Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2012.2606

37(2012)364–372
January

Competitive adsorption of phenol and heavy metal ions onto titanium dioxide (Dugussa P25)

Salim Bekkouche[a,b], Stéphane Baup[b], Mohamed Bouhelassa[a,*], Sonia Molina-Boisseau[c], Christian Petrier[b]

[a]*Faculty of Engineering Science, Laboratory LIPE, Department of Industrial Chemistry, Mentouri University, Route Ain El-bey Constantine, Algeria*
Tel. +213774135135; email: mbouhela@hotmail.com
[b]*Université Joseph Fourier, LEPMI - GP2E, 1130 Rue de la piscine, BP 75, 38402 St Martin d'Hères Cedex, France*
[c]*Université Joseph Fourier, CERMAV, 601 Rue de la chimie, BP 53, 38041 St Martin d'Hères Cedex 9, France*

Received 29 January 2011; Accepted 22 September 2011

ABSTRACT

Single-solute adsorption of phenol (chosen as an organic pollutant) and single-solute adsorption of four heavy metal ions (Cu(II), Zn(II), Cd(II) and Fe(II) chosen as minerals pollutant) onto titanium dioxide (Dugussa P25) nanoparticles in aqueous suspension are studied. Temperature effect is studied for copper and for phenol. Furthermore, competitive adsorption between phenol and each metal cation is also studied. Phenol is dosed via HPLC while heavy metals are quantified by Atomic Adsorption Spectrophotometry. The single-solute adsorption results were well fitted by Freundlich, Langmuir, Temkin and Kiselev isotherm models. This study showed that adsorption of the different pollutants onto TiO_2 is favourable and adsorption energy was calculated as well. Moreover it is concluded that phenol adsorption and heavy metal cation adsorption do not proceed with the same mechanism. In the case of competitive adsorption in the 4 studied bisolute systems (phenol in presence of each heavy metal ion), the adsorption is decreased from 30% to 60% in comparison to single-solute results. Moreover, the Shiendorf-Rebuhn-Sheintuch (SRS) - a Freundlich type modified equation - was successfully applied. This competitive model described and simulated well the bisolute isotherms results for both phenol and metal ion. The competition influence is based on competitive coefficients a_{ij}.

Keywords: Adsorption; Isotherm; Competition; TiO_2; Phenol; Heavy metal

1. Introduction

Because of human, industrial and agriculture activities, multitude of organics and heavy metal ions are present in the environment. Organics are mainly non biodegradable and heavy metal ions are generally stable and non-degradable, so they are concentrated in food chain to reach toxic levels, tend to bioaccumulate and cause some serious health troubles [1]. For instance, it is well documented that phenol and cadmium are highly toxic and carcinogenic agents while copper, zinc and iron cations are likely to initiate toxic effects [2–5].

Some conventional methods, such as precipitation, ion exchange, adsorption onto activated carbon, membrane techniques, are widely applied to treat aqueous effluent. Nevertheless these traditional methods are limited, for instance physical methods are only pollutants transfer towards another phase while chemical methods can generate by-products more toxic than the original pollutant.

---

*Corresponding author.

Within this framework, photocatalysis is widely use to eliminate organic chemicals: it consists in the excitation of a photocatalytic material by ultraviolet light, which generates electron-hole pairs, able to undergo secondary reactions due to very reactive intermediary compounds. If molecules likely to be oxidized or reduced are present on the semiconductor surface, they will be attacked and finally turned into water and carbon dioxide [6]. These molecules are all the more present because TiO_2 involves surface hydroxylation and hydration (dissociative and non-dissociative water chemisorption) and that the surface lattice titanium atoms are considered as adsorption sites [7,8].

As a consequence photocatalytic efficiency depends not only on material characteristics (bandgap energy, size distribution) and oxidation reactions but also on the adsorption step of pollutants onto the semiconductor surface [9].

Solid-liquid single solute adsorption of organics onto titanium dioxide has been studied in various aspects either for organics or heavy metals. Robert et al. put in evidence that organic acid chemisorption proceeds very fast via titanium carboxylate formation, whereas adsorption phenol was less important and leads to Ti-phenolate adsorbates [10]. In the case of heavy metal ions, it was suggested that a hydroxyl group on the TiO_2 surface is involved in metal ions adsorption while chemisorbed water is exchanged in metal adsorption [11].

Many studies have been carried out to investigate the competitive adsorption on TiO_2 between organic-organic molecules or metal-metal ions [12–14]. However few of them deal with competitive adsorption between organic molecules and metal ions whereas natural and waste waters contain both organics and metal ions [15]. For instance, Janusz and Matysek estimate that the presence of oxalate ions affects the adsorption of Cd(II) ions onto TiO_2, with an important influence of pH [14].

Within this framework, the objective of this study is to investigate suitable adsorption isotherms for phenol and 4 heavy metals Cu(II), Zn(II), Cd(II) and Fe(II) on titanium dioxide (Dugussa P25). Not only single adsorption but also competitive adsorption (phenol in presence of each of the 4 heavy metal cations) will be studied.

2. Materials and methods

2.1. Chemicals

All chemicals were analytical grade: phenol (Sigma); $CuSO_4$ $5H_2O$ (Fluka); $ZnSO_4$ $7H_2O$ (Fisher Scientific); $3CdSO_4$ $8H_2O$ (Prolabo) and $FeSO_4$ $7H_2O$ (Aldrich). Solutions were prepared with ultra-pure water (18 MΩ). Mother solutions were prepared at 1.0 g/l concentration, stored at 4°C and then diluted to appropriate concentrations. HCl and NaOH (analytical grade) were used for pH adjustment.

Commercial P25 Dugussa TiO_2 is used for all the experiments, without any further treatment.

2.2. Analysis

Phenol was analysed by High Performance Liquid Chromatography (Waters® 510 HPLC pump) coupled with an UV-detector (Waters® 484 Detector, adjusted at 270 nm) and a Supelcosil® column (C18 column, particle diameter 5 µm, length 25 cm, diameter 4.6 mm). The eluant (60/40 (v/v) methanol/water with 1% of acetic acid added) flows at 1 ml/min. Data were recorded thanks to ASUR® software.

Heavy metals concentrations were measured with a Perkel-Elmer® A Analyst 200 atomic absorption spectrophotometer (AAS) operating with an air-acetylene flame (air 10 l/min and acetylene 2.5 l/min) and equipped with a Cu (324.7 nm), Fe (248.3 nm), Zn (213.9 nm) and Cd (228.8 nm) hollow cathode lamps.

To complete adsorbent characterization, specific surface (determined by BET technique) and nitrogen adsorption/desorption isotherms were performed using a Coulter SA 3100 Surface Area and Pore Size Analyzer. Moreover zeta-potentials of the TiO_2 particles dispersed in water were measured at 25°C using a laser-doppler-electrophoresis type apparatus (Nanosizer ZS Malvern Instruments). Data were averaged over 4 measures.

2.3. Adsorption equilibrium

Adsorption isotherm equilibria were performed by addition of 0.2 g of titanium dioxide (Dugussa P25) adsorbent into 200 ml of pollutant solutions in a 250 ml corked conical flask, at 25°C (Julabo thermostat), with a concentration of pollutants ranging from 10 ppm to 140 ppm. pH was adjusted at 6 for all experiments except for experiments involving Fe (II) where pH is 4.76 to avoid its precipitation. Suspensions were magnetically stirred in darkness for 60 min to reach adsorption equilibrium. Samples (1 ml) are filtered (Whatmann 0.20 µm) before HPLC and AAS analysis in order to eliminate TiO_2 particles.

Experiments are carried out for single-solute adsorption (each component separately) and for multicomponent adsorption (simultaneous presence of phenol and one metal cation).

2.4. Influence of temperature

To study influence temperature, addition of 0.4 g of titanium dioxide (Dugussa P25) adsorbent into 400 ml of pollutant solutions are made, with a concentration of phenol or copper ions of 100 ppm. pH was adjusted at 6 for all experiments and solutions were magnetically stirred at 300 rpm in darkness. Temperature is adjusted via a Julabo thermostat and experiments were carried out at 20°C, 25°C, 30°C, 35°C and 40°C.

3. Results and discussion

3.1. Preliminary studies

pH plays a major role in adsorption, particularly when the adsorbent is a semiconductor such as TiO_2, because of the ionisation state of the surface functional groups and because of the different ionic forms of the metal ions. So the pH-dependence of copper adsorption onto TiO_2 was studied (Fig. 1) for a 1–6 pH range, all other conditions remaining constant. This range was chosen because above 6, copper elimination is due to precipitation [16].

For very acidic pH, low adsorption happens because Cu^{2+} ion is the dominant species, repulsed by positively charged TiO_2 surface. Moreover there is a competition between Cu^{2+} and H^+ ions for adsorption sites onto TiO_2 nanoparticles surface [17].

When the pH increases from 1 to 6, adsorbed quantities increases from 0.05 to 0.25 mmol/g. As it can be seen, the optimum copper ions removal occured at pH = 6. Other studies confirm phenol adsorption onto TiO_2 with an optimum removal occuring for a pH between 5 and 6 (close to natural pH) [18].

Furthermore, zeta potential evolution with pH was also measured in order to determine the zero point of charge (ZPC) for the used titanium dioxide (Fig. 2). Above this isoelectrical point, TiO_2 surface is negatively charged while it is positively charged under this value. The obtained ZPC is 6.3 thus adsorption experiments are carried out at pH 6, closed to the ZPC, because adsorption is supposed to be favoured at the ZPC.

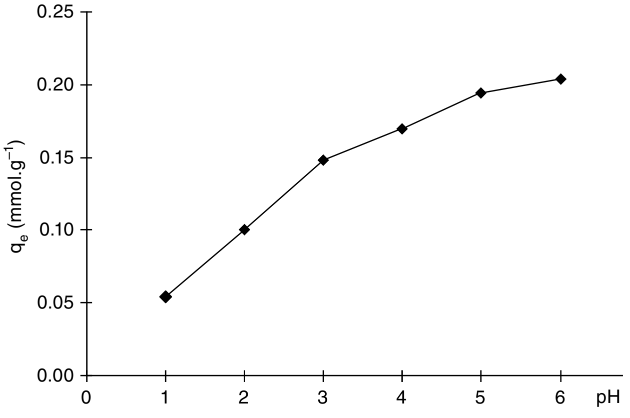

Fig. 1. Influence of pH on copper adsorption onto TiO_2.

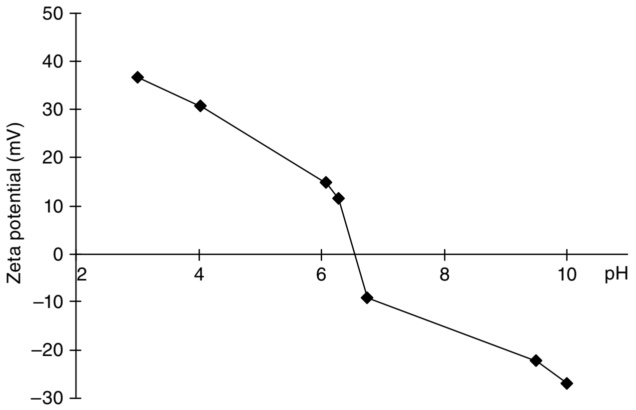

Fig. 2. Determination of ZPC for the used TiO_2.

Finally, BET experiments are carried out in order to characterize the adsorbent surface. For the used TiO_2, the obtained average specific surface was at 45.4 m²/g, closed to the value usually cited in the literature.

3.2. Single-component adsorption onto TiO_2

Single-component adsorption equilibria were carried out for phenol, Cu(II), Zn(II), Cd(II) and Fe(II) from aqueous solutions onto TiO_2 (Fig. 3). These data show a very good adsorption of copper and zinc while phenol and cadmium are less adsorbed. Nevertheless, the L-shaped curves of the experimental isotherms mean that adsorption is favoured and that there is no competition between adsorbate molecules and solvent to occupy adsorption sites on TiO_2 surface [19].

In order to characterize single-solute equilibrium, different models were used (Table 1) whose aim is to find a mathematical relation between C_e (equilibrium liquid concentration of adsorbate, mmol/l) and q_e (equilibrium adsorbed quantity of adsorbate, mmol/g). The interest to use different models is to obtain information

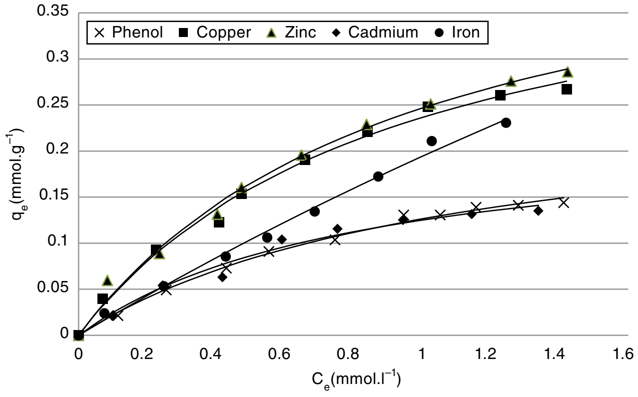

Fig. 3. Experimental (plots) and Langmuir calculated (lines) adsorption isotherms onto TiO_2.

Table 1
Models of single-solute equilibrium

	Equation	Linear equation	Parameters
Langmuir	$q_e = \frac{q_{\max} b C_e}{1 + bC_e}$	$\frac{C_e}{q_e} = \frac{1}{b\,q_{\max}} + \left(\frac{1}{q_{\max}}\right) C_e$	$q_{\max}$; b ; R_L
Freundlich	$q_e = K_F C_e{}^n$	$\ln(q_e) = \ln(K_F) + n\ln(C_e)$	K_F ; n
Temkin	$\theta = \frac{q_e}{q_m} = \frac{R¤}{\Delta Q}\ln\left(K_0 C_e\right)$	$\theta = \frac{q_e}{q_m} = \frac{R¤}{\Delta Q}\ln(K_0) + \frac{R¤}{\Delta Q}\ln(C_e)$	ΔQ ; K_0
Kiselev	$K_1 C_e = \frac{\theta}{(1-\theta)(1+K_n\theta)}$	$\frac{1}{(1-\theta)C_e} = K_1 K_n + K_1\left(\frac{1}{\theta}\right)$	K_1 ; K_n

about maximal adsorption capacity, but also dealing with intercations between adsorbates for example or adsorption energy.

In the case of equilibrium modelled by the Langmuir equation, the adsorption is assumed to occur on a homogenous surface by monolayer adsorption without any interaction between the adsorbed species [20]. The value of $q_{\max}$ and b, the maximum adsorption capacity (mmol/g) and the adsorption intensity (l/mmol) respectively, are obtained (Table 2) via the linearized form cited in Table 1, which is the most adapted linearized equation [21,22]. The adsorption isotherms were fairly well in agreement with the Langmuir isotherm model except for the adsorption of Fe(II) which has a low correlation coefficient. The obtained values of $q_{\max}$ are in agreement with the observed experimental results. In addition, the equilibrium adsorbed amounts were recalculated by Langmuir equation using the obtained parameters in order to check its validity (Fig. 3). Experimental points and calculated data were found to be in good agreement.

It is usually accepted that the high-energy sites have low maximum adsorption capacity $q_{\max}$ and reciprocally [23]. As it can be seen, the adsorbates with higher molar mass (cadmium and phenol) have low value of $q_{\max}$ indicating that the adsorption of these adsorbates implies high-energy sites while compounds with lower molar mass have higher values of $q_{\max}$, indicating that the adsorption of these adsorbates implies low energy.

Moreover, equilibrium described by Langmuir equation can be conveniently represented by a dimensionless constant separation factor (R_L) defined by Hall et al. as follows [24]:

$$R_L = \frac{1}{1 + bC_0}$$

where C_0 is the initial solute concentration (mmol/l) and b the Langmuir constant. This coefficient is used to evaluate the feasibility of adsorption: the isotherm is assumed to

Table 2
Calculated parameters of studied adsorbates onto TiO_2 for the different used models

		Phenol	Copper	Zinc	Cadmium	Iron
Langmuir	$q_{\max}$ (mmole/g)	0.286	0.427	0.444	0.242	0.292
	b (l /mmol)	0.789	1.231	1.248	1.062	1.160
	R^2	0.96	0.96	0.93	0.91	0.84
	R_L (C_0=10 mg/l)	0.92	0.83	0.84	0.91	0.94
	R_L (C_0=140 mg/l)	0.41	0.32	0.33	0.47	0.44
Freundlich	K_F (mmol/g)(mmol/l)$^{-n}$	0.127	0.236	0.241	0.130	0.187
	N	0.75	0.65	0.59	0.71	0.83
	R^2	0.97	0.99	0.98	0.96	0.99
Temkin	ΔQ (KJ/mol)	13.5	12.9	12.6	12.7	26.6
	K_0 (l/mol)	11.0	16.6	15.8	13.8	11.4
	R^2	0.98	0.94	0.93	0.96	0.84
Kiselev	K_1	0.70	1.50	1.99	1.26	0.43
	K_n (l/mol)	0.43	−0.47	−0.82	−0.21	−1.87
	R^2	0.99	0.98	0.91	0.97	0.98

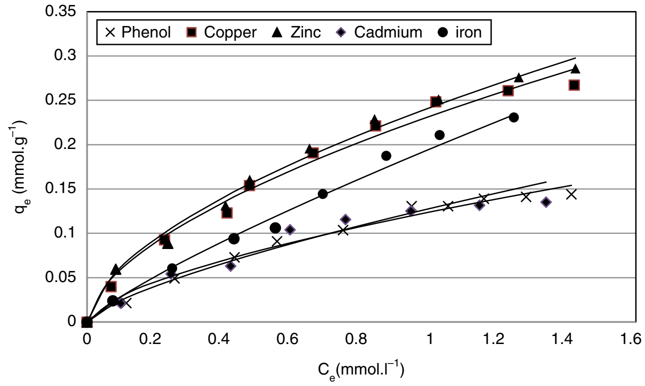

Fig. 4. Experimental (plots) and Freundlich calculated (lines) adsorption isotherms onto TiO_2.

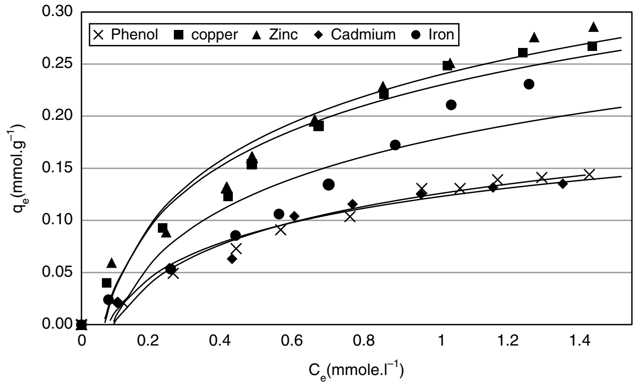

Fig. 5. Experimental (plots) and Temkin calculated (lines) adsorption isotherms onto TiO_2.

be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$) [24,25]. In our case, the R_L values were calculated for the lowest initial concentration (10 mg/l) and for the highest (140 mg/l) initial concentration. For the five studied compounds, the obtained R_L values are in 0.32–0.94 range (Table 2), indicating a favourable adsorption of these compounds onto TiO_2 surface.

The equilibrium data were also fitted to Freundlich isotherm, a semi-empirical equation widely used for adsorption description. In the case of Freundlich isotherm, adsorption is assumed to occur on a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [26]. The Freundlich isotherm constants K_F ((mmol/g)$\cdot$ (mmol/l)$^{-n}$) and n incorporate all factors describing the adsorption. The obtained parameters are presented in Table 2, and the linear correlation coefficients (R^2) are very good. Moreover experimental equilibrium and modeled isotherm are drawn (Fig. 4) leading to a good agreement.

The parameter n is linked to the intensity of adsorption and indicates favourable adsorption (high adsorption intensity) for all the concentration studied if $n < 1$ [27]. As noticed in Table 2, the value of n for each adsorbate is lower than 1, thus it confirms the conclusion of R_L calculations from Langmuir model.

The value of K_F indicates high adsorption capacity, as noticed for Zn (II) and Cu (II) which have higher adsorption capacity than the other adsorbates.

Furthermore, equilibrium data were studied using the Temkin model (Table 1). This model takes into account the presence of adsorbate/adsorbent interactions so that the heat of adsorption in the layer decreases linearly with coverage [28,29]. The fractional coverage θ is linked to the equilibrium liquid concentration C_e (mol/l) in relation with the adsorption energy variation ΔQ (kJ/mol) and the Temkin constant K_0 (l/mol).

According to the correlation coefficient values obtained (Table 2) Temkin isotherm model fits well the adsorption isotherm of phenol and heavy metal ions onto TiO_2 (Fig. 5). ΔQ values are in a 12.6–26.6 kJ/mol range showing an exothermic adsorption for these studied compounds.

Finally, experimental equilibrium data were also fitted by to Kiselev equation (Table 1 and Fig. 6), assuming monomolecular layer adsorption. The interest of this equilibrium model is to obtain information about a possible formation of complex between adsorbed molecules in the adsorption mechanism, related to K_n, the constant of complex formation and K_1 (l/mol), the Kiselev constant [30]. The calculated Kiselev parameters and the corresponding coefficient of correlation, which are good, are shown in Table 2.

The equilibrium constant of complex formation between adsorbate and adsorbent, K_n, is negative for all of the 4 studied metal ions. It indicates that there is no complex formation between metal ions and TiO_2 surface. On the contrary, the K_n constant is positive in the case of phenol adsorption onto TiO_2 surface. It is supported by several studies which have demonstrated that

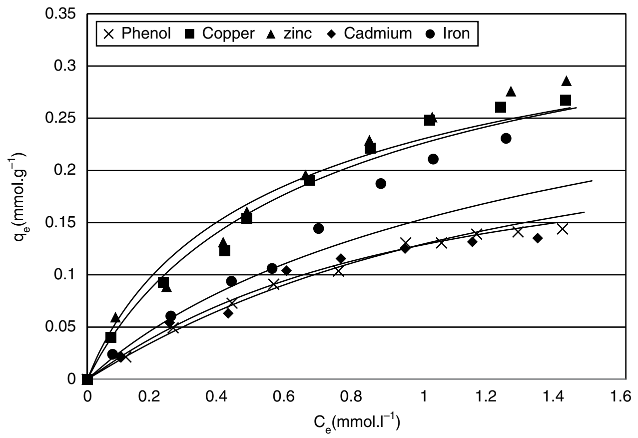

Fig. 6. Experimental (plots) and Kiselev calculated (lines) adsorption isotherms onto TiO_2.

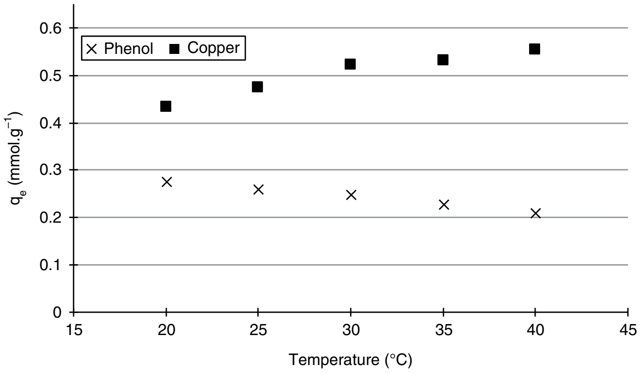

Fig. 7. Influence of temperature on copper and phenol adsorption onto TiO_2.

adsorption of phenol onto TiO_2 surface occurs by a chemisorption mechanism via binding ligand complex and the adsorption of heavy metal ions onto TiO_2 proceeds via cation exchange [1,10]. For instance, cadmium ions adsorption is said to proceed via exchange of hydrogen ions from surface hydroxyl groups [14].

3.3. *Influence of temperature on single-solute adsorption*

Temperature influence has been studied for phenol and copper adsorption equilibrium. Five temperatures were used: 20, 25, 30, 35 and 40°C. The experiments were carried out in the same conditions for other parameters (pH, mass of TiO_2, initial concentration of pollutant) than for the systematic isotherm studies carried out at 25°C. The variation of adsorbed quantities at equilibrium (q_e) of phenol and copper versus temperature were calculated (Fig. 7).

In the case of phenol, results indicate phenol adsorption onto TiO_2 decreases with increasing temperature. When the temperature increases from 20 to 40°C, q_e decreases from 0.28 to 0.21 mmol/g of TiO_2. Thus the adsorption of phenol is an exothermic process.

On the other hand, results for copper indicate copper equilibrium adsorption increases substantially with temperature increase. From 20 to 40°C, q_e increases from 0.43 to 0.55 mmol/g. As a consequence the temperature promotes the adsorption of copper on TiO_2 that is in contradiction with ΔQ values obtained with Temkin model. Nevertheless, it was put in evidence that the adsorption of Cu(II) onto TiO_2 nanoparticles is an endothermic process [1]. Moreover, Li et al. found that the adsorption of Zn(II) onto TiO_2 particles is strongly temperature dependent [31]. Their results revealed that a temperature rise causes a marked increase of zinc adsorption capacity. As a consequence, the adsorption of heavy metal ions onto TiO_2 nanoparticles seems to be an endothermic process.

In order to quantify the influence of temperature, experiments were carried out at temperatures of 20, 25, 30, 35, and 40°C. The following thermodynamic parameters were used [32]:

$$K_C = \frac{q_e}{C_e} \tag{1}$$

$$\Delta G = -RT \ln K_c \tag{2}$$

$$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{3}$$

where K_c is an equilibrium constant between the adsorbed equilibrium concentration and the aqueous equilibrium concentration (l/g), R is the gas constant (8,314 kJ/mol K). Furthermore, ΔG (kJ/mol); ΔH (kJ/mol); ΔS (kJ/mol K) are the variation of free energy, enthalpy and entropy respectively. ΔH and ΔS values are calculated (Table 3) from the slope and the intercept of $\ln K_C$ evolution versus de $1/T$ of Eq. (3).

The negative values of free energy change (ΔG) show that adsorption is a spontaneous process in the studied temperature range, whereby no energy input is required. Moreover, the obtained values in the case of phenol decrease, indicating that adsorption of phenol become less favourable at higher temperature. On the contrary, ΔG values increase with increasing temperature, showing that adsorption of Cu(II) is favoured at higher temperature (Table 3 and Fig. 7).

In the case of phenol, the negative value of ΔH (Table 3) indicates that adsorption of phenol onto TiO_2 is exothermic. In the case of copper, the positive value of ΔH shows an endothermic nature of adsorption.

Table 3
Thermodynamic parameters of phenol and copper adsorption onto TiO_2

Temperature (°C)	Phenol					Copper				
	20	25	30	35	40	20	25	30	35	40
ΔG (kJ/mol	−2.55	−2.79	−3.01	−3.33	−3.63	−2.35	−2.09	−1.76	−1.73	−1.59
ΔH (kJ/mol)			−13,25					13,44		
ΔS (kJ/mol K)			−53,58					−38,09		

Finally, negative values of ΔS show a good affinity of TiO_2 for both studied adsorbates, which is corroborated by the equilibrium models showing a favourable adsorption. Furthermore it shows a decreased disorder at the interface during adsorption [31,32].

3.4. Competitive adsorption onto TiO_2

Phenol adsorption and cations adsorption seem to obey different mechanisms, as it was underlined by Kiselev isotherm study. Nevertheless, these two types of pollutants require adsorption sites on TiO_2 surface, thus competition is relevant to be studied and quantified. As a consequence competitive adsorption of the organic target was studied in presence of each cation adsorbate and compared to single-solute adsorption.

Compared to phenol single-solute adsorption onto TiO_2, competitive adsorption implies a significant decrease in phenol adsorption for each phenol/cation couple, from 30% for phenol/zinc or phenol/iron couples to 60% in the case of phenol/cadmium (Fig. 8).

Furthermore, results of adsorption of heavy metal cations onto TiO_2 surface in presence of phenol were achieved. In comparison with single-solute adsorption of metal cations, the presence of phenol in solution also clearly reduces cations adsorption onto TiO_2. For instance, adsorption of cadmium and zinc in single-solute and in phenol bisolute systems is shown (Fig. 9). Adsorption decreases from 30% (in the case of cadmium) to 50% (in the case of copper). As exhibited, the presence of phenol in solution creates an obstruction at the TiO_2 surface which reduces the quantities of heavy metal ions likely to interact with the sites. It has been recently reported that the presence of oxalate ions cause changes in Cd(II) adsorption edge, increasing the adsorption at low pH and decreasing the adsorption at high pH [14].

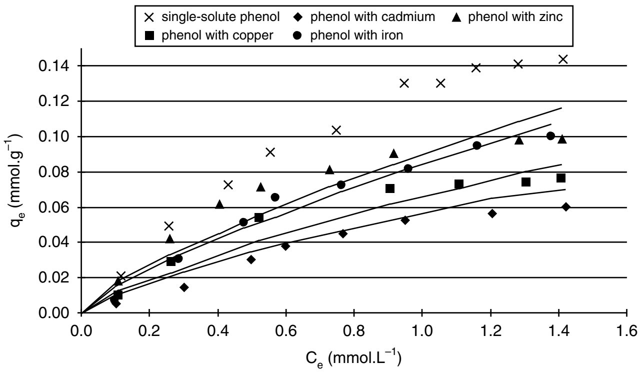

Fig. 8. Phenol adsorption equilibrium onto TiO_2 in single-solute and in Cu(II), Zn(II), Cd(II) or Fe(II) bisolute systems.

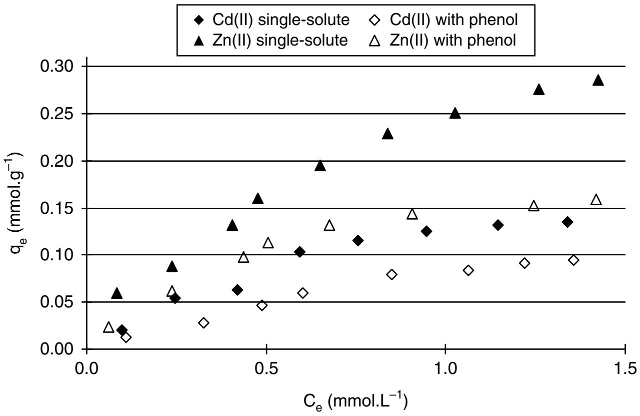

Fig. 9. Zn(II) and Cd(II) adsorption equilibrium onto TiO_2 in single-solute (black symbols) and in phenol bisolute (open symbols) systems.

Different equilibrium models were used to describe these bi-solute results. ideal adsorbed solution theory (IAST) based on Freundlich equilibrium and extended Langmuir equation revealed to be unsuccessful. However the shiendorf-rebuhn-sheintuch (SRS), derivated from an adaptation of Freundlich equation to bi-solute adsorption, was used in this study [33,34]. This model is based on the following equation:

$$q_{ei} = K_{Fi} C_i (\sum a_{ij} C_{ej})^{(ni-1)} \tag{4}$$

where q_{ei} is the equilibrium adsorbed quantity of adsorbate i (mmol/g), C_{ei} is the equilibrium liquid concentration of adsorbate i (mmol/l), K_{Fi} and n_i are the Freundlich coefficients obtained in single-solute isotherm for the component i, and a_{ij} is the competition coefficient for the adsorption of the adsorbate i in presence of the competitive component j.

Using SRS modeling of experimental data, interaction coefficients were computed (Table 4). In this table $a_{phenol/ion}$ traduces the competition of phenol adsorption and $a_{ion/phenol}$ deals with the ion adsorption. According to the a_{ij} competition coefficient is all the more high since the competition is efficient and a nil value traduces a lack of competition [33]. This is corroborated by the experimental isotherms of phenol with and without competition and the evolution of $a_{phénol/ion}$ (Fig. 8 and Table 4).

Table 4
Competition coefficients for the 4 studied bisolute systems

	$a_{phenol / ion}$	$a_{ion / phenol}$
phenol / copper	12.19	7.73
phenol /zinc	2.85	2.44
phenol / cadmium	20.47	4.14
phenol / iron	4.13	6.14

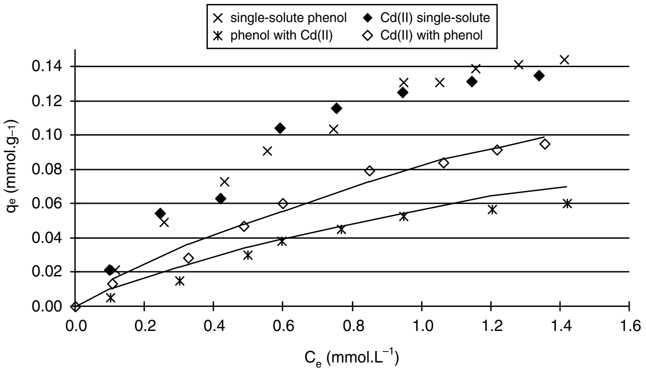

Fig. 10. Phenol and Cd(II) adsorption equilibrium onto TiO_2 in single-solute systems, bisolute system, and simulated bisolute system (lines).

Using these a_{ij} coefficients, simulations are drawn and competition is likely to be modeled. These calculations are compared to experimental data, for instance in the case of phenol /copper bisolute system (Fig. 10). Simulations for phenol in the 4 bisolute systems are also plotted (Fig. 8). For the adsorption of mixtures, the calculated data are similar to the experimental values, which validate the calculations.

4. Conclusions and perspectives

The adsorption of phenol and copper, zinc, cadmium and iron bivalent ions onto titanium oxide (Dugussa P25) was investigated, in single-solute but also in bi-solute phenol-metal system. For single-solute adsorption, the obtained results from the adsorption isotherms studies were fitted with various isotherm models: Langmuir, Freundlich, Temkin, and Kiselev models. Langmuir and Freundlich models show that adsorption is favourable, thanks to the calculated values of R_L (between 0 and 1) and n (lower than 1). Furthermore Temkin model gives values of adsorption energy. Finally Kiselev model allows concluding that phenol adsorption and metal adsorption does not proceed with the same mechanism because K_n is positive in the case of phenol adsorption whereas K_n values are negative in the case of metal ions adsorption.

In the case of bisolute adsorption of phenol in presence of each of four heavy metal ions (Cu, Zn, Cd or Fe) onto TiO_2, it was found that phenol adsorption onto TiO_2 was decreased in the presence of heavy metal ions and reciprocally. Moreover, the shiendorf-rebuhn-sheintuch (SRS) was successfully applied. This competitive model allows to simulate bisolute isotherms for both phenol and metal ion and to quantify the competition influence via competitive coefficients a_{ij}.

This study allows a better understanding of adsorption onto titanium oxide surface, in order to characterize single-solute and bisolute adsorption of organics and metallic ions. This better knowledge will allow a better anticipation of organic compounds photocatalysis onto TiO_2 in presence of metallic salts, like it happens in real wastewaters. Moreover this better knowledge is likely to be applied in TiO_2 doping process via metal ions, to improve the wavelength range of this photocalatytic material.

References

[1] S.-S. Liu, C.-K. Lee, H.-C. Chen, C.-C. Wang and L.-C. Juang, Application of titanate nanotubes for Cu(II) ions adsorptive removal from aqueous solution, Chem. Eng. J., 147 (2009) 188–193.

[2] J.-H. Kim, K.-K. Oh, S.-T. Lee, S.-W. Kim and S.-I. Hong,Biodegradation of phenol and chlorophenols with defined mixed culture in shake-flasks and a packed bed reactor, Process Biochem., 37 (2002) 1367–1373.

[3] B.A. Fowler, Monitoring of human populations for early markers of cadmium toxicity: A review, Toxicol. Appl. Pharmacol., 238 (2009) 294–300.

[4] K. Azetsu-Scott, P. Yeats, G. Wohlgeschaffen, J. Dalziel, S. Niven and K. Lee, Precipitation of heavy metals in produced water: In?uence on contaminant transport and toxicity, Marine Environmental Research, 63 (2007) 146–167.

[5] B. Wei and L. Yang, A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China, Microchem. J., 94 (2010) 99–107.

[6] S. Horikoshi, N. Serpone, S. Yoshizawa, J. Knowland and H. Hidaka, Photocatalyzed degradation of polymers in aqueous semiconductor suspensions. IV Theoretical and experimental examination of the photooxidative mineralization of constituent bases in nucleic acids at titania/water interfaces, J. Photochem. Photobiol., A, 120 (1999) 63–74.

[7] M.A. Blesa, A.D. Weisz, P.J. Morando, J.A. Salfity, G.E. Magaz and A.E. Regazzoni, The interaction of metal oxide surfaces with complexing agents dissolved in water, Coordination Chemistry Reviews, 196 (2000) 31–63.

[8] H.S. Wahab, T. Bredow and S.M. Aliwi, Computational modeling of the adsorption and photodegradation of 4-chlorophenol on antase TiO_2 particles, J. Mol. Struct. THEOCHEM, 863 (2008) 84–90.

[9] H.Y. Chen, O. Zahra, M. Bouchy, F. Thomas and J.Y. Bottero, Adsorption properties of TiO_2 related to the photocatalytic degradation of organic contaminants in water, J. Photochem. Photobiol., A, 85 (1995) 179–186.

[10] D. Robert, S. Parra, C. Pulgarin, A. Krzton and J.-V. Victor Weber, Chemisorption of phenols and acids on TiO_2 surface, Appl. Surf. Sci., 167 (2000) 51–58.

[11] J.-K. Yang and A. P. Davis, Competitive Adsorption of Cu(II)-EDTA and Cd(II)-EDTA onto TiO_2, J. Colloid Interface Sci., 216 (1999) 77–85.

[12] A.D. Weisz, L. Garcia Rodenas, P.J. Morando, A.E. Regazzoni and M.A. Blesa, 'FTIR study of the adsorption of single pollutants and mixtures of pollutants onto titanium dioxide in water: oxalic and salicylice acids', Catal. Today, 76 (2002) 103–112.

[13] Maria Konstantinou and Ioannis Pashalidis, 'Competitive sorption of Cu(II), Eu(III) and U(VI) ions on TiO_2 in aqueous solutions- A potentiometric study', Colloids and Surfaces A: Physiochemical and Engineering Aspects, 324 (2008) 217–221.

[14] W. Janusz and M. Matysek, Coadsorption of Cd(II) and oxalate ions at the TiO_2/electrolyte solution interface, J. Colloid Interface Sci., 296 (2006) 22–29.

[15] Zhao-Fu Meng, Yi-Ping Zhang and Zeng-Qiang Zhang, 'Simultaneous adsorption of phenol and cadmium on amphoteric modified soil', J. Hazard. Mater., 159 (2008) 492–498.

[16] K. Rahman and M.R. Islam, Effect of pH on isotherms modelling for Cu(II) ions adsorption using maple wood sawdust, J. Hazard. Mater., 149 (2009) 273−280.

[17] K. Kabra, R. Chaudhary and R.L. Sawhney, Effect of pH on solar photocatalytic reduction and deposition of Cu(II), Ni(II), Pb(II) and Zn(II): Speciation modelling and reaction kinetics, J. Hazard. Mater., 149 (2007) 680−685.

[18] S. Bekkouche, M. Bouhelassa, N. Hadj Salah and F.Z. Meghlaoui, Study of adsorption of phenol on titanium oxide (TiO_2), Desalination, 166 (2004) 355−362.

[19] C.H. Giles, T.H. Mc Ewan, S.N. Nakhwa and D. Smith, Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurements of specific surface areas of solids, J. Chem. Soc., 10 (1960) 3973–3993.

[20] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. American Chemical Society, 38 (1916) 2221–2295.

[21] M.L. Zhou, Modelisation de l'adsorption sur charbon actif. PhD Thesis, University of Rennes 1 n° 724, France (1992).

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

[23] E. Eren, Removal of copper ions by modified Unye clay, Turkey, J. Hazard. Mater., 159 (2008) 235–244.

[24] K.R. Hall, L.C. Eagleton, A. Acrivos and T. Vermeulen, Pore and solid diffusion kinetics in fixed-bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam., 5 (1966) 212–223.

[25] A.K. Bhattacharya, S.N. Mandal and S.K. Das, Adsorption of Zn(II) from aqueous solution by using different adsorbents, Chem. Eng. J., 123 (2006) 43−51.

[26] H. Freundlich, On adsorption in solutions, Z Physik. Chem., 57 (1906) 385−471.

[27] R.E. Treybal, Mass-transfer Operations, 3rd Ed., McGraw-Hill (1981).

[28] M. Arami, N.Y. Limaee and N.M. Mahmoodi, Investigation on the adsorption capability of egg shell membrane towards model textile dyes, Chemosphere, 65 (2006) 1999–2008.

[29] M.I. Temkin, Adsorption equilibrium and the kinetics of processes on nonhomogeneous surfaces and in the interaction between adsorbed molecules, J. Phys. Chem. (USSR) 15 (1941) 296−332.

[30] A.V. Kiselev, Vapor adsorption in the formation of adsorbate molecule complexes on the surface, Kolloid Zhur, 20 (1958) 338–348.

[31] W. Li, G. Pan, M. Zhang, D. Zhao, Y. Yang, H. Chen and G. He, EXAFS studies on adsorption irreversibility of Zn(II) on TiO_2: Temperature dependence, J. Colloid Interface Sci., 319 (2008) 385−391.

[32] W.S. Wan Ngah and M.A.K.M. Hanafiah, Adsorption of copper on rubber (*Hevea brasiliensis*) leaf powder: Kinetic, equilibrium and thermodynamic studies, Biochem. Eng. J., 39 (2008) 521–530.

[33] C. Shiendorf, M. Rebhum and M. Sheintuch, A Freundlich-type multicomponent isotherm, J. Colloid Interface Sci., 79 (1981) 136–142.

[34] C.-H. Wu, C.-Y. Kuo, C.-F. Lin and S.-L. Lo, Modeling competitive adsorption of molybdate, sulfate, selenate, and selenite using a Freundlich-type multi-component isotherm, Chemosphere, 47 (2002) 283–292.