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Assessment of organic chlorinated compound removal from aqueous matrices by adsorption on activated carbon

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ABSTRACT

Adsorption on activated carbon is currently the most frequently used technology to remove organic chlorinated pollutants from wastewaters. The present study examines the ability of five commercially available types of activated carbon to remove organic chlorinated compounds from the effluent of a chemical plant. The various types were tested on the basis of Freundlich adsorption isotherms for 14 pure organic chlorinated compounds, of molecular weight ranging from that of dichloromethane ($MW = 84.93\,g\,mol^{-1}$) to hexachlorobenzene ($MW = 284.78\,g\,mol^{-1}$). The best was selected and used in a laboratory fixed-bed column to assess its removal efficiency with respect to the tested organic chlorinated compounds. Removal efficiency was always higher than 90%. These results provide information necessary to optimize scale-up from the pilot plant to the real one.

1. Introduction

Organic chlorinated compounds are chemicals used on a large scale even in everyday life, and they may be industrial effluent contaminants (Yu and Chou, 2000; Shawwa et al., 2001). Some of them are toxic and are slow to biodegrade, so that they accumulate in the environment. Adsorption on activated carbon is one of the most frequently used and efficient technologies for removing volatile, semi-volatile and non-volatile chlorinated organic pollutants from aqueous industrial sludge, surface waters and drinking water (Sotelo et al., 2002; Yun et al., 1998; Eckenfelder, 1992). The amount and rate of adsorption involve thermodynamic aspects (Chianga et al., 2002) and are functions of the chemical nature of the activated carbon (Chuanga et al., 2003; Karanfil and Kilduff, 1999; Kunio et al., 2001; Othman et al., 2000), which depends on the activation method employed (Cheremisinoff, 1980). An equation often used to describe solute/adsorbed equilibrium adsorption capacity Q_e ($mg\,g^{-1}$) isotherms (Eckenfelder, 1992) derives from Freundlich's semi-empirical model:

$$\frac{X}{M} = KC^{1/n}, \tag{1}$$

where X is the weight of adsorbed compound (mg), M the weight of adsorbent substrate (g), K the adsorption constant ($mg^{1-1/n}\,l^{1/n}\,g^{-1}$), C the residual compound concentration in solution ($mg\,l^{-1}$) and n the adsorption constant (dimensionless). Non-ideal competitive interactions (Smith, 1991) explain observed deviations from this model. Although Freundlich adsorption isotherms indicate the best activated carbon, they are not sufficient to design a full-scale plant adsorption column that works in non-ideal equilibrium conditions. Inside the column absorbing bed, the thickness of the mass transfer zone (MTZ) in cm (Eckenfelder, 1992; La Grega et al., 1994) depends on various parameters. The relationship between output pollutant concentration C_e ($mg\,l^{-1}$) vs time may be represented by the so-called "breakthrough curve" (Fig. 1).

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Nomenclature

$a = \frac{N_0}{C_0 V}$	fixed-bed operative parameter ($\mathrm{h\,m^{-1}}$)
$b = -\frac{1}{KC_0}\ln(\frac{C_0}{C_B} - 1)$	fixed-bed operative parameter (h)
BDST	bed depth service time (h)
bp	boiling point (°C)
C	residual compound concentration in solution ($\mathrm{mg\,l^{-1}}$)
C_b	breakthrough concentration ($\mathrm{mg\,l^{-1}}$)
C_e	output pollutant concentration ($\mathrm{mg\,l^{-1}}$)
C_l	operative limit concentration ($\mathrm{mg\,l^{-1}}$)
C_0	input concentration ($\mathrm{mg\,l^{-1}}$)
d	relative density (dimensionless)
D	dipole moment (Debye)
K	reaction kinetics constant ($\mathrm{l\,h^{-1}\,mg^{-1}}$)
K	adsorption constant ($\mathrm{mg^{1-1/n}\,l^{1/n}\,g^{-1}}$)
k	time constant (h)
LOD	limit of detection ($\mathrm{ng\,l^{-1}}$) as three times the signal-to-noise ratio
$\log K_{ow}$	logarithm of octanol–water partition coefficient (dimensionless)
LOQ	limit of quantification ($\mathrm{ng\,l^{-1}}$) as six times the signal-to-noise ratio
M	weight of adsorbent substrate (g)
mp	melting point (°C)
MTZ	mass transfer zone (cm)
MW	molecular weight ($\mathrm{g\,mol^{-1}}$)
n	adsorption constant (dimensionless)
nD_{20}	refractive index (dimensionless)
N_0	activated carbon adsorbent capacity ($\mathrm{kg\,m^{-3}}$), i.e., mass of contaminant removed per unit of column volume ($\mathrm{m^3}$)
$Q_e = \frac{X}{M} = KC^{1/n}$	equilibrium adsorption capacity ($\mathrm{mg\,g^{-1}}$)
t	service time (h)
V	superficial velocity through column, i.e., flow ($\mathrm{m^3\,h^{-1}}$) per unit section of column ($\mathrm{m^2}$)
X	weight of adsorbed compound (mg)
Z	bed depth (m)
$Z_0 = \frac{V}{KN_0}\ln(\frac{C_0}{C_b} - 1)$	critical bed thickness (m)

Greek letter

$\eta = \frac{Z-Z_0}{Z} \times 100$	percent adsorption efficiency (dimensionless).

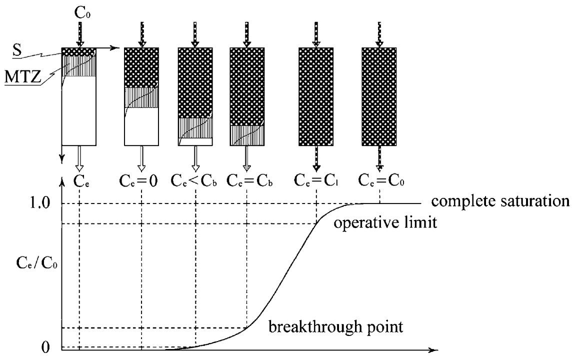

Fig. 1 – Breakthrough curve. S: saturation zone; MTZ: adsorbing zone; C_0: input concentration; C_e: output concentration; C_e/C_0: ratio between output and input concentrations. Above C_b, so-called breakthrough concentration, C_e is no longer acceptable and adsorbing bed needs to be regenerated. In particular, "breakthrough point" here is defined as point reached when concentration is 10–5% of initial one. C_l: operative limit concentration; $C_e = C_0$: complete saturation.

This curve can be fitted by the following equation:

$$\frac{C_{out}}{C_{in}} = \frac{t^n}{k^n + t^n}, \tag{2}$$

where t is the elapsed time (h), while the constant k (time constant, h) and the dimensionless exponent n depend on the system under study. A simplified relationship (Hutchins, 1973), involving the desired "service time t" (h) of a filtering unit, its "bed depth Z" (m) and the "bed depth service time" (BDST) (h), allows us to design an adsorbing bed, provided that C_0 and C_b ($\mathrm{mg\,l^{-1}}$) are known. At this point, BDST can be used to determine fixed-bed operative parameters a and b:

$$t = aZ + b, \tag{3}$$

where $a = N_0/C_0V$ "fixed-bed operative parameter" ($\mathrm{h\,m^{-1}}$), N_0 being the activated carbon "adsorbent capacity" ($\mathrm{kg\,m^{-3}}$), i.e., mass of contaminant removed per unit of column volume ($\mathrm{m^3}$), C_0 = input concentration ($\mathrm{mg\,l^{-1}}$) and V = superficial velocity through the column, i.e., flow ($\mathrm{m^3\,h^{-1}}$) per unit section of column ($\mathrm{m^2}$); $b = -(1/KC_0)\ln(C_0/C_B - 1)$ is the "fixed-bed operative parameter" (h) with K = reaction kinetics constant ($\mathrm{l\,h\,mg^{-1}}$) and C_b = "breakthrough concentration" ($\mathrm{mg\,l^{-1}}$).

Considering only the class of chlorinated organic compounds examined here, the aims of the present work are as follows: (1) to study the removal efficiency of five commercial activated carbons by determining their Freundlich adsorption isotherms and choosing the best among them; (2) to verify the removal efficiency of the chlorinated compounds by continuum absorption on a fixed bed of granular activated carbon; (3) to optimize parameters useful for scaling-up from the pilot adsorbing column to the full-scale plant.

2. Materials and methods

2.1. Materials and reagents

Reagents used for activated carbon adsorption tests were sodium chloride 99.5% RPE (Carlo Erba reagents), sodium hydroxide 98% Arista R® (BDH) and Milli-Q water (WP 4100 reagent-grade water purifier-SMEG). Reagents used to wash