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Bioregeneration of granular activated carbon in simultaneous adsorption and biodegradation of chlorophenols

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ABSTRACT

The objectives of this study are to obtain the time courses of the amount of chlorophenol adsorbed onto granular activated carbon (GAC) in the simultaneous adsorption and biodegradation processes involving 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP), respectively, and to quantify the bioregeneration efficiency of GAC loaded with 4-CP and 2,4-DCP by direct measurement of the amount of chlorophenol adsorbed onto GAC. Under abiotic and biotic conditions, the time courses of the amount of chlorophenol adsorbed onto GAC at various GAC dosages for the initial 4-CP and 2,4-DCP concentrations below and above the biomass acclimated concentrations of 300 and 150 mg/L, respectively, were determined. The results show that the highest bioregeneration efficiency was achieved provided that the initial adsorbate concentration was lower than the acclimated concentration. When the initial adsorbate concentration was higher than the acclimated concentration, the highest bioregeneration efficiency was achieved if excess adsorbent was used.

1. Introduction

Chlorinated organics particularly chlorophenols (CPs) are known to be xenobiotic, carcinogenic and mutagenic. They are also environmentally persistent and recalcitrant in nature (Quan et al., 2004). Some of these compounds have been listed as priority pollutants by US Environmental Protection Agency (EPA). In the treatment of chlorinated organics, adsorption is the most commonly employed method due to its effectiveness and economical advantages (Dąbrowski et al., 2005; Wang et al., 2007; Hameed et al., 2008). However, since adsorption is merely a process of concentrating the pollutants onto the surface of the adsorbent, the adsorbent will no longer be functional once the active sites have been exhausted. The spent adsorbent becomes a secondary waste and will need to be either discarded or regenerated.

The use of microorganisms to renew the surface of the adsorbent for further adsorption is known as bioregeneration. Studies on the bioregeneration process in extending the lifetime of the adsorbent have been reported by many researchers (de Jonge et al., 1996; Orshansky and Narkis, 1997; Silva et al., 2004; Lee and Lim, 2005; Aktaş and Çeçen, 2006, 2007, 2009; Ng et al., 2009, 2010). The main objectives of these studies were the quantification of bioregeneration under two situations: (i) sequential adsorption and biodegradation and (ii) simultaneous adsorption and biodegradation. In general, the researchers did not face much difficulty in quantifying bioregeneration efficiency in the sequential adsorption and biodegradation processes using various techniques. This is, however, not the case in simultaneous adsorption and biodegradation. Using the respirometry technique, bioregeneration efficiency of powdered activated carbon (PAC) in the simultaneous adsorption and biodegradation of alkyl-substituted phenolic compounds was successfully quantified by Lee and Lim (2005). In another study using the same technique, Ng et al. (2009) succeeded in quantifying the bioregeneration of PAC in the simultaneous adsorption and biodegradation of phenol and *p*-nitrophenol. In both studies, the adsorption was almost instantaneous and adsorption equilibrium was attained before the commencement of biodegradation, thus mimicking the sequential adsorption and biodegradation processes. For many other systems, the condition for the prior establishment of adsorption equilibrium before biodegradation is normally not satisfied. Under this situation, the respirometry technique appears to be a poor choice as it is difficult to determine the initial substrate loading of the adsorbent. Direct determination of the substrate amount on the adsorbent after the completion of bioregeneration had been conducted by various researchers either by reloading the bioregenerated adsorbent or solvent extraction (Ha et al., 2000; Vinitnantharat et al., 2001; Aktaş and Çeçen, 2009). However, to date, there was no report of studies to track the change of the amount of substrate adsorbed onto the adsorbent during simultaneous adsorption and biodegradation processes.

In light of the above observation, the objectives of this study are: (i) to obtain the time courses of the amount of chlorophenol

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adsorbed onto granular activated carbon (GAC) in the simultaneous adsorption and biodegradation processes involving 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP), respectively, and (ii) to quantify the extent of bioregeneration of GAC by direct measurement of the amount of chlorophenol adsorbed onto GAC. For this study, the biomass used was a mixed culture acclimated to 4-CP and 2,4-DCP, respectively. Mixed cultures have been found to be more efficient for the complete mineralization of toxic organics. Studies using pure culture have revealed that toxic intermediates accumulate during the biodegradation process leading to low COD removal efficiency (Wang and Loh, 1999; Dos Santos et al., 2009; Banerjee and Ghoshal, 2010).

2. Methods

2.1. Adsorbent and chemicals

The adsorbent used in this research was the commercially available GAC (NORIT 830) which is a steam-activated wood-based carbon. The GAC was carefully sieved to the sizes of 10–20 mesh and was kept in the oven at 104 °C. Prior to the studies, the GAC was allowed to cool in the desiccator before weighing. The 4-CP and 2,4-DCP used were purchased from Merck and Sigma–Aldrich, respectively, and were of synthesis grade with >98% purity.

2.2. Culturing of the chlorophenol-adapted biomasses

Two 5-L beakers were used as the laboratory-scale sequencing batch reactors (SBRs) to culture the 4-CP and 2,4-DCP-adapted biomasses. The seed of the biomass was obtained from a local municipal sewage treatment plant. The SBRs were operated with FILL, REACT, SETTLE, DRAW and IDLE periods in the ratio of 2:10:1:1:10 for a 24-h cycle time. The reactors were operated with a 4-L working volume and the sludge age was controlled at 30 days. In each cycle, 3 L of the synthetic wastewater containing the respective chlorophenol as the sole carbon source and nutrients with the following composition (in mg/L): $(NH_4)_2SO_4$ (212), KH_2PO_4 (32), K_2HPO_4 (180), $MgSO_4$ (49), $NaHCO_3$ (354), $FeCl_3{\cdot}6H_2O$ (18.8) and $CaCl_2$ (40) was introduced into the reactor during the FILL period while 3 L of the treated effluent was drawn out during the DRAW period. Once the SBRs had attained the steady state, the acclimated biomass from the reactor was collected for the bioregeneration studies. The biomasses were adapted to 300 mg/L 4-CP and 150 mg/L 2,4-DCP, respectively.

2.3. Adsorption and desorption studies

Preliminary studies were carried out to determine the characteristics of adsorption and desorption of 4-CP and 2,4-DCP onto GAC. The initial contact time studies revealed that 72 h was required to establish the adsorption equilibrium for the chlorophenols. For the adsorption isotherm study, 0.05 g of GAC was agitated at 300 rpm at various initial concentrations of chlorophenols (100–600 mg/L) for a period of 72 h at 25 ± 1 °C in the presence of nutrients with the composition as described above. On the other hand, the desorption experiment was carried out by preloading the GAC with excess chlorophenol (400 mg/L of 4-CP and 500 mg/L of 2,4-DCP, respectively, for every 1 g/L of GAC) at various dosages (1.0–3.5 g/L for 4-CP and 1.0–2.0 g/L for 2,4-DCP) in nutrients and the loaded GAC was resuspended into a nutrient solution. The selected chlorophenol concentrations were sufficiently high to exhaust the active sites. The concentration of the chlorophenol was determined after the attainment of desorption equilibrium which took 24 h.

2.4. Bioregeneration studies

Batch bioregeneration studies were conducted to investigate the extent of bioregeneration of GAC. For the biotic experiments involving GAC dosage of 1.0 g/L, exactly 0.05 g of GAC was weighed and placed in a series of 140-mL amber glass reaction vessels. Solutions containing different concentrations of 4-CP (100–600 mg/L) or 2,4-DCP (100–300 mg/L), 100 mg/L of chlorophenol-adapted biomass and nutrients with the composition described above were prepared. Before the commencement of the experiments, the initial dissolved oxygen (DO) and pH of the solution were determined. Then, 50 mL of the solution was added into each of the reaction vessels and was shaken at 300 rpm using an orbital shaker (IKA KS Basic 260) at 25 ± 1 °C. Concurrently, in each of the experiments, three other samples, namely solution containing chlorophenol and GAC but without biomass (the abiotic experiment), solution containing chlorophenol and biomass, and solution containing chlorophenol only (the blank experiment), were also shaken under the same conditions.

A sample was taken for analysis at suitable time intervals. As the GAC particles were heavier, they could easily be separated from the supernatant by decantation. The adsorbent was then autoclaved to deactivate the microbial activities and resuspended in a solution of excess chlorophenol, namely 400 mg/L of 4-CP and 500 mg/L 2,4-DCP, respectively, for every 1.0 g/L of GAC in order to determine the amount of chlorophenol adsorbed onto GAC at different time intervals. The loss of chlorophenols from GAC due to autoclaving was estimated to be less than 5%. The amount of chlorophenol adsorbed at various times, Q_t, was then calculated using Eq. (1).

$$Q_t = Q_v - (C_{io} - C_{ie})\mathrm{V/m} \quad (1)$$

where Q_v is the amount of chlorophenol required to saturate the fresh GAC, C_{io} the initial concentration of chlorophenol in reloading, C_{ie} the equilibrium concentration after reloading, V the volume of solution and m the mass of GAC. The decanted supernatant was filtered using a GF/C filter and the concentration of residual chlorophenol was determined. For the abiotic system, the bulk solution was sampled frequently at suitable time intervals for the determination of the residual chlorophenol concentration until the concentration was almost constant. The total volume sampled was estimated to be less than 5% of the initial volume of bulk solution. The amount of chlorophenol adsorbed at time t was calculated from the difference between the initial and the residual amounts of chlorophenol at time t per unit mass of GAC.

For the initial 4-CP and 2,4-DCP concentrations of 600 and 300 mg/L, respectively, the bioregeneration experiment was repeated by varying the GAC dosages from 1.0 to 3.5 g/L for 4-CP and from 1.0 to 2.0 g/L for 2,4-DCP.

2.5. Studies on biodegradation of chlorophenols

The extent of biodegradation of chlorophenols was investigated by determining the mass of chloride released after bioregeneration. A series of 140-mL reaction vessels at different initial concentrations of chlorophenols (100–600 mg/L of 4-CP and 100–300 mg/L of 2,4-DCP at 1.0 g/L of GAC) and at varying GAC dosages (1.0–3.5 g/L and 1.0–2.0 g/L GAC for 600 mg/L of 4-CP and 300 mg/L of 2,4-DCP, respectively) were prepared and run according to the procedure as described above. Sampling was carried out at 72 h after the commencement of the biotic experiment for the determination of the amount of chloride released due to the biodegradation of chlorophenols. The experiment results were compared with the calculated results based on the stoichiometric mass of chloride released in the complete degradation of chlorophenols.