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Activated Carbons Application to Remove Nonionic Surfactants from Wastewater Produced by an Italian Metallurgic Plant

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ABSTRACT

The performance of different activated carbons for the removal of nonionic surfactants from metallurgic wastewater was assessed through lab scale experiments. Two different matrices were used: a simple one, obtained by dissolving different amounts of a single nonionic surfactant (Triton X100) in distilled water, and a complex matrix, prepared as above but using surfactants-free wastewater from an Italian metallurgic plant as solvent. In this way the main operative parameters that affect the adsorption process in the simple matrix have been studied avoiding the interference due to the complex matrix; then the results were utilized to define and optimize the tests carried out on the complex matrix. The adsorption equilibrium experimental data were best fitted with a Langmuir isotherm, allowing defining the contact time and the proper design parameters for the adsorption column. The different tests were performed on four different activated carbon types, and the removal efficiency and the treatment cycle duration for each of the tested carbons were discussed and compared. The

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experimental results showed that the saturation adsorption capacity is not notably correlated either with the pH value or with the water matrix, whereas the slope of the isotherm, defined by the Henry constant, is sensibly higher at strong acidic or alcaline conditions, with a minimum value at nearly neutral pH. Therefore, it was concluded that the removal efficiency is maximized when the operative pH was in the 2–4-unit value range. The best activated carbon, in terms of removal efficiency, resulted to be a mineral activated carbon, characterized by the highest iodine number, and thus with the largest porosity. Removal efficiencies were in the 60 to 80% range.

Key Words: Nonionic surfactants; Industrial wastewater; Activated carbon; Adsorption; Metallurgic plant.

INTRODUCTION

Surfactants may be efficiently removed from wastewater through conventional biological processes together with COD removal without the need of any supplementary treatment unit.[1] When the wastewater is characterized by an high content of inorganic matter (i.e., heavy metals) and by initial pH values in a strongly acidic or alkaline range, such as those from a metallurgic plant, the biological treatments cannot be applied, since the biomass, that is strongly affected by non-suitable environmental conditions (pH and temperature) and by the presence of toxic compounds (heavy metals), is unable to activate itself. In these conditions, the biological treatment looses its effectiveness so that the fixed legislative limits (COD and surfactant concentration) cannot be met. Therefore, alternative technologies such as ion exchange,[2] Fenton's oxidation[3] or ozonation[4,5] have to be utilized.

A really alternative process, fulfilling the requirements of low management and capital costs and reduced size and volume of the facilities to be installed, based on surfactants removal by adsorption on activated carbon columns, was studied in this work. The adsorption isotherms of a nonionic surfactant (Triton X100), utilized by an Italian metallurgic plant, on different activated carbon types were determined using two different water matrices: distilled water and the wastewater collected upstream the final processing step of metallic laminates production of the same metallurgic plant. The influence of different operating parameters, such as pH, type of activated carbon was also investigated. As a result, the proper conditions for a packed column process were defined and assessed through lab-scale breakthrough experiments.

MATERIAL AND METHODS

Reagents

The compound chosen in this work as representative of nonionic surfactants is Triton X-100, characterized by relatively low biodegradability and high toxicity.

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Table 1. Characterization of Triton X100 surfactant.

Physical state	Odor	Boiling point (°C)	Melting point (°C)	Flammability point (°C)	Vapor pressure (hPa)	Density (g $(cm^3)^{-1}$)	Solubility
Clear liquid	Light	270	7	288	<0.01	1.07	Infinite

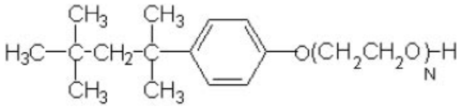

Figure 1. Structure of Triton X-100.

The chemical and physical properties of Triton X100 are reported in Table 1, whereas its structure is reported in Fig. 1.

Wastewater Properties

The wastewater used in this study, obtained from an Italian metallurgic plant, is already treated through a chemical process, where iron chloride is added, allowing the formation and precipitation of different insoluble compounds, such as phosphates, fluorides and heavy metals. Such precipitation takes place in a sedimentation tank, where a polyelectrolyte compound is added to enhance the sludge settlement properties. The wastewater, whose main characteristics are reported in Table 2, was collected just downstream this sedimentation unit.

Activated Carbon Properties

The properties of the four different activated carbons used in this work are reported in Table 3. All tested media are of mineral origin, except type-B, which has vegetal origin.

Experimental Set-Up

Batch Experiments

Batch tests were performed in 500 mL bottles using a magnetic stirrer by Ikamag (Italy) with a 550-rpm stirring rate. The adsorption kinetics was determined by mixing a 25 g L^{-1} solution of X-Triton 100 in distilled water with a 1.0 g amount of type-A activated carbon and by collecting liquid samples at increasing contact times. Adsorption equilibrium was studied by mixing a 25 g L^{-1} solution of X-Triton 100, in either distilled or wastewater, with different amounts of activated carbon, until

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Table 2. Characteristics of wastewater collected from an Italian metallurgic plant.

T (°C)	pH	F^- (mg L^{-1})	PO_4^{3-} (mg L^{-1})	Fe (mg L^{-1})	Cr (mg L^{-1})	Ni (mg L^{-1})	Zn (mg L^{-1})	Ca (mg L^{-1})
22	11.4	3.3	0.7	0.078	<0.01	<0.01	0.076	330

Table 3. Properties of four activated carbon types.

Parameter	Method	Dimension	Carbon A	Carbon B	Carbon C	Carbon D
Methylene Blu index	Cefic DAB	mL	180–230	> 22	15	>20
Iodine index	Awwa B 604-74	mg I_2 (g ac)$^{-1}$	900–1050	>1050	1000	>800
Ash content	Unichim M33	%	<1	<5	<8	n/a
Apparent density	ASTM D2854	g (cm^3)$^{-1}$	0.48–0.52	0.47–0.52	0.43–0.47	0.47–0.53
Humidity	ASTME 2867	%	<5	<7	<5	n/a
Hardness	ASTM D 3802	%	93-96	98	>85	>90
pH	ASTM D 3838		7–8	8–10	8–10	8–10
Grain size distribution	ASTM 2862-82	mesh mm^{-1}	12/40	8/30	12/30	8/30

equilibrium was achieved. The surfactant concentration in the adsorbed phase was then determined from the material balance of X-Triton 100 in the liquid phase. In this way, the influence of some key operating parameters, such as pH and carbon type, was examined.

Column Tests

The column tests were performed in a stainless steel column (length = 98 cm, i.d. = 4.8 cm), packed with 767 g of type-A activated carbon, resulting in a 1025 mL pore volume. The surfactant solution was fed to the column by means of a peristaltic pump at a 7.7 L h^{-1} flow rate corresponding to an 8 min contact time.

Analysis

Determination of Triton X100 concentration in both distilled and wastewater was performed with a modified Unichim 10511-1 method,[6] without the sublation and purification procedures as described in more detail below.

Among the analytical techniques commonly used in Italy for the determination of nonionic surfactants in water, the Unichim method 10511-1 is the one preferred by local Italian sanitary authorities.

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Such a method is specifically aimed to the determination of nonionic ethoxylated surfactants (BIAS) containing from 6 to 30 oxyethylenic groups, in both water and wastewater quality control. The surfactants are extracted in ethylacetate from the aqueous matrix through a sublation process that is by flowing nitrogen through the matrix. Ethylacetate is in this way evaporated and after removal of ionic surfactants by means of ion exchange resins, the residual matrix is dissolved in water and analyzed. Analysis is based on colorimetric titration with a 0.0005 M Tetrakis solution. The volume, C, of titration solution required per mg of surfactant is determined through the following equation:

$$C = \frac{A - B}{N} \tag{1}$$

where A is the volume (mL) required to titrate N mg of surfactant in 20 mL of water containing 1.5 g KOH and few drops of "Victoria Blu" indicator; B is the volume required to titrate 20 mL of water (blank sample). The concentration of surfactant, as Tetrakis active substance (TAS), is obtained from the following equation:

$$\mathrm{TAS} = \frac{(T - P)}{C} * \frac{V_1}{V_2} * \frac{1000}{V} \tag{2}$$

where:

V: sample volume (mL);
V_1: total volume of the surfactant solution after sublation and purification (mL);
V_2: volume of the surfactant solution taken for titration (mL);
T: volume of titration agent used (mL);
P: volume of titration agent used for the blank sample.

Such a method requires long and time expensive procedures for sublation and purification, which some times also affect the reliability and precision of the method. For these reasons we have developed a simplified procedure, in which basically both sublation and purification are neglected. We checked the results of this modified Unichim method by applying it for the determination of ionic surfactant in the real wastewater, whose properties were reported above, and comparing them with those obtained using the standard Unichim procedure. The results are summarized in Table 4, where it can be noticed that the agreement between the standard Unichim method and the modified Unichim method is fairly good. Besides, it is worth noting that the average error observed for the modified method is generally lower than that observed for the standard Unichim method, even at low surfactant concentration where the precision of the method decreases sharply for both methods.

EXPERIMENTAL RESULTS

Batch Tests

Adsorption Kinetics

The kinetics of Triton X100 uptake by type-A activated carbon is reported in Fig. 2. It can be observed that after about one hour contact time, equilibrium

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Table 4. Performance of Unichim and modified Unichim methods for nonionic surfactants determination.

Experimental	Unichim		Modified Unichim	
Surfactant concentration ($mg\,L^{-1}$)	Surfactant concentration ($mg\,L^{-1}$)	Error (%)	Surfactant concentration ($mg\,L^{-1}$)	Error (%)
1	1.7	75.6	1.3	33.6
2	2.3	16.7	2.7	38.5
3	2.8	5.4	3.7	25.3
6	4.2	29.8	6.0	0.06
11	7.3	33.2	10.1	8.0
21	16.3	22.4	20.5	1.9
31	24.0	22.3	31.6	2.1

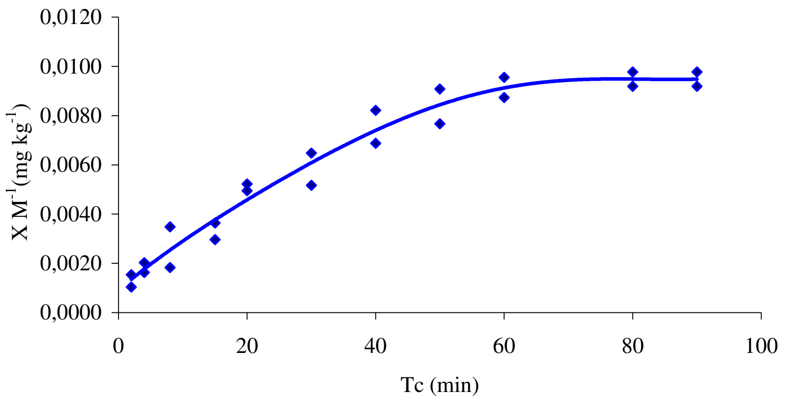

Figure 2. Adsorption kinetics of Triton 100 on type-A activated carbon in distilled water: concentration in the adsorbed phase ($g\ kg^{-1}$) vs. time (min).

between fluid and adsorbed phase was achieved. Therefore, all batch equilibrium tests, whose results are reported in the following, were performed with a 60 min equilibration time. Besides, the column tests were also designed for a contact time near to 60 min.

Adsorption Isotherms

The adsorption equilibrium data of Triton X100 on type-A activated carbon from distilled and wastewater, reported in Fig. 3a and b, respectively, were best fitted with a Langmuir isotherm:

$$q = \frac{abC_E}{1 + bC_E} \tag{3}$$

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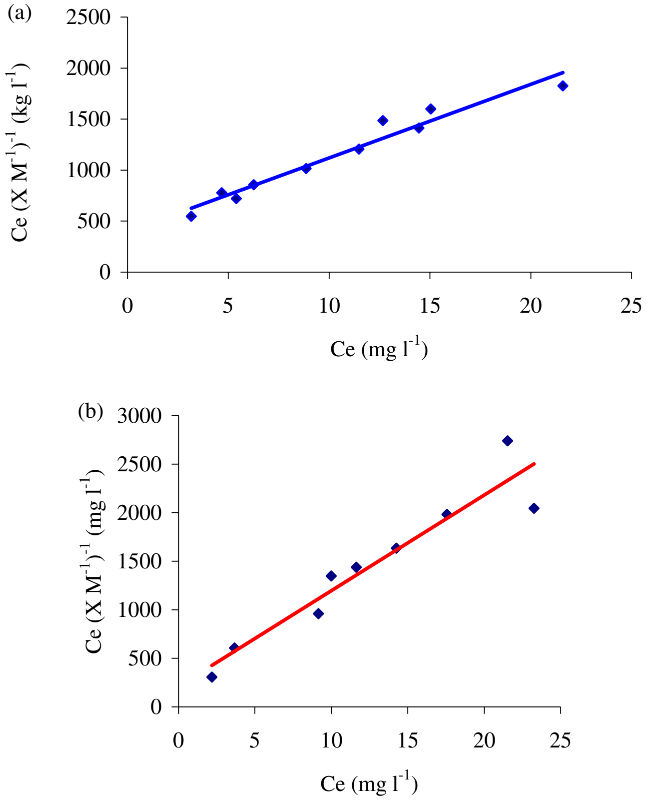

Figure 3. Langmuir adsorption isotherm on type-A activated carbon of Triton 100 in (a) distilled water, (b) wastewater from metallurgic plant.

where q and C_E are the Triton X100 equilibrium concentration in adsorbed phase (mg g^{-1} carbon) and liquid phase (mg L^{-1}), respectively.

Namely, the saturation concentration was equal to 0.0138 mg g^{-1} of activated carbon in distilled water, which was reduced to 0.01 mg g^{-1} in wastewater. Even if the observed difference is still in the range of experimental error, it may be also attributed to competing species that may be present in the wastewater, and eventually also to the different pH value of the two matrices: 6.5 for distilled water and 11.4 for wastewater.

Influence of pH

The results of batch adsorption equilibrium experiments, performed in distilled water at different pH values, reported in linearized form in Fig. 4a, indicate that pH plays a strong role in determining the adsorption capacity of the carbon. Namely, it is worth noting that the type-A activated carbon exhibited the highest adsorption capacity at strongly acidic pH values. This is confirmed by the results reported in

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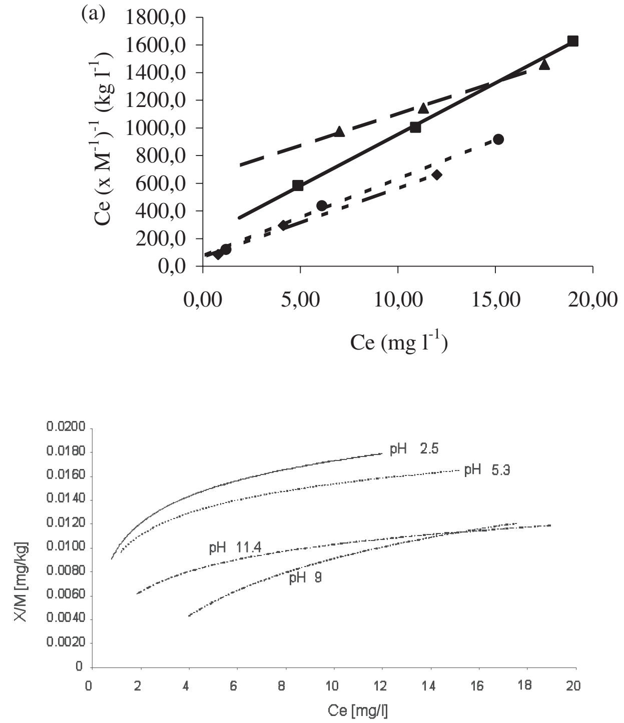

Figure 4. Langmuir adsorption isotherm on type-A activated carbon of Triton 100 in distilled water at different pH values in: (a) linearized form, ▲ pH = 9; ■ pH = 11.4; ● pH = 5.4; ◆ pH = 2.5; (b) standard form.

Table 5. Parameters of Langmuir adsorption isotherm of Triton X100 on type-A activated carbon at different pH values (see Eq. (1)). H = Henry constant.

pH	2.5	5.3	6.5	9.0	11.5	11.5 (waste)
a (mg g^{-1})	0.0198	0.0177	0.0138	0.0215	0.0135	0.01
b (g mg^{-1})	0.809	0.799	0.182	0.072	0.352	0.470
H = ab	0.0160	0.0141	0.0025	0.0015	0.0047	0.0047

Fig. 4b, where it can be clearly observed that the slope of the adsorption isotherm at low concentration is higher when operating at acidic pH values. Besides, also the activated carbon capacity was observed to be larger at pH = 2.5 with respect to the other pH conditions. The values of Langmuir isotherm parameters, reported in Table 5, also indicate that the Henry constant, given by the product *ab,* is sensibly higher at acidic pH or in strongly alcaline conditions, whereas at near neutral pH values the carbon is less effective in adsorbing Triton X100. Finally, at the same pH = 11.5, the Henry constants measured in distilled and waste water are similar, thus indicating that the adsorption behavior of Triton X100 is not notably affected by the matrix type, when the other operating conditions are the same.

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Influence of Activated Carbon Type

The adsorption isotherms of Triton X100 on four different activated carbon types, whose properties are reported in Table 2, are shown in Fig. 5a. It can be observed that among the tested media, type-A activated carbon was the one characterized by the highest adsorption capacity at least among the mineral activated carbons (type-A, C, and D). This can be easily observed by looking at Fig. 5b, where it can be noticed that using the type A activated carbon the slope of the adsorption isotherm was larger at low surfactants concentration in the liquid phase; in the mean time, the adsorption capacity of the type A activated carbon was comparable with that of the type B and much larger of the other ones.

Efficiency of Triton X-100 Removal

The equilibrium adsorption data, described above, allowed to evaluate the removal efficiency of the investigated surfactant at different pH values, when using different amounts of activated carbon. The results, summarized in Fig. 6a to c, clearly show that the best results in terms of removal efficiency were always obtained when operating at lower pH values, namely at pH = 2.5.

Besides, the removal efficiency was observed to increase as long as larger quantities of activated carbon were used. Nevertheless, if the removal efficiency is

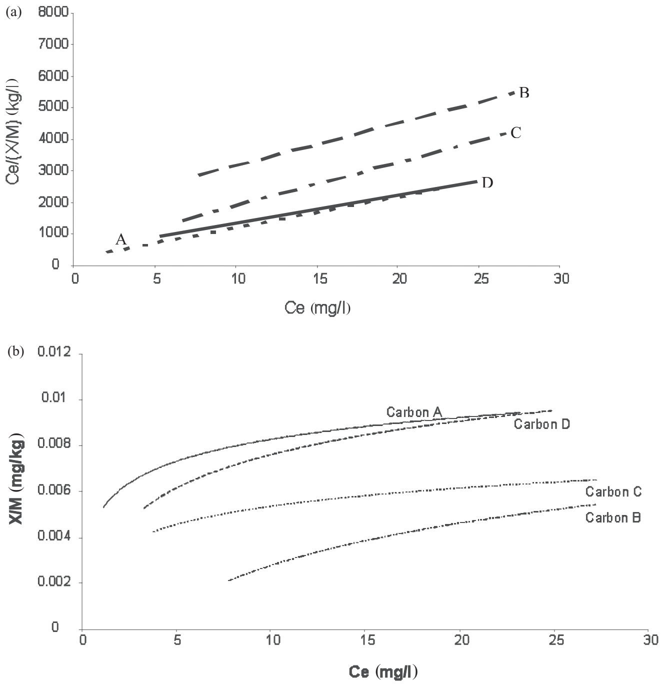

Figure 5. Langmuir adsorption isotherm of Triton X 100 in distilled water on different activated carbon types in (a) linearized and (b) standard form.

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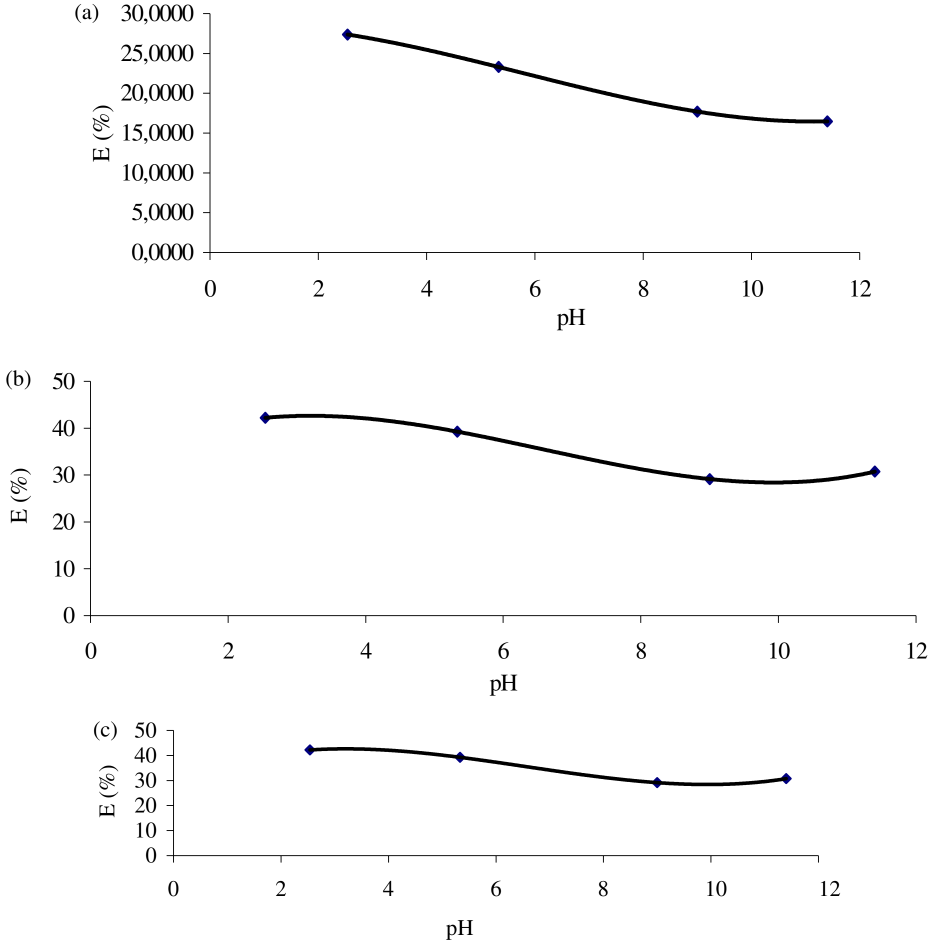

Figure 6. Efficiency of Triton X100 removal at different pH values using (a) 400 mg, (b) 800 mg, (c) 1400 mg of type A activated carbon.

normalized to the amount of activated carbon used, the highest normalized removal efficiency is obtained for the conditions corresponding to the lower amount of activated carbon (see Fig. 6a), This means that when larger amounts of activated carbon are used, only a fraction of the extra activated carbon is really useful for the Triton X100 removal.

Column Tests

A breakthrough experiment of a 25 g L^{-1} solution of Triton X 100 in wastewater was performed in a column packed with type-A activated carbon. The geometric

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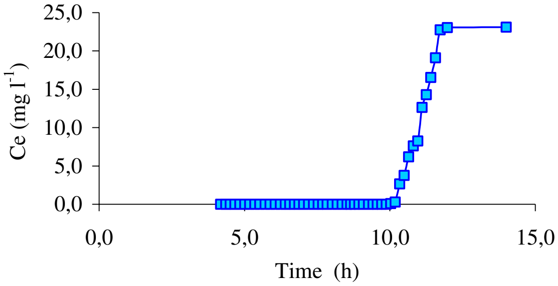

Figure 7. Breakthrough curve of Triton 100 on a column packed with type A activated carbon.

description and the applied flow rates were reported above. The results of this experiment, reported in Fig. 7, indicate that the nonionic surfactant starts eluting from the column after about 10 h, when the outlet concentration of Triton X100 increased above 1 mg L^{-1}. The breakthrough time, estimated from the adsorption capacity data, was calculated using the following equation:

$$t_b = \frac{(x/m)_b M_c}{Q(C_i - C_b/2)} \tag{4}$$

where $(x/m)_b$ is the activated carbon capacity at breakthrough concentration [mg mg^{-1}], M_c is the amount of activated carbon packed in the columns [mg], Q is the volumetric flow rate of water fed to the column [L h^{-1}, C_i and C_b are the inlet and breakthrough concentrations [mg L^{-1}], respectively.

By comparing the breakthrough time, estimated with Eq. (4) with the experimental one, it may be concluded that the experimental capacity of the bed at breakthrough is around 75% of the estimated value (Fig. 7). This result is different from the indications found in the literature, where it ranges typically between 25 and 50% of the value provided by the batch equilibrium data and could be directly used for a short-cut design of the adsorption column, with no need for conducting further column experiments.

CONCLUSIONS

The adsorption equilibria of Triton X100 on activated carbon from distilled and wastewater was best described using a Langmuir isotherm. The calculated parameters of the Langmuir isotherm indicated that the adsorption efficiency was not notably affected by the water matrix itself (i.e., its constituents), but rather from the pH value, which is strongly alcaline (pH = 11.5) in the wastewater. In fact, adsorption isotherms were approximately the same for distilled and wastewater, when the former one was amended in order to increase its pH to 11.5.

Besides, the experimental results showed that the saturation adsorption capacity was not notably correlated either with the pH value or with the water matrix,

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whereas the slope of the isotherm, defined by the Henry constant, was sensibly higher at strong acidic or alcaline conditions, with a minimum value at nearly neutral pH. Therefore, it was concluded that the removal efficiency is maximized when the operative pH was in the 2–4-unit value range. The best activated carbon, in terms of removal efficiency, resulted to be a mineral activated carbon (type-A), characterized by the highest iodine index, and thus with the largest porosity. Namely, it was possible to achieve a removal efficiency of Triton X100 around 64% with an initial concentration of $25\,\mathrm{g\,L^{-1}}$, which increased to 84% for a $6\,\mathrm{g\,L^{-1}}$ initial concentration.

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