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Enhanced mitigation of para-chlorophenol using stratified activated carbon adsorption columns

*Michael Fan Fu Sze, Gordon McKay**

Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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ABSTRACT

The adsorptive removal of toxic para-chlorophenol using activated carbon adsorption columns is a proven effective engineering process. This paper examined the possibility to stratify an adsorbent bed into layers, in order to enhance the adsorption process performance in terms of increased column service time and adsorbent bed saturation. Four different types of fixed-bed adsorption columns are used and compared under the same operating conditions, but with the variation of column geometry and activated carbon particle size stratification. The Type 3 column – a cylindrical column with particle stratification packing, is found to be the most efficient choice, as the extent of column service time and adsorbent bed saturation are the largest. This could eventually decrease the frequency of adsorbent replacement/regeneration and hence reduce the operating cost of the fixed-bed adsorption process. The Homogeneous Surface Diffusion Model (HSDM) was applied successfully to describe the dynamic adsorption of para-chlorophenol onto Filtrasorb 400 (F400) activated carbon in different types of columns. The Redlich-Peterson isotherm model equation, an experimentally derived external mass transfer correlation and a constant surface diffusivity are used in the HSDM. The optimised surface diffusivity of para-chlorophenol is found to be 1.20E-8 cm^2/s, which is in good agreement with other phenolics/F400 carbon diffusing systems in literature.

1. Introduction

Chlorophenols are a large group of chemicals with chlorine atoms (between one and five) attached to the phenolic structure, and there are 19 congeners exist in total. They are normally used in herbicides (Tsyganok et al., 1999), insecticides, wood preservatives and industries as synthesis intermediates or as raw materials in the manufacturing of pharmaceuticals and dyes (Pera-Titus et al., 2004). According to Pera-Titus et al. (2004), the world market of chlorophenols is fairly stable and is ca. 100 kilo-tones per year, in which the production of heavy and light chlorophenols is ca. 25–30 and 60 kilo-tones per year respectively.

Due to their poor bio-degradability (Dorn et al., 1974), the environment has little assimilative capacity towards chlorophenols. Some recent researches have demonstrated the potential to degrade recalcitrant chlorinated hydrocarbons using fungus (Marco-Urrea et al., 2009) and bacteria (Adebusoye et al., 2007). Chlorophenols' half life in aerobic waters can exceed 3 months and exceed several years in organic sediments (Keane, 2005). Chlorophenols do not just cause severe adverse effects such as toxicity and

* *Corresponding author*. Tel.: + 852 2358 8412; fax: + 852 2358 0054.
E-mail address: kemckayg@ust.hk (G. McKay).
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Nomenclature

Alphabet

C	adsorbate concentration in liquid phase (mg dm^{-3})
C_o	initial adsorbate concentration in liquid phase (mg dm^{-3})
C_s	liquid phase adsorbate concentration at adsorbent external surface (mg dm^{-3})
d_p	particle diameter (m)
D	mass transfer coefficient (cm^2 s^{-1})
D_{mol}	molecular diffusivity (cm^2 s^{-1})
D_p	average pore diameter (nm)
D_s	surface diffusivity (m^2 s^{-1})
J_d	mass transfer coefficient factor (dimensionless)
k_f	external film mass transfer coefficient (m s^{-1})
L	bed length or characteristic length (cm)
Pe	Peclet number (dimensionless)
q	solid phase pollutant concentration at time t (mg g^{-1})
Q	pollutant volumetric flowrate (dm^3 h^{-1})
r	radial position within adsorbent particle (m)
R_p	radius of adsorbent particle (m)
Re	Reynolds number (dimensionless)
R^2	R-squared value of trendline plot (dimensionless)
S_{BET}	BET surface area (m^2 g^{-1})
S_{meso}	mesopore surface area (m^2 g^{-1})
S_{micro}	micropore surface area (m^2 g^{-1})
Sc	Schmidt number (dimensionless)
Sh	Sherwood number (dimensionless)
t	service time/operating time of the column (hr)
v	interstitial adsorbate velocity (m s^{-1})
V_{total}	total pore volume (cm^3 g^{-1})
V_{meso}	mesopore volume (cm^3 g^{-1})
V_{micro}	micropore volume (cm^3 g^{-1})
Z	bed height (m)

Greek alphabet

λ_{max}	maximum absorbance wavelength (nm)
ρ	density of adsorbate solution (kg m^{-3})
ρ_p	density of adsorbent particle (kg m^{-3})
ρ_s	skeleton density (kg m^{-3})
μ	viscosity of adsorbate solution (kg m^{-1} s^{-1})
ε	bed porosity (dimensionless)

carcinogenicity (Jorens and Schepens, 1993; Huff, 2001), but also degradation of the water quality for consumptive use in terms of taste and odour problems even at concentrations below 0.1 μg/L (Verschueren, 2001). Therefore, several phenolic compounds have been listed as a group of toxic pollutants by the US Environmental Protection Agency and by the European Decision 2455/2001/EC.

According to the Agency for Toxic Substances and Disease Registry, chlorophenols can bio-accumulate in organisms in different extents, and pentachlorophenol has a higher tendency to bio-accumulate in aquatic organisms, with a bio-concentration factor (an indicator for the extent of bio-accumulation) 1000 for goldfish, 324 for mussels and 78 for oysters (ATSDR, 2001). The high bio-concentration factor implies that chlorophenols could be bio-concentrated from one species to another, and hence posing the greatest risk to human beings through food chain transport. Chronic exposure to low molecular weight chlorophenols results in liver and kidney damage, loss in weight, general fatigue and low appetite (Savant et al., 2006).

Numerous researches study the oxidation of chlorophenols with reagents, for example, potassium permanganate (Zhang et al., 2003; Bruchet and Duguet, 2004), hydrogen peroxide and ozone (Ormad et al., 1997; Pi et al., 2007), electrochemical oxidation (Gherardini et al., 2001) and hydrodechlorination (Molina et al., 2010; Sun et al., 2011). For complete mineralisation of chlorophenols into carbon dioxide, water and chloride anions or less harmful intermediates, the techniques of advanced oxidation processes, such as with Fenton's reagent (H_2O_2/Fe^{2+}) (Chamarro et al., 2001; Zimbron and Reardon, 2009), photo-Fenton's reagent (H_2O_2/Fe^{2+}/UV) (Bauer et al., 1999) and photocatalysis (Chu, 1999) have been employed to chlorophenols.

Activated carbon adsorption column operation has been studied extensively (Garcia-Mendieta et al., 2003; Sulaymon and Ahmed, 2008; Sze et al., 2008) for remediating moderately bio-degradable chlorophenols. Basmadjian (1983) proposed a reverse stratified tapered adsorber with varying cross-sectional area and different adsorbent particles arranged in a reverse layering of adsorbent size. This bed geometry provides a unique superficial velocity profile for the adsorbate solution, which influences the residence time of adsorbate and the extent of the external mass transfer film thickness around the adsorbent particles. Pota and Mathews (2000) and Mathews (2005) demonstrated that adsorption columns with particle layering/stratification perform better than columns using uniform particle size. This research is particularly designed to verify the possibility of enhancing the efficiency of an adsorption column under the effects of bed geometry and adsorbent particle stratification packing, which is advantageous in terms of reduced frequency of adsorbent regeneration/replacement and lower operating cost of the wastewater treatment plant.

2. Theoretical section

2.1. *Equilibrium adsorption isotherm*

The experimental procedure and results of the single component equilibrium adsorption isotherm study of para-chlorophenol adsorption onto F400 activated carbon were discussed in previous work (Sze and McKay, 2010). The Redlich-Peterson isotherm model was found to be the best fit model for the experimental equilibrium adsorption isotherm data obtained (Sze and McKay, 2010).