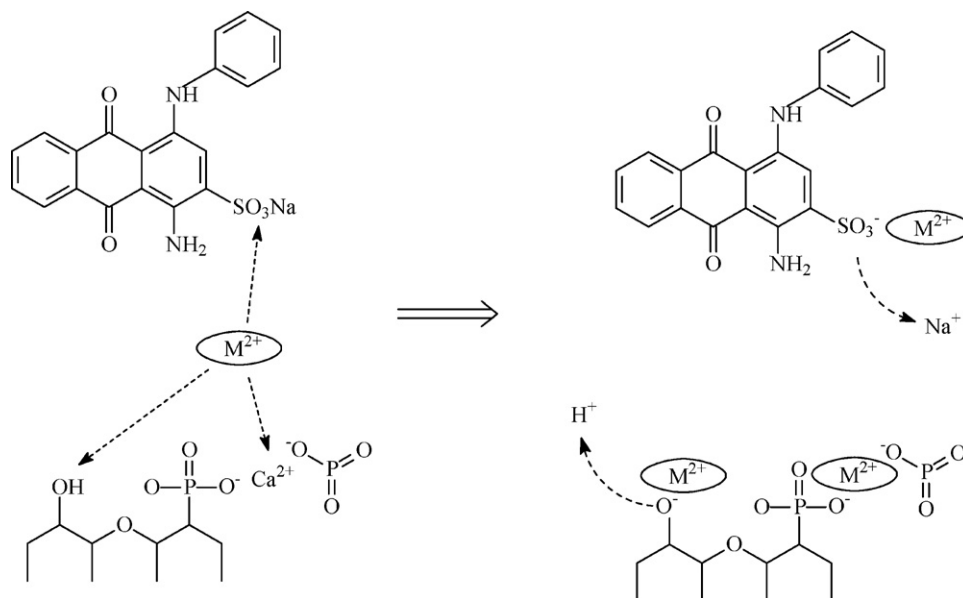


Fig. 7. Proposed mechanism for the simultaneous removal of AB25 and heavy metals using $\text{Ca}(\text{PO}_3)_2$ -modified carbon.

dye is firstly adsorbed on the substrate and after that copper ion is effectively adsorbed on this new layer.

4. Conclusions

In this study, multi-component kinetic and equilibrium adsorption studies of AB25 and heavy metals using a $\text{Ca}(\text{PO}_3)_2$ -modified carbon have been performed. Our results show that the presence of AB25 significantly affects the uptake of Cd^{2+} , Ni^{2+} and Zn^{2+} ions in the bi-pollutant system. This synergic adsorption depends on both the metal ion and dye concentrations and its magnitude is also different for tested heavy metals. However, the dye adsorption is not significantly affected by the presence of these metal ions and, practically, the adsorbed amount of AB25 on $\text{Ca}(\text{PO}_3)_2$ -modified carbon is the same in both single and binary solutions. This adsorption performance may be caused by the fact that the anionic dye favors the electrostatic interactions with metal ions or may create new specific sites for adsorption process. In particular, characterization results suggest that the heavy metals may interact with the $-\text{SO}_3^-$ group of AB25 and with the hydroxyl and phosphoric groups of $\text{Ca}(\text{PO}_3)_2$ -modified carbon. However, it is important to remark that the study and analysis of multi-component adsorption process is complex because adsorption is affected by several factors. In fact, there are various mechanisms involved in the removal of both dyes and heavy metal ions, which may occur simultaneously. Therefore, further studies are necessary to confirm and validate the proposed mechanism in this study. Finally, an empirical model based on response surface methodology provided better correlations for our experimental data than those obtained using non-modified Sips, non-modified Langmuir and extended Langmuir multi-component models. In summary, this study provides new insights about the simultaneous removal of dyes and heavy metals using activated carbons, and our results could be further employed in the optimization and implementation of effective adsorption processes for treatment of wastewaters polluted by both hazardous species.

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References

- [1] B.K. Korbahti, K. Artut, C. Gecgel, A. Ozer, Electrochemical decolorization of textile dyes and removal of metal ions from textile dye and metal ion binary mixtures, *Chem. Eng. J.* 173 (2011) 677–688.
- [2] N.F. Cardoso, E.C. Lima, I.S. Pinto, C.V. Amavisca, B. Royer, R.B. Pinto, W.S. Alencar, S.F.P. Pereira, Application of cupuassu shell as biosorbent for the removal of textile dyes from aqueous solution, *J. Environ. Manage.* 92 (2011) 1237–1247.
- [3] D. Das, D. Charumathi, N. Das, Bioaccumulation of the synthetic dye basic violet 3 and heavy metals in single and binary systems by candida tropicalis grown in a sugarcane bagasse extract medium: modelling optimal conditions using response surface methodology (RSM) and inhibition kinetics, *J. Hazard. Mater.* 186 (2011), 1541–1522.
- [4] C. Namasivayam, D. Sangeetha, Recycling of agricultural solid waste, coir pith: removal of anions, heavy metals, organics and dyes from water by adsorption onto ZnCl_2 activated coir pith carbon, *J. Hazard. Mater.* B135 (2006) 449–452.
- [5] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, *J. Environ. Manage.* 92 (2011) 407–418.
- [6] S. Wang, M. Soudi, L. Li, Z.H. Zhu, Coal ash conversion into effective adsorbents for removal of heavy metals and dyes from wastewater, *J. Hazard. Mater.* B133 (2006) 243–251.
- [7] M.S. Venkata, P. Sailaja, M. Srimurali, J. Karthikeyan, Color removal of monoazo acid dye from aqueous solution by adsorption and chemical coagulation, *Environ. Eng. Pol.* 1 (1999) 149–154.
- [8] J. Wu, M.A. Eiteman, S.E. Law, Evaluation of membrane filtration and ozonation processes for the treatment of reactive dye wastewater, *J. Environ. Eng.* 124 (1998) 272–277.
- [9] A. Méndez, R. Tovar, M.M. Davila, M.P. Elizalde, Degradation of reactive black 5 and basic yellow 28 on metallic-polymer composites, *Portugaliae Electrochim. Acta* 26 (2008) 89–100.
- [10] V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal – a review, *J. Environ. Manage.* 90 (2009) 2313–2342.
- [11] W.S. Wan Ngah, L.C. Teong, M.A.K.M. Hanafiah, Adsorption of dyes and heavy metals ions by chitosan composites: a review, *Carbohydr. Polym.* 83 (2011) 1446–1456.
- [12] A. Demirbas, Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review, *J. Hazard. Mater.* 167 (2009) 1–9.
- [13] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, *Water Res.* 33 (1999) 2469–2479.
- [14] W.S.W. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, *Bioresour. Technol.* 99 (2008) 3935–3948.
- [15] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – a review, *Bioresour. Technol.* 99 (2008) 6017–6027.
- [16] A. Demirbas, Heavy metal adsorption onto agro-based waste materials: a review, *J. Hazard. Mater.* 157 (2008) 220–229.
- [17] M.P. Elizalde González, V. Hernández Montoya, Fruit seeds as adsorbents and precursors of carbon for the removal of anthraquinone dyes, *Int. J. Chem. Eng.* 1 (2008) 243–253.
- [18] L.S. Chan, W.H. Cheung, G. McKay, Adsorption of acid dyes by bamboo derived activated carbon, *Desalination* 218 (2007) 304–312.
- [19] I.A. Aguayo-Villarreal, A. Bonilla-Petriciolet, V. Hernández-Montoya, M. Montes-Morán, H.E. Reynel-Avila, Batch and column studies of Zn^{2+} removal

- from aqueous solution using chicken feathers as sorbents, *Chem. Eng. J.* 167 (2011) 67.
- [20] J.M. Dias, M.C.M. Alvim-Ferraz, M.F. Almeida, J. Rivera-Utrilla, M. Sánchez-Polo, Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review, *J. Environ. Manage.* 85 (2008) 833.
- [21] Y. Al-Degs, M.A.M. Khraisheh, S.J. Allen, M.N. Ahmad, G.M. Walker, Competitive adsorption of reactive dyes from solution: equilibrium isotherm studies in single and multisolute systems, *Chem. Eng. J.* 128 (2007) 163–167.
- [22] F. Pagnanelli, A. Esposito, F. Veglio, Multi-metallic modelling of biosorption of binary systems, *Water Res.* 36 (16) (2002) 4095–4105.
- [23] V.C. Srivastava, I.D. Mall, I.M. Mishra, Equilibrium modeling of single and binary adsorption of cadmium and nickel onto bagasse fly ash, *Chem. Eng. J.* 117 (1) (2006) 79–91.
- [24] H.E. Reynel-Avila, D.I. Mendoza-Castillo, V. Hernandez-Montoya, A. Bonilla-Petriciolet, Multicomponent removal of heavy metals from aqueous solution using low-cost sorbents, in: *Water Production and Wastewaters Treatment*, Editorial Nova Science Publisher, 2011, pp. 69–99.
- [25] S.R. Shukla, R.S. Pai, Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust, *Sep. Purif. Technol.* 43 (2005) 1–8.
- [26] M. Visa, C. Bogatu, A. Duta, Simultaneous adsorption of dyes and heavy metals from multicomponent solutions using fly ash, *Appl. Surf. Sci.* 256 (2010) 5486–5491.
- [27] A. Guijarro-Aldaco, V. Hernandez-Montoya, A. Bonilla-Petriciolet, M.A. Montes-Moran, D.I. Mendoza-Castillo, Improving the adsorption of heavy metals from water using commercial carbons modified with egg shell wastes, *Ind. Eng. Chem. Res.* 50 (2011) 9354–9362.
- [28] S.K. Papageorgiou, F.K. Katsaros, E.P. Kouvelos, N.K. Kanellopoulos, Prediction of binary adsorption isotherms of Cu²⁺, Cd²⁺ and Pb²⁺ on calcium alginate beads from single adsorption data, *J. Hazard. Mater.* 162 (2–3) (2009) 1347–1354.
- [29] N. Fiol, I. Villaescusa, M. Martínez, N. Miralles, J. Poch, J. Serarols, Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste, *Sep. Purif. Technol.* 50 (1) (2006) 132–140.
- [30] M. Prasad, H. Xu, S. Saxena, Multi-component sorption of Pb(II), Cu(II) and Zn(II) onto low-cost mineral adsorbent, *J. Hazard. Mater.* 154 (2008) 221–229.
- [31] T. Sismanoglu, Y. Kismir, S. Karakus, Single and binary adsorption of reactive dyes from aqueous solutions onto clinoptilolite, *J. Hazard. Mater.* 184 (2010) 164–169.
- [32] A. Ahmadpour, K. Wang, D.D. Do, Comparison of models on the prediction of binary equilibrium data of activated carbons, *AIChE J.* 44 (3) (1998) 740–752.
- [33] S. Al-Asheh, F. Banat, R. Al-Omari, Z. Duvnjak, Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data, *Chemosphere* 41 (5) (2000) 659–665.
- [34] A. Bonilla-Petriciolet, M.G. Lira-Padilla, C.A. Soto-Becerra, Aplicación del método de recocido simulado en la regresión de isotermas de adsorción, *Revista Internacional de Contaminación Ambiental* 21 (4) (2005) 201–206.
- [35] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [36] Y.S. Ho, D.A.J. Wase, C.F. Forster, Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat, *Environ. Technol.* 17 (1996) 71–77.
- [37] D. Mohan, S. Chander, Single, binary and multicomponent sorption of iron and manganese on lignite, *J. Colloid Interface Sci.* 299 (1) (2006) 76–87.
- [38] V.M. Srivastava, I.D. Mall, I.M. Mishra, Equilibrium modeling of ternary adsorption of metal ions onto rice husk ash, *J. Chem. Eng. Data* 54 (2009) 705.
- [39] V.C. Srivastava, I.D. Mall, I.M. Mishra, Removal of cadmium (II) and zinc (II) metal ions from binary aqueous solution by rice husk ash, *Colloid Surf. A* 312 (2008) 172.
- [40] W.B. Lu, W.C. Kao, J.J. Shi, J.S. Chang, Exploring multi-metal biosorption by indigenous metal-hyperresistant enterobacter sp. J1 using experimental design methodologies, *J. Hazard. Mater.* 153 (1–2) (2008) 372–381.
- [41] C.J. Durán-Valle, M. Gómez-Corzo, J. Pastor-Villegas, V. Gómez-Serrano, *J. Anal. Appl. Pyrol.* 73 (2005) 59.