PVA entrapped activated sludge beads coated with PAC for bioremediating 4-chlorophenol-bearing wastewater

Kuan-Shiong Khoo, Houy-Yng Lam, Zhen-Yin Lau, Alyna Ong Ching Wuie,
Anissa Binti Azlan, Hoe-Guan Beh, Jun-Wei Lim*
Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia

Abstract

This study compares the effectiveness of powdered activated carbon (PAC) to adsorb 4-chlorophenol (4-CP) from wastewater via coated onto and homogenised into polyvinyl alcohol (PVA) bead surface. The bioregeneration of spent PAC for repeated uses via entrapment with 4-CP acclimated biomass of activated sludge was also unveiled. Results showed that the maximum capacity of PAC adsorbing 4-CP was 0.2 g 4-CP/g PAC. It was confirmed that the PAC coated onto the bead surfaces with biomass entrapment could be used for eight cycles with the removal efficiency ranging from 80-85%. The removal rate of 4-CP was best fitted by the pseudo-first-order reaction kinetic, permitting plausibly projection to upscale for industrial application in treating wastewater containing chlorophenol more effectively.

Keywords: Activated sludge; adsorption; bioregeneration; PAC coated beads; biomass entrapment; 4-chlorophenol

1 Introduction

Nowadays, an industrial sector which has used 22% of water on Earth per year is recorded as the second largest consumer of water after agriculture [1]. A large quantity of water that undergoes industrial processes contaminated with various pollutants. Accordingly, up to 90% of wastewater is untreated before discharged [2]. Hence, the industrial wastewater also known as effluence served as a source of water pollution. Different industrial sectors such as pulp and paper, iron and steel, petrochemicals, pharmaceutical, meat and poultry, etc. produce the various combination of pollutants such as suspended solids, dissolved inorganics, phenols, acids, heavy metals and others. Among the pollutants, chlorophenols have been listed as the first-priority pollutants and were classified in the 132 dangerous substances category due to its toxicity, genotoxicity, mutagenicity and carcinogenicity by the EU and US EPA [3].

Owing to the uneconomic costing and production of toxic intermediate by the conventional treatment technologies [4], a cost-effective, practical and highly reliable method, namely, biological treatment is preferred. Biological wastewater treatment, as a secondary treatment process relies on microorganisms or biomass to break down contaminants or toxic substances laden into the wastewater. Microorganisms that undergo cultivation in the aerated treatment system such as sequencing batch reactor (SBR) are known as activated sludge. The SBR is an activated sludge process for wastewater treatment and is operated with FILL, REACT, SETLLE, DECANT and IDLE phases. It is an effective treatment system with simple operation, single-tank configuration and high removal efficiency of pollutants [5]. During the REACT phase, the microorganisms are in contact with toxic substances. Pollutants are then broken down into less toxic metabolites and assimilated.

However, high concentrations of toxic compounds in industrial wastewaters usually inhibit the biological activity of activated sludge [6]. To prevent the treatment process from impairing, activated carbon addition during the pre-treatment step is necessary to protect other treatment units. During the REACT phase in SBR, adsorption occurs. Pollutants adhered on the surface of activated carbon and being trapped in the pores of it. However, the occurrence of activated sludge and powdered activated carbon (PAC) wash out during the DECANT period also arises. This leads to the non-recyclability of PAC and activated sludge. In this situation, researches in immobilisation of activated sludge or simply biomass via entrapment by polymeric materials had escalated recently. In enhancing the removal of pollutant or toxicant via simultaneous adsorption and biodegradation processes, PAC is a supplement to the immobilised biomass in beads. Itis known as homogenised PAC with biomass beads. Nonetheless, [7] found that this type of beads had impoverished the PAC effectiveness in reducing the toxicity. Therefore, in our study, PVA beads with PAC attached on the external layer were synthesised and recyclability of the beads was eventually confirmed.

*Corresponding author.
E-mail address : junwei.lim@utp.edu.my

2 Methodology

A. Culturing of 4-CP acclimated activated sludge

A 5-L beaker with 1.8 L working volume was inoculated with activated sludge obtained from a domestic wastewater treatment plant. Sequencing batch reactor (SBR) mode was operated for a cycle of 24 hours started with FILL, 0.5 hr; REACT, 16 hr; SETTLE, 3 hr; DRAW, 0.5 hr and IDLE, 4 hr. In each cycle, 1.4 L of feed solution containing 49 mg/L $FeCl_3.6H_2O$, 105 mg/L $CaCl_2$, 556 mg/L $(NH_4)_2SO_4$, 128 mg/L $MgSO_4$ and 929 mg/L $NaHCO_3$ were introduced into the reactor at a constant rate during FILL period and 4-chlorophenol was then spiked into it at an increasing concentration until 65 mg/L. The pH was maintained in the range between 6.5 and 7.5 throughout the REACT period. During SETTLE period, the aeration pump was switched off and an activated sludge would be left to settle down. During the DRAW period, 1.4 L of effluence which is known as exchanged volume would be decanted and the 0.4 L of residual volume would be remained for the next cycle. Throughout the IDLE period, the biomass was not agitated.

B. Synthesising Beads

i. Beads with PAC on the external surface

The method of synthesising beads followed the procedures reported by See [7] with modification. The chemical composition used was chosen from preliminary works in which intact beads could be produced with unnoticeable disintegration when beads were agitated in aqueous medium." Eight grams of PVA powder was mixed with 40 ml of distilled water in a 250-ml beaker and placed in a water bath with an initial temperature of 30-40°C. The mixture was constantly stirred by using a magnetic stirrer by increasing the temperature to 60°C and maintained until it is completely dissolved. A 60 ml of distilled water was then added to the solution. After mixing well, it was immediately filled in a 60 ml syringe and extruded on a non-stick aluminised steel tray. This was followed by subjecting them to two iterations of 4 hours freezing at -20°C and 2 hours thawing at 4°C to improve the cross-linking and pore formations of PVA gel structure. The beads were then gently dropped into a solution of sodium alginate and PAC, isolated and finally dropped into the calcium chloride solution. It was stirred for approximately 20 minutes to ensure complete calcification and adhesion of PAC on the external surface of beads. The beads were then washed for several times with distilled water to elutriate the free Ca^{2+}. Calculation for the amount of PAC coated on the surface of 100 ml cryogel beads was the final amount of PAC left subtracted by the initial amount of PAC. Figure 1 shows the diagram of beads with PAC on the external surface.

ii. Beads with homogenised PAC

From Section Bi., one gram of PAC was found attached on the external surface of 100 ml PVA beads. The same amount of PAC was added into 8 g of PVA powder and mixed 40 ml of distilled water. After the mixture was completely homogenised, 60 ml of distilled water was added. Two iterations of 4 hours freezing at -20°C and followed by 2 hours thawing at 4°C was subjected to improve the cross-linking and pore formations within PVA gel structure. The homogenised PVA and PAC gel beads were introduced into a sodium alginate solution, prepared by dissolving 2 g of sodium alginate powder in 60 ml of distilled water. This was followed by dropping them into a calcium chloride solution, prepared by dissolving 0.8 g of calcium chloride powder into 200 ml of distilled water. The beads were then washed for several times with distilled water to elutriate the free Ca^{2+} ions. Figure 2 shows the diagram of beads with homogenised PAC.

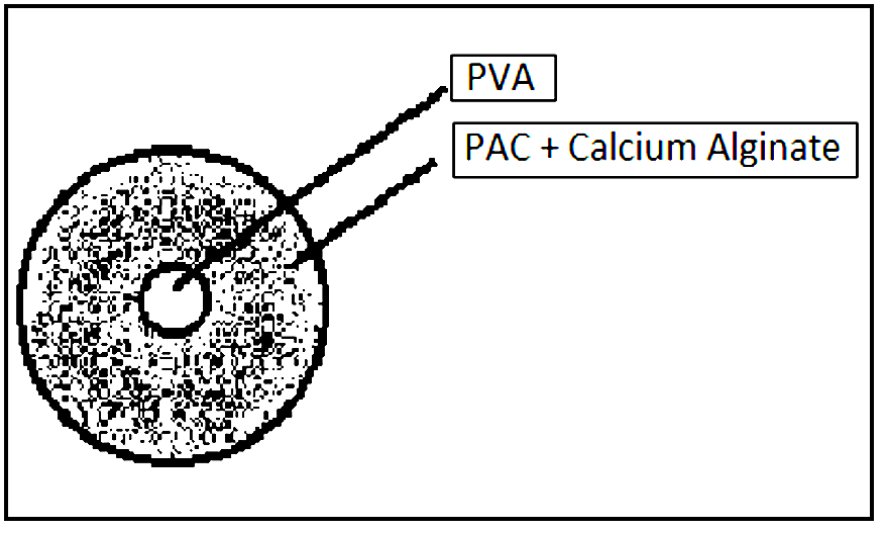

Figure 1 Beads with PAC on the external surface.

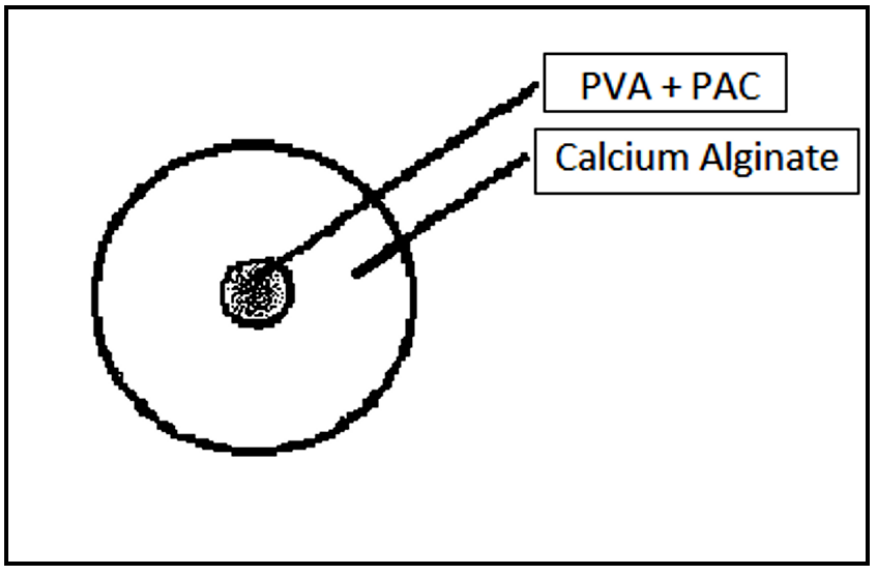

Figure 2 Beads with homogenised PAC

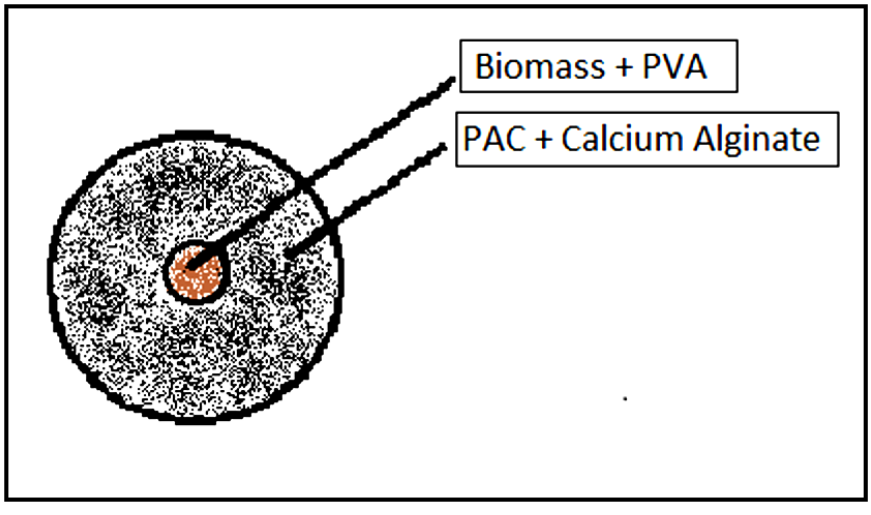

Figure 3 Beads with immobilised biomass

iii. Beads with immobilised biomass

The 4-CP acclimated biomass wasted from SBR during the steady state in Section A was washed repeatedly with distilled water to remove the soluble components. The PVA mixture was constantly stirred by using a magnetic stirrer with increasing temperature to 60ºC and maintained until it was completely dissolved. A two grams of activated sludge was extracted and then added into the cooled to room temperature solution of PVA. The distilled water was then added to the solution until it reaches100 mL. After mixing well, it was immediately filled into a 60 ml of syringe and being extruded on a non-stick aluminised steel tray. This was followed by subjecting them to two iterations of 4 hours freezing at -20°C and 2 hours thawing at 4ºC to improve the cross-linking and pores formation within PVA gel structure. The solution of sodium alginate was prepared by dissolving 2g of sodium alginate powder in 60 ml of distilled water while calcium chloride solution was prepared by dissolving 0.8 g of calcium chloride powder in 200 ml of distilled water. After the freezing and thawing process, the PVA droplets were instilled into a mixture of 1.0 g of PAC and sodium alginate solution. The PVA droplets coated with sodium alginate and PAC were then dropped into calcium chloride solution. It was stirred for approximately 20 minutes to ensure complete calcification and adhesion of PAC on the external surface of beads. The beads were then washed for several times with distilled water to elutriate the free Ca^{2+} ions. Figure 3 shows the diagram of beads with immobilised biomass.

C. Experimental Setups

i. Time course of 4-CP adsorption onto PAC

The 4-CP concentration was analysed using the 4-Aminoantipyrine Calorimetric method. In determining the maximum adsorption capacity of PAC, 0.1 g of PAC powder was added into a 1 L aerated tank of water containing 40 mg/L of 4-CP. The pH was maintained in the range of 6.5 to 7.5 throughout the experiment. Ten samples were collected over the course of 30 minutes to determine the adsorption of 4-CP by PAC and the maximum capacity of 4-CP adsorption by PAC adsorbent. The procedures were then repeated to ensure the reliability of the result obtained. Noted that each sample was filtered to remove the PAC presented in the samples prior to the analysis of remaining 4-CP concentration.

ii. Comparative study on effectiveness of PAC to adsorb 4CP from wastewater via coated onto and homogenised into PVA beads surface

A 10 mL of each type of beads were prepared by using a water displacement method. For each type of beads, it was individually introduced into a tank of 1 L of water containing 20 mg/L of 4-CP with aeration. Seven samples were taken over the course of 1 hour (0, 0.5, 3, 12, 18, 30, 60 min). The pH was maintained in the range of 6.5 to 7.5 throughout the experiment. By using the 4-aminoantipyrine calorimetric analysis method, the remaining 4-CP concentration was analysed at each particular time. The procedures were repeated to confirm the reliability of the result.

iii. Recyclability of PAC beads

A 10 mL of PAC externally-coated beads with entrapment of biomass were prepared by using the water displacement method. The beads were then introduced into a 1 L aerated water tank that contains 10 mg/L of 4-CP. The pH was maintained in the range of 6.5 to 7.5 throughout the experiment. Samples were analysed every hour to determine the removal of 4-CP by the beads. In the first cycle, the time taken for the beads to complete the removal of 4-CP was recorded. The completion of 4-CP removal was indicated by the stagnant reading of 4-CP concentration in the tank. The efficiency of the beads was then calculated. Ten cycles in total were experimented using the same batch of beads to investigate the recyclability of the beads. In ensuring reliability, the two batches of experiments were run at the same time and the average was calculated.

Results And Discussions

i. Capacity of PAC in adsorbing 4-CP

By using the analytic method as elaborated in the methodology, the capacity of PAC in adsorbing 4-CP was determined and found to be 0.2 g 4-CP/g PAC. Figure 4 shows the time course of 4-CP adsorption while determining the adsorption capacity of PAC.

ii. Comparative study on the effectiveness of PAC to adsorb 4-CP from wastewater via coated onto and homogenised into PVA beads surface

The performances of each type of beads are shown in Figure 5.

It can be concluded that the PAC on the external beads was better than the PAC in internal beads in adsorbing 4-CP, where PAC on external beads adsorbed 8 mg/L of 4-CP while PAC on internal beads adsorbed around 6 mg/L of 4-CP. Beside, PAC on external beads adsorbed 4-CP faster than PAC in internal beads, which indicated that the PAC on external beads was more efficient. To prove that, the removal rate analysis using a pseudo-zeroth-order and pseudo-first-order reaction kinetic studies are employed and herein, unveiled in the following section.

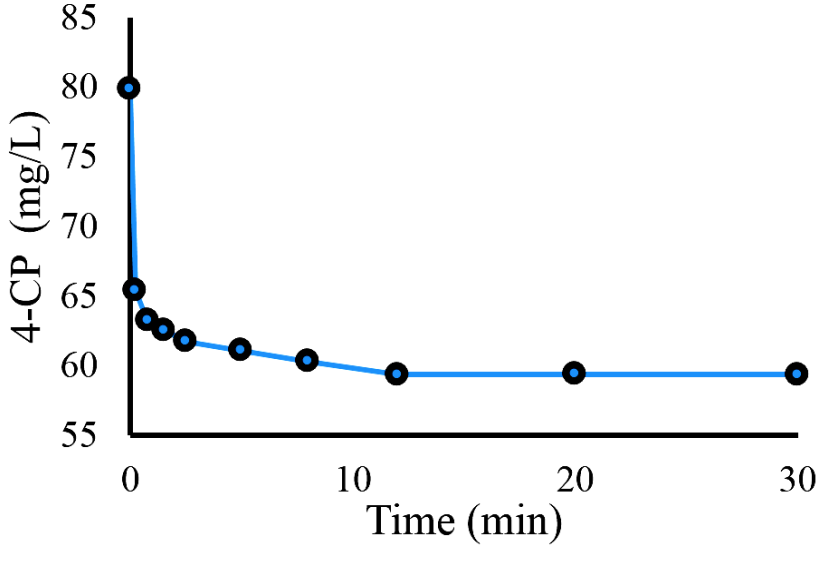

Figure 4 Time course of 4-CP adsorption by PAC

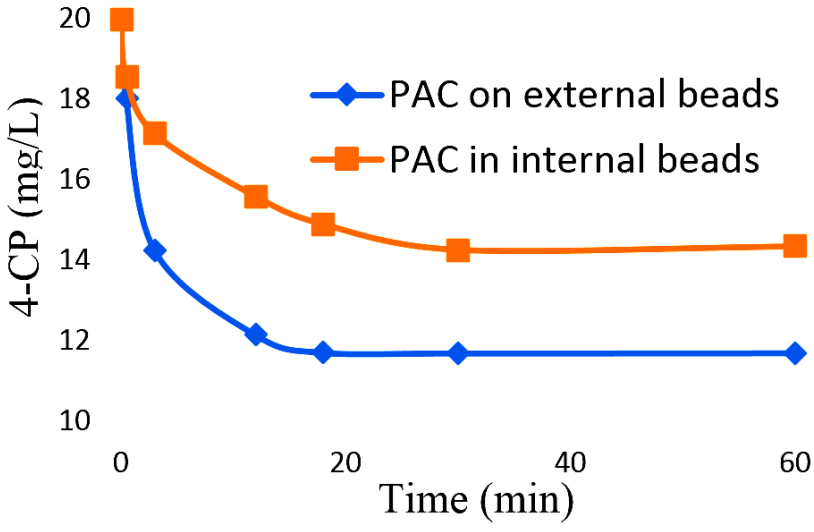

Figure 5 Comparative study on two types of PAC beads

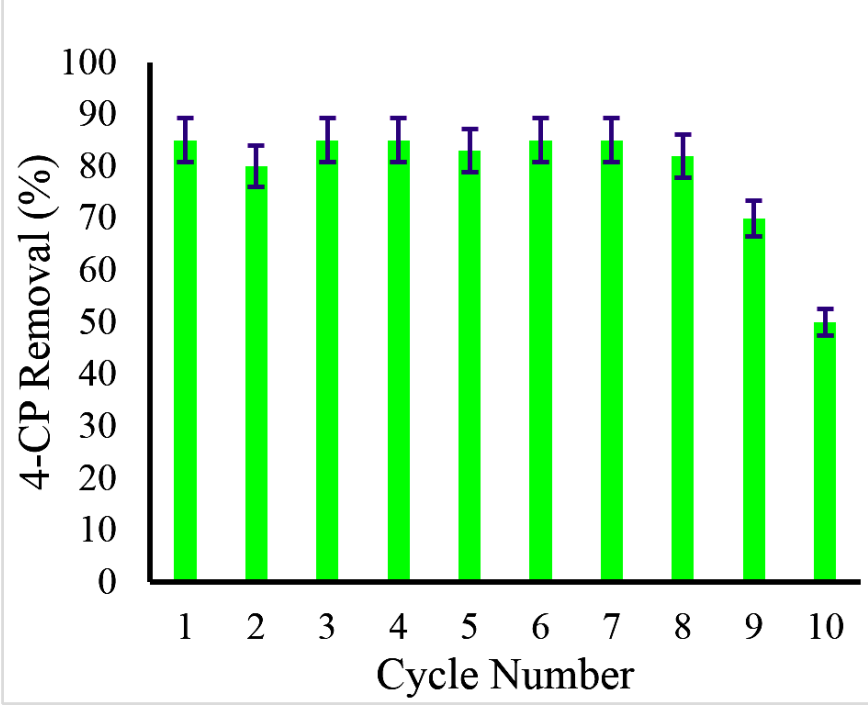

Figure 6 Recyclability of PAC coated beads

iii. Kinetics of removal of 4-CP via adsorption by PAC coated onto and homogenised into PVA beads

According to the results of kinetic studies on the removal of 4-CP using pseudo-zeroth-order and pseudo-first-order (Eqs. 1 and 2, respectively), it was found that the PAC on external beads rate constant for pseudo-zeroth-order rate constant was 1.7817 mg/L min with R^2 of 0.9646 and pseudo-first-order rate constant of 0.1066 /min with R^2 of 0.9781. On the other hand, PAC in internal beads rate constant for pseudo-zeroth-order was 0.8255 mg/L min with R^2 of 0.8669 and pseudo-first-order rate constant of 0.0449 / min with R^2 of 0.8816. The rate constants for both zeroth order and first order of pseudo kinetic studies of PAC on external beads were higher than the rate constants of PAC in internal beads. Hence, it could be concluded that the PAC on external beads was better than PAC in internal beads in terms of 4-CP removal rate. The result shows that the R^2 values of pseudo-first-order reaction kinetic were higher than that of pseudo-zeroth-order reaction kinetics. Hence, the 4-CP removal rate by the externally-coated

PAC beads, could be represented by the pseudo-first-order equations.

$$C_t = -k_0 t + C_0 \quad (1)$$

$$\ln C_t = -k_1 t + lnC_0 \quad (2)$$

where t is the time, C_t and C_0 are the concentrations of 4-CP at the arbitrary time and at t = 0, respectively, and k_0 and k_1 are the zeroth and first order rate constants, respectively.

iv. Recyclability of PVA beads

The recyclability of externally-coated PAC beads with entrapment of biomass was determined. Figure 6 shows the results obtained for 10 cycles of testing on the same batch of beads. Each cycle was experimented around 5-6 hours in determining the 4-CP removal capacity.

Based on the results, the beads could be reused for 8 cycles continuously with a 4-CP removal efficiency of around 80-85% before they have dropped to 72% in the 9th cycle and 47% in the 10th cycle. The flop of efficiency was due to the disintegration of beads.

Conclusion

In this study, it was found that the effectiveness of PAC to adsorb 4-CP from wastewater coated onto PVA beads was better than homogenised beads. From the kinetic study on the removal rate of 4-CP, it could be represented by the pseudo-first-order reaction kinetics. The numbers of cycles for PAC coated-externally beads with entrapment of biomass showed the beads could be reused for 8 cycles with the removal efficiency of 80-85%. Therefore, PAC coated beads with entrapment of activated sludge was effective and applicable for bioremediation of 4-chlorophenol-bearing wastewater generated from industries.

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