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Sonochemical extraction and biological treatment of pentachlorophenol contaminated wood

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Abstract

More than 450 million cubic feet of pentachlorophenol (PCP) treated wood products are discarded in municipal landfills or burned in power generating plants in the USA alone. The reported carcinogenicity of PCP is expected to result in more stringent controls and limit the disposal options of PCP treated wood. A treatment process has been developed in the laboratory scale to decontaminate PCP treated wood. In the first step of this process, the wood is chipped into small pieces. Then PCP is extracted using commercial grade ethanol. A three-step counter-current extraction under sonication removes more than 99% of the PCP from wood. In the next step, the remaining PCP is biodegraded utilizing a two stage bioreactor containing a white rot fungus. The PCP concentration in wood decreases to below detection limit (< 0.01 mg kg) within 5 days. The various reactor configurations namely batch, semi-batch, and fluidized-bed were studied to minimize the treatment time. No toxic biotranformation products were detected during the biodegradation process. The extracting ethanol was regenerated for reuse. © 1997 Elsevier Science B.V.

Keywords: Pentachlorophenol; Treated wood; Decontamination; Sonication; Biological treatment; *Phanerochaete chrysosporium*

1. Introduction

Nearly 130 million utility poles are currently in use throughout the continental USA with an average life ranging from 20 to 35 years [1,2]. Among all treating chemicals, PCP is used to treat about 60% of those poles to prevent microbial attack. On average

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2.5 million poles are disposed annually. PCP treated wood is also used worldwide as railroad line cross arms, crates, boxes and pallets. Nearly 15 million railroad ties are replaced annually in the US alone. In addition, the US Army uses significant amounts of treated wood and 80% of this wood has been treated with PCP [1]. Some US military bases dispose of more than 5 million pounds of treated pallets, shook and boxes per year [1]. To date treated wood has been predominately disposed in landfills or burned in power generation plants. However, due to reported carcinogenicity of PCP [3], in May 1992 the USEPA proposed a substantial revision to the hazardous waste identification system which would lower the TCLP (toxicity characteristics leaching procedure) level of PCP from $100\,mg\,kg^{-1}$ of dry wood to $0.1\,mg\,kg^{-1}$ of dry wood [4]. This level, if adopted, would make disposal of PCP treated wood in municipal waste landfills problematic. Furthermore, the number of landfill sites that accept chemically treated lumber has dropped from 15 000 in 1970 to 3000 in 1992 [1]. The cost of transport and clean air requirements exceeds the BTU value of wood, and burning in power generation plants is uneconomical [5]. Furthermore, the disposal costs of the generated ash discourage the power generation plants for such use [5]. Therefore, controlled incineration is likely to be the only alternative for disposal of these poles at a cost approaching $\$2000\,ton^{-1}$ [2]. In addition, approximately 450 million cubic feet of wood is wasted [2] in the US alone.

A number of approaches have been tested in the recent years for removing PCP/creosote deposits. US Patent 4,734,138 [6], disclosed a method for surface removal of creosote deposits from wood using a biodegradable "wood restorative" composition. US Patent 5,262,004 [7], disclosed a method for extracting chemical preservatives from wood impregnated with PCP and/or creosote using alkali hydroxide solution. Another technology includes the extraction of PCP and carrier oil by heating it to 370–410 °C under a nitrogen atmosphere [1]. This results in very brittle, carbonized wood chips limiting their reuse potential.

Recycling of treated wood is considered to be the ecologically preferable and economically sound option. Recently, Microtera Inc. at Boca Raton, Florida developed a combined physical–chemical–biological method for treatment of the PCP treated wood [2,5]. In this process, wood chips are first washed with sodium hydroxide solution to remove creosote and PCP. The creosote and PCP are separated by air flotation and the wood chips containing remaining creosote and PCP are fed to a bioreactor. The remaining PCP concentration drops to 5 ppm in 21 days [2]. Approximately 98.7% of the initial PCP can be removed in 21 days at an approximate cost of $\$160\,ton^{-1}$ [8]. However, literature reveals that this process takes 3 months and costs around $\$200\,ton^{-1}$ [5].

PCP and creosotes, due to their inert nature, are usually found precipitated in the interstices of the wood matrix and do not form chemical bonds with wood constituents. PCP has been shown to be adsorbed on biomass such as bacteria [9]. Thus, it could conceivably be adsorbed to lignin and cell walls in the wood. A number of solvents are found to have high solubility for PCP. However the main problem is to release precipitated PCP from wood matrices. Low frequency (20–100 kHz) high power (10–15 kW) ultrasound has long been used to release adsorbed particles from solid surfaces. In 1982, ultrasound was used to restore wooden artifacts from Tudor Warship, "*Mary*

Rose'' which was impregnated with iron deposits [10]. Such low frequency ultrasound is usually not adequate to facilitate any chemical transformations [10]. Although most of the PCP can be removed under sonication, for complete removal other final polishing steps are necessary.

Biological treatment of low concentration PCP has shown great promise. A number of bacterial species (both mixed and pure cultures) have shown significant potential for PCP degradation [11]. The major limitation of using bacterial cultures to decontaminate chemically treated wood is due to presence of PCP in the interstices of the wood matrix, thereby reducing the bioavailability. In addition, aerobic cultures cannot grow in these interstices due to oxygen limitations. Although, anaerobic cultures can successfully degrade PCP in wood, this has been shown to be an extremely slow process. Furthermore, toxicity of PCP on bacterial cultures is another limitation for bacterial degradation. For example, a PCP concentration of $0.04\,mg\,l^{-1}$ was found to exhibit significant toxicity on enriched activated sludge [11].

A number of investigators reported biodegradability of PCP by a wood rotting fungus *P. chrysosporium*,[12–14] both in soil as well as in the aqueous phase. Lamar and Dietrich [15] showed *P. chrysosporium* to be equally effective for mineralizing wood-bound PCP. They also showed that the loss of weight during the degradation processes was minimal (6.5% in 4 weeks of treatment). This fungus has the natural ability to attach on wood and penetrate the wood by its long filaments, thereby reaching the interstices. This fungus secretes a series of non-specific enzymes [16,17] to initiate the *in situ* degradation of wood-bound PCP. Toxic biotransformation byproducts are not produced when proper conditions are maintained [17,18]. In addition, the fungus has shown no inhibitory effects at concentrations as high as $500\,mg\,l^{-1}$ [13]. It has been shown that in the case of chlorophenols, the initial step is an extracellular enzymatic reaction, producing an intermediate that is subsequently mineralized by biomass [17,19]. The intermediate compound (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione, TCHD) produced from the initial attack by extracellular enzyme on PCP [13,19] is highly soluble in water. Therefore the problem that arises from the low solubility of PCP at acidic conditions is eliminated. In addition, wood is a natural attachment surface for this lignin degrading fungus [20]. All these properties make this fungus uniquely suitable for this purpose.

2. Materials and methods

2.1. Wood

Sections of PCP treated utility poles with an average diameter of 8 in were used for this study. The poles were in service for about 18 years. Before being put into service, the poles are treated only on the outer 2 in radius of the pole. However, while in service (15–30 years), PCP reaches the center of the poles mainly by diffusion. The concentration of PCP in the outer surface was about $12\,000–16\,000\,mg\,kg^{-1}$ of dry wood, and that at the center of the pole was around $10\,000\,mg\,kg^{-1}$. For this study, wood chips having dimensions of 0.4 inch length $\times$ 0.8 inch width $\times$ 0.08 inch thickness were chipped

from the pole with the stainless steel chisel. To minimize the variation in PCP concentration, chips were prepared from the same peripheral location of the pole for a particular experiment.

2.2. Pentachlorophenol, ethanol and methanol

Pentachlorophenol was obtained from Aldrich Chemicals having a purity of above 99.5%. Commercial grade denatured ethanol used in this study was obtained from Fisher Scientific, contained 95% ethanol, 2.5% methanol, and 2.5% isopropyl alcohol. HPLC grade methanol was obtained from Fisher Scientific.

2.3. Extraction of PCP from wood matrix

The PCP concentration in the wood was determined by stirring about 2 g of wood sample in 100 ml methanol on a thermolyne type stirrer (Fisher Scientific, Model no. 7200) continuously for 3 days at room temperature. The wood chips were separated by a glass fiber filter, washed with distilled water and the extraction was repeated for 24 h with 100 ml of fresh ethanol. The PCP extraction efficiency was found to exceed 99.9% by this method. This was confirmed by Soxhlet extraction of the wood chips in methylene chloride. The wood chips were then filtered, washed and dried at 60 °C for 48 h in a convection oven. The resultant filtrate was analyzed for PCP concentration using HPLC. The detection limit of PCP in wood was 0.01 mg kg^{-1} of dry wood. The PCP concentration is reported in milligrams of PCP per kilogram of dry wood.

2.4. Quantification of PCP, chloride ion concentration

Liquid samples were centrifuged for 10 min at 16 200 g. The PCP concentration in the samples was determined by an HPLC (Varian 9010) equipped with a diode array detector (Polychrom 9065), a solvent delivery system, and an autosampler. A reverse phase C-18, 5 μm column (Alltech Associates) was used with acetonitirle, H_2O and glacial acetic acid as the mobile phase at a ratio of 75:24.875:0.125 and a flow rate of 1 ml min^{-1}. The absorbance was monitored at a wavelength of 239 nm. The detection limit for this instrument was 0.2 mg l^{-1} and the reproducibility of the analysis was within ± 0.28 mg l^{-1}. In case where PCP concentrations were less than 2 mg l^{-1}, the samples were concentrated using solid phase extraction technique. The estimation procedure for chloride ion was described elsewhere [18].

2.5. GC / MS method for identification of PCP and other transformation intermediates

After completion of biodegradation of PCP in wood, the wood samples were tested for presence of any transformation byproducts of PCP. About 10 g of wood samples were extracted in 25 ml methylene chloride and analyzed using USEPA method 8270 [21]. A 30 m long 0.25 mm i.d. capillary column with DB-5 film (Altech), was used with GCMS (Varian model no. Saturn II).

3. Experimental procedure

3.1. Selection of solvent

Four solvents, namely acetonitrile, ethanol, methanol and 2 M NaOH solution were tested to select the most suitable solvent. Wood samples each having a weight of 2 ± 0.005 g were placed in four identical 250 ml conical flasks and 200 ml of solvent was added to each flask. The flasks were then placed on a gyratory shaker (New Brunswick Scientific, NJ) operating at 30 °C and 150 rpm. Liquid samples were analyzed after 24 h.

3.2. Optimization of solvent to wood ratio

In order to determine the optimum volume of solvent requirement, 2 ± 0.005 g of wood sample were placed in five 250 ml Erlenmeyer flasks. Then 20, 30, 45, 75 and 125 ml of ethanol was added to these flasks, respectively. All five flasks were placed on a gyratory shaker at 30 °C. Samples (< 1.0 ml) of solvent were collected from each flask at regular intervals for analysis.

3.3. Effect of sonication on PCP extraction efficiency

To determine the effect of sonication on the PCP extraction, 6.0 ± 0.005 g wood chips were placed in two identical 250 ml conical flasks and 135 ml of ethanol was added. One flask was placed in the sonicator (Fisher Scientific, Model FS 15, frequency 43 kHz, power 270 W) and the other was placed on stirrer at room temperature. Samples of the extract were collected from each of these flasks at regular intervals for analysis of PCP.

3.4. Effect of temperature on extraction efficiency of PCP

To determine the effect of temperature on the PCP extraction efficiency, accurately weighted (2 ± 0.005 g) wood and 100 ml ethanol was placed in two 250 ml Erlenmeyer flasks. One flask was maintained at room temperature (≈ 20 °C) and the other at 35 °C equipped with magnetic stirrer. Samples were periodically collected and analyzed.

3.5. Growing the fungus

Phanerochaete chrysosporium (ATCC 24725) was obtained from the American Type Culture Collection (ATCC) and maintained on yeast malt agar. The fungus was grown in growth medium [18] in a Erlenmeyer flask placed on a gyratory shaker at 30 °C. After growing for 5 days this fungal culture was used as inoculum as described later.

3.6. Batch reactor studies

The batch experiments were conducted in 250 ml Erlenmeyer flasks. Pre-weighed wood chips (about 5 g) were added to 100 ml of growth media and inoculated with 5 ml

of pre-grown fungal culture and incubated at room temperature on a gyratory shaker at 45 rpm. A few wood chips and a small amount of aqueous solution were taken out at regular intervals for analysis. The wood chips were washed, dried and weighed before extraction and analysis.

In a separate experiment, the biodegradation of PCP was tested in liquid phase to determine the first-order rate constant. For this purpose PCP was spiked ($16.7\,mg\,l^{-1}$) in 4-day-old broth and the PCP concentration was analyzed regularly.

3.7. Experiment to determine biodegradability of PCP by P. chrysoporium in fixed-film bioreactor

The biodegradability of PCP by *P. chrysosporium* was tested, in the absence of wood, using a packed-bed reactor. Previous studies showed that degradation of chlorophenols does not reach completion in batch systems due to depletion of energy sources and subsequent accumulation of enzyme inhibitors [16,22]. Those problems can be successfully eliminated in a continuous bioreactor system [16]. A schematic of the setup is shown in Fig. 1. A cylindrical glass reactor equipped with a feed pump and air sparger at the bottom, and provided with an external recirculation, was used for this experiment. The length and diameter of the reactor were 65 and 4 cm respectively. Clear polyethylene terephthalate (PET) flakes (irregular in shape and size, cross-sectional area = 2–15 mm^2; thickness ≈ 0.5 mm) were used as random packing material and maintained at room temperature by circulating water. The reactor was continuously fed

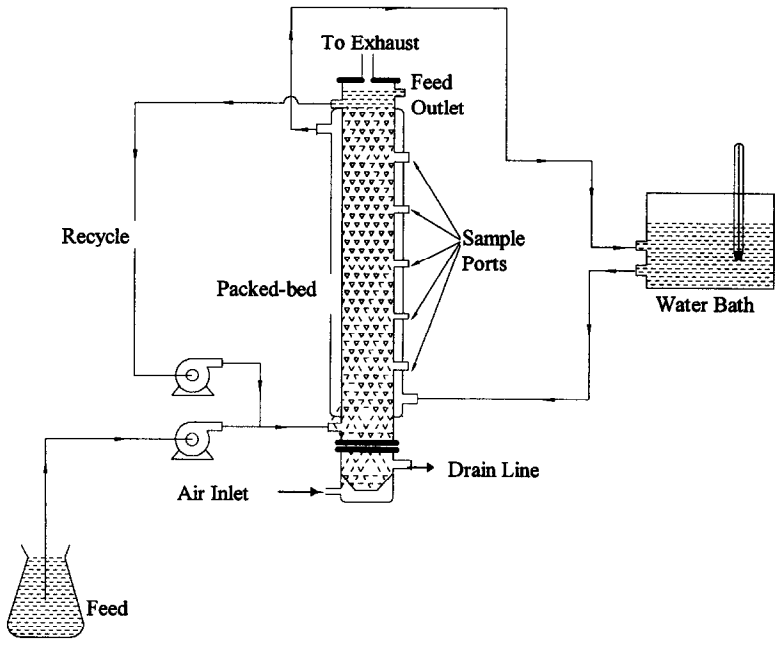

Fig. 1. Schematic of the packed-bed bioreactor system (after Pal et al. [15]).

at a rate of 1.139 ml min^{-1}. The external recirculation rate was 6 ml min^{-1}, and was always much larger than the feed rate to ensure that the liquid content of the reactor was always well mixed. To immobilize the fungus in the packed-bed reactor, a 5-day-old fungal culture broth from the shaker flask was transferred to the reactor with the simultaneous addition of PET flakes. The fungus was allowed to grow for an additional period of 10 days while continuously feeding growth medium and maintaining external recirculation. Then, the feed was switched from growth medium to induction medium containing PCP solution (time zero for the experiment). These media differed only in their glucose and $NaNO_3$ compositions as described elsewhere [18]. The induction medium was used to stimulate the secretion of extracellular enzymes by limiting the availability of nutrients to the fungus. The induction medium fed to the reactor was supplemented with a 23.4 mg l^{-1} PCP solution. The inlet glucose and nitrogen concentrations were 600 and 10 mg l^{-1} respectively. To minimize shear-stress effects, the volumetric flux was maintained at 1.0 ml $(min\ cm^2)^{-1}$ [18]. Samples from different ports along the length of the reactor were collected and analyzed for PCP, nitrogen, glucose, pH and chloride concentrations. To confirm biodegradability of PCP, the experiment was continued until steady state was achieved. The attainment of a steady-state condition was confirmed when no significant change in outlet concentrations was observed throughout a period of at least 3–4 days.

For experiments with biodegradation of PCP in wood, three samples were collected from the various locations of the reactor and the PCP concentration in the combined sample was determined and reported as the average PCP concentration and corresponding standard deviation. To check the heterogeneity of PCP in various locations of the reactor, samples were collected and processed separately.

3.8. Experiments with silo type reactor packed with wood chips

A glass column (length 72.5 cm; i.d. = 5.0 cm) with multiple ports along the length of reactor was used for these experiments. The glass column was loosely packed with wood chips. The reactor was inoculated with pre-grown fungal culture and growth medium trickled from the top and air was introduced from the bottom of the reactor. Samples of wood chips were collected from different ports of the reactor for analysis.

3.9. Combined slurry and packed-bed reactor studies

The schematic diagram of the combined slurry and packed-bed reactor is given in Fig. 2. The slurry reactor made of acrylic polymer consists of two connected sections. The bottom section is hollow conical section with the cross section continuously increasing from 4.4–9.6 cm i.d. having a length of 27 cm. The top section consists of the cylindrical form of height 24.7 cm and i.d. 9.6 cm. The bottom and top of the reactor are sealed and provided with inlet/outlet opening, one for air and another for induction media inlet at the bottom, and a vent and an induction medium outlet at the top. The outlet liquid from the slurry reactor enters at the bottom of a packed-bed reactor, as described before.

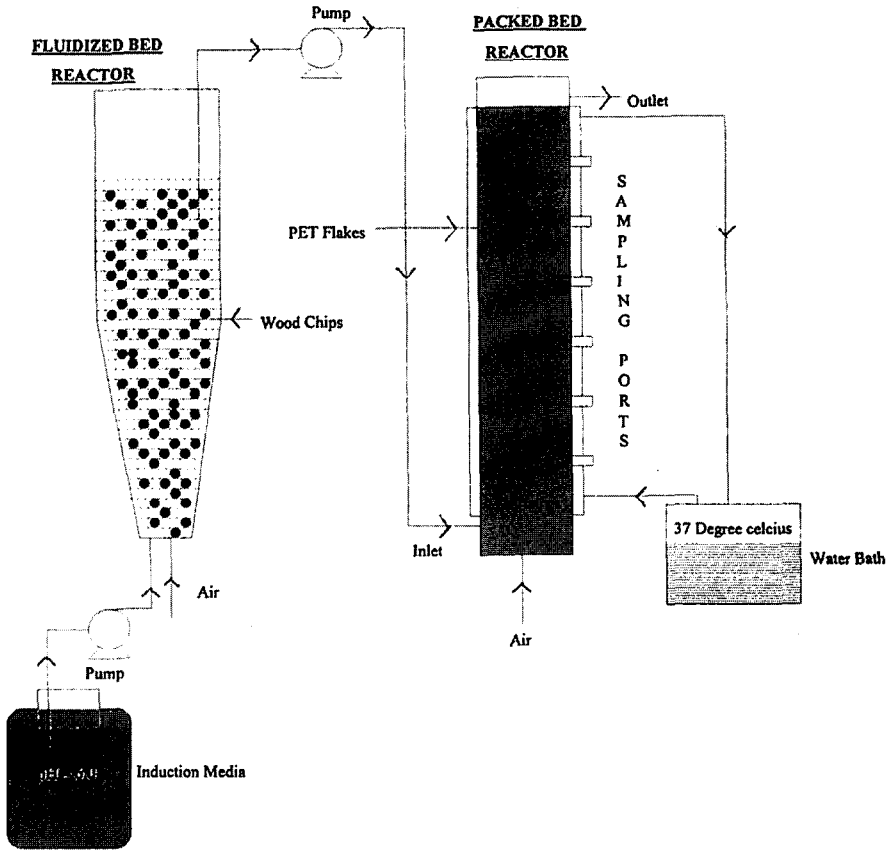

Fig. 2. Setup for the combined reactor system.

3.10. Separation of PCP from spent ethanol solution

The spent ethanol solution containing approximately 0.1% (w/v) of PCP was regenerated by distillation. Since the boiling points of PCP (310 °C) and ethanol (78.4 °C) differ substantially. A batch distillation process resulted in complete separation of ethanol from ethanol–PCP extract mixture. To avoid formation of an azeotropic mixture, anhydrous calcium sulfate was used to remove water. For batch distillation, a 2 l sample of spent ethanol was placed in a 4 l round-bottom flask, connected to a spiral condenser. The outlet was connected to another 2.5 l round-bottom receiving flask. Tap water was used as the cooling fluid. The flask content was heated to about 78 °C and the distillate was collected in the receiving flask until all the liquid was evaporated. Precautions were taken to minimize any losses during the distillation.

4. Determination of biodegradation kinetics

The mechanism of biodegradation process for the PCP embedded in wood is quite complex. As per previous studies [17], the following steps are probably involved. The degradation of PCP is initiated by an extracellular enzyme [17,18] producing a water soluble intermediate. The intermediate is further mineralized in contact with biomass [17]. In case of PCP embedded in wood, the mechanism of contact of PCP with extracellular enzyme is not known. It is probable that attached *Phanerochaete chrysosporium* on wood releases the extracellular enzyme and catalyzes the degradation process. In the next step the intermediate TCHD is transported to liquid phase and is mineralized in contact with biomass. The rate-limiting step in this process is not known. Either the rate of diffusion of TCHD from wood pellets to water or the rate of reaction can be the rate-limiting step. Due to complexity of the process, we approximate a first-order kinetics for the degradation process, to gain a quantitative understanding of the kinetics involved.

The differential mass balance equation of PCP embedded in wood chips for a batch reactor is given by:

$$-\frac{dc_s}{dt} = K_w C_s \tag{1}$$

where C_s is the concentration of PCP in wood ($mg\,kg^{-1}$), t is the time, and K_w is the first-order degradation rate constant (day^{-1}) in wood phase.

In the case of a continuous reactor (fixed-film bioreactor) the mass balance equation of PCP in liquid phase at steady state can be written as:

$$qC_{in} - qC_{out} - K_L C_{out} V_l = 0 \tag{2}$$

where C_{in} and C_{out} are inlet and outlet concentration of PCP in liquid phase ($mg\,l^{-1}$), q is the steady-state volumetric flow rate ($l\,day^{-1}$), V_l is the liquid volume, K_L is the first-order liquid phase rate constant (day^{-1}).

In the case of a slurry reactor, the system can be modeled as a semi-batch reactor where the liquid flows through in continuous mode and wood chips remain in the reactor as in batch mode.

The mass balance of PCP embedded in wood can be written as:

$$V_w \frac{dC_s}{dt} = -K_w C_s V_w - r_{sol} V_l \tag{3}$$

where V_w is the volume of wood and V_l is the reactor volume, r_{sol} is the rate of transfer of PCP from wood to liquid phase ($mg\,(day\text{-}liter\ of\ liquid)^{-1}$). K_w is the first-order degradation rate. During our study, the PCP concentration was observed to be very low ($< 0.6\,mg\,l^{-1}$) and remained constant throughout the experiment. Therefore we can replace

$$r_{sol} V_l = qC_l \tag{4}$$

where q is the steady-state liquid flow rate and C_l is the liquid phase concentration of PCP and the liquid phase degradation is neglected. Such an assumption is justified since rate of transfer of PCP from wood to growth medium or water is very minimal.

To quantify the effect of sonication, first-order kinetics was also approximated where K_s and K_{ws} are the first-order rate constants denoting with and without sonication.

5. Results and discussion

5.1. Selection of solvent

The results of extraction for four solvents are shown in Fig. 3. The criterion for selection of solvent is amount of PCP removed from wood per unit volume of solvent, higher is better. In addition, the time required for the extraction was also a significant consideration. The result of the experiment for a 24 h extraction is shown in Fig. 4. It was observed that acetonitrile, methanol and ethanol perform equally well for removal of PCP, however no significant PCP removal was observed in the case of 2 M NaOH solution. In this case, less than 1% of PCP was removed in 3 days, even though the solubility of PCP at that pH (≈ 12) is more than 10 000 mg l^{-1}. Since the performance of ethanol, acetonitrile, and methanol is comparable, due to toxicity of both acetonitrile and methanol, ethanol was selected as the solvent for extraction.

5.2. Selection of wood to solvent ratio

In the next phase the optimal wood to ethanol ratio was determined. The result of this set of experiments is shown in Fig. 5. From the results, it was concluded that the

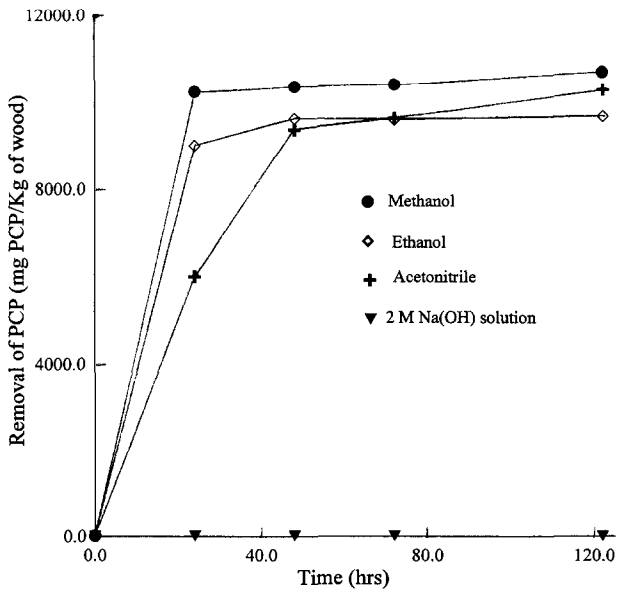

Fig. 3. Comparative PCP extractability by four solvents (the initial PCP concentration in wood was 10702 ± 183 mg kg^{-1} of dry wood).

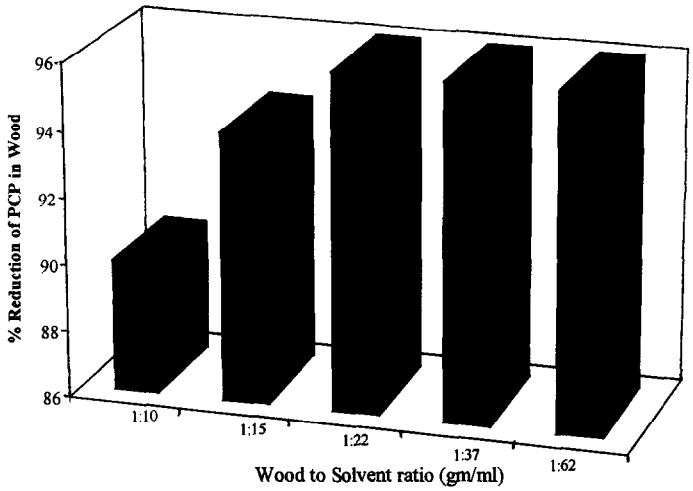

Fig. 4. Results of PCP extraction using various ratios of wood and ethanol.

optimum ratio of wood (g) to ethanol (ml) is around 1:22. In all further studies, this ratio was used.

5.3. *Effect of sonication on extraction of PCP*

The results of PCP removal under sonication are presented in Fig. 6 and compared with that in absence of sonication. The result of three samples analyses is shown with

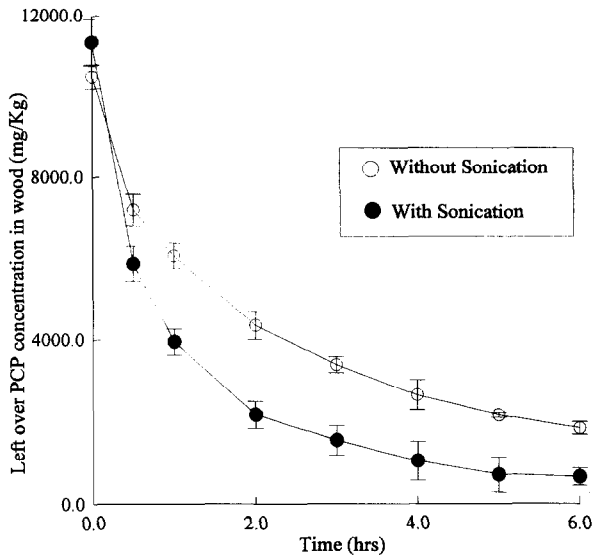

Fig. 5. Comparison of PCP removal with and without sonication.

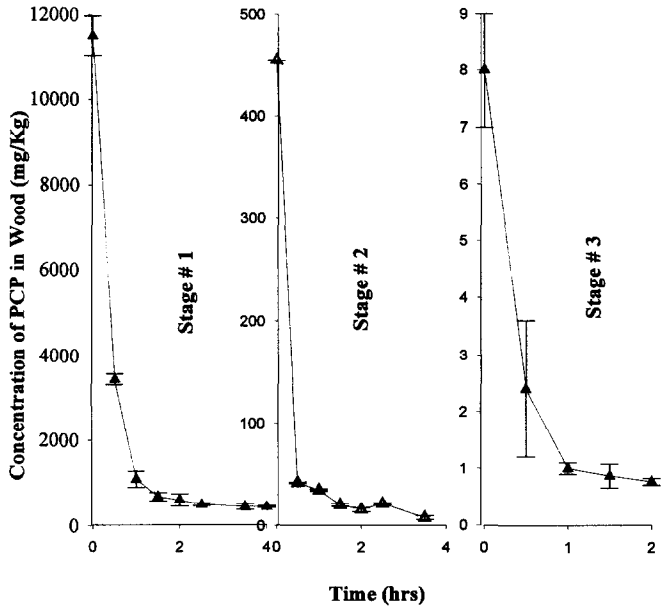

Fig. 6. Effect of successive stages of extraction on removal of PCP from wood.

corresponding standard deviation by error bars. Under the influence of sonication, a significant reduction in extraction time was achieved. Approximation of a first-order kinetics for PCP removal yields a first-order rate constant (K_s) of 13.44 day^{-1} under the influence of sonication compared to 7.81 day^{-1} (K_{ws}) in absence of sonication when all other parameters remained identical. Further more under sonication, a much higher concentration (20% greater) of PCP in ethanol was achieved as compared to that without sonication due to the added mechanical energy from sonicator that reaches the interstices of the wood. These results indicate that the rate of transport of PCP is a diffusion-limited process. Addition of sonication increases the mixing in the interstices and increases the mass transfer rate. Experiments also show that a three-stage counter-current extraction under sonication can reduce the PCP concentration in the wood to less than 1 mg kg as shown in Fig. 5. Such a reduction requires more than 3 days in a three-stage process and requires 40–50% more solvent without sonication. Furthermore it is expected that the time and efficiency can be further reduced when a higher sonication power is used.

5.4. Effect of temperature on extraction efficiency

To increase the solubility and to reduce time, extraction of PCP under higher temperature is another alternative. The results of a comparative study are shown in Fig. 7. Here the wood concentration in wood was calculated from corresponding liquid phase PCP concentration. Since the liquid phase concentration showed no spatial variability, statistical analyses were not performed. From Fig. 6, one can observe that temperature can enhance the extraction efficiency, however the extraction time does not reduce

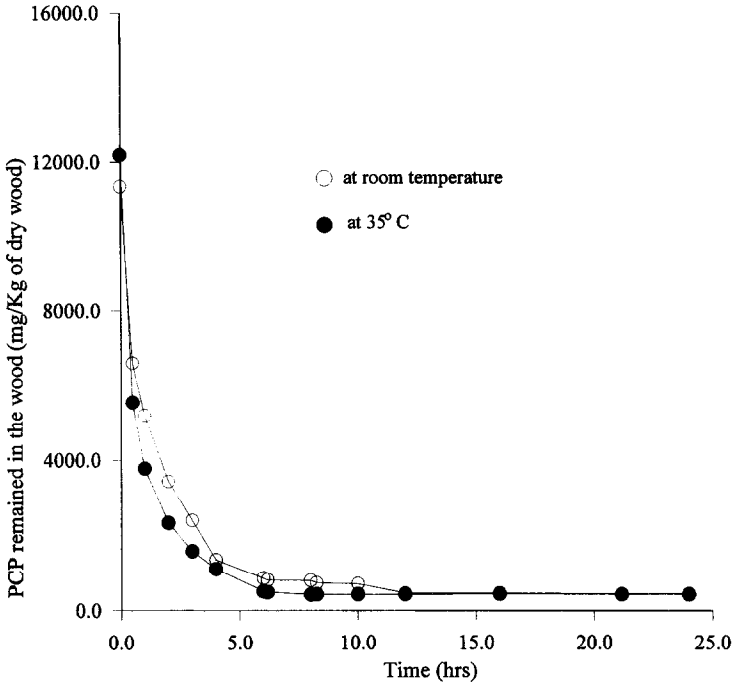

Fig. 7. Effect of temperature on removal of PCP from wood.

significantly for a 15 °C increase in temperature. In addition, laboratory experiments have shown that extraction of PCP at temperatures (close to the boiling point of ethanol), extracts other natural wood ingredients, blackish tar like substances (mostly wood creosotes). The separation of this chemical from ethanol is quite difficult, reducing reusability potential of ethanol. Therefore extraction must not be carried out at high temperature. A number of studies tried to increase the extraction efficiency by performing at boiling point [7,8].

5.5. Biodegradation of PCP in packed-bed reactor

The results of the biodegradation study using *P. chrysosporium* is shown in Fig. 8. Complete mineralization of PCP with release of stoichiometrically compatible amounts of chloride ion (1 mg PCP ≈ 0.66 mg Cl^-) was achieved. This conclusively proves the fungal ability to mineralize PCP. Previous studies have shown that the degradation rate can be enhanced by an order of magnitude utilizing fixed-film reactor in continuous operational mode compared to suspended growth system in the case of chlorophenols [18]. First-order rate approximation of the degradation kinetics yields a rate constant (K_L) of 2.915 day^{-1}.

5.6. Biodegradation in batch reactor

In these set of experiments wood samples were first subjected to a three-step batch extraction with ethanol and then were introduced to the reactor. The results of this study

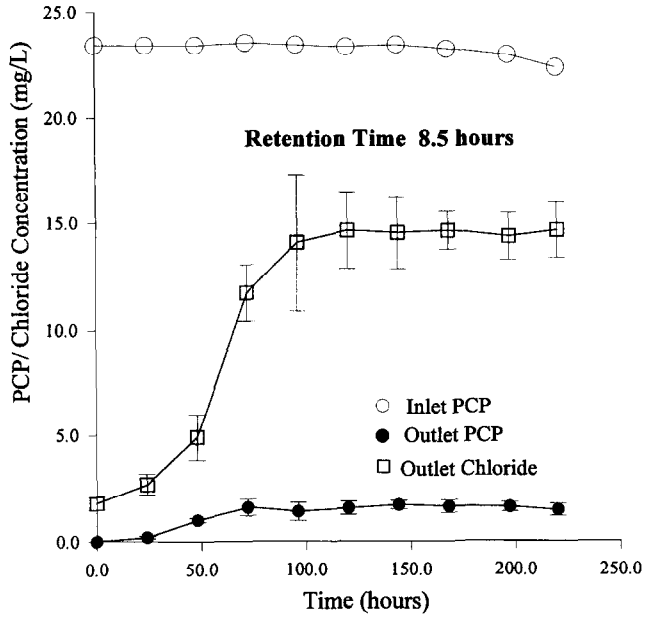

Fig. 8. Mineralization of PCP by *P. chrysosporium* in packed-bed bioreactor.

are shown in Fig. 9. It can be observed that the rate of degradation of PCP decreases. Approximation of a first-order rate constant (K_s) yields a value of $0.088\,day^{-1}$. In another experiment for biodegradation of PCP in liquid phase the first-order rate

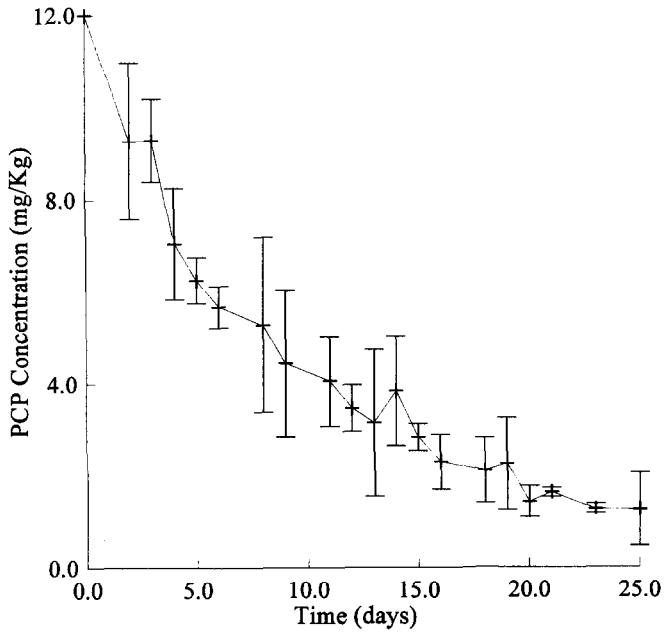

Fig. 9. Degradation of PCP in wood in batch reactor.

constant (K_1) was found to be 0.72 day^{-1}. Moreover, the degradation ceases after 10 days for all practical purposes and never reaches completion. Similar observations were made by other researchers [16,18]. Those researchers have shown that such a phenomenon is caused by depletion of nutrients and production and accumulation of inhibitors [22]. In order to sustain the degradation process, a continuous supply of nutrients are required. These objectives can be achieved in a reactor where the feed containing growth media flows through in a continuous mode [18].

5.7. Degradation of PCP treated wood in silo type packed-bed reactor

In this experiment, treated wood chips were used as the packing material and the results are shown in Fig. 10. It can be observed that the PCP concentration in the wood reaches non detectable levels after two weeks of treatment. The value of first-order degradation rate constant (K_w) in this case is 0.1374 day^{-1}, compared to 0.088 day^{-1} in the batch reactor. The concentration of PCP in the bed was non-homogeneous as depicted by large standard deviation of triplicate samples. Several regions of high PCP concentrations were observed during the experiments. This is attributed to improper distribution (channeling effects) of both the growth medium and the air. Channeling effects can be more severe in large scale silo reactors and large sections would remain untreated. Therefore this configuration was not found to be a viable option. Another problem was the liquid stream coming out of the silo reactor had a PCP concentration of

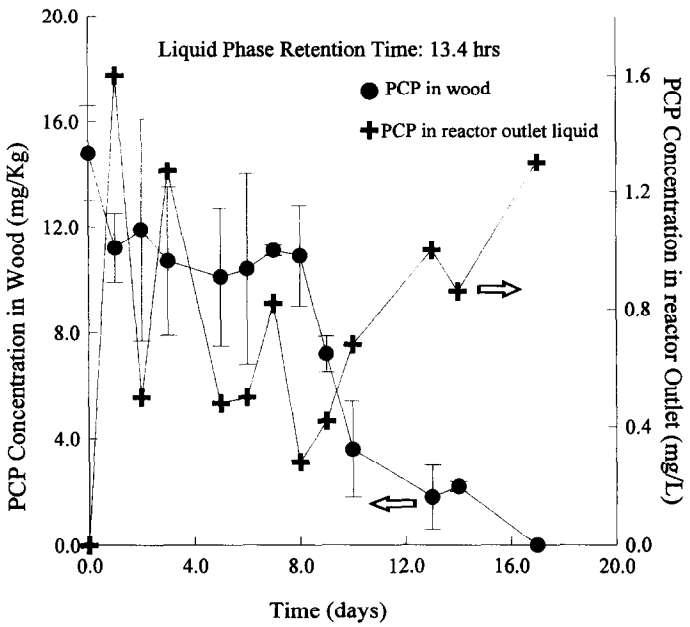

Fig. 10. Biodegradation of PCP in wood in silo reactor.

about $0.50\,mg\,l^{-1}$. Therefore the liquid needed to be treated before final discharge. These problems were alleviated in a combined slurry–packed bed system.

5.8. Biodegradation in combined–slurry reactor and packed-bed system

The results of the combined reactor tests are shown in Fig. 11. One can observe that the PCP concentration in the wood was reduced to below detectable levels within 5 days of operation. The first-order rate constant of PCP degradation (K_w) in this case was found to be $0.3182\,day^{-1}$ compared to $0.088\,day-1$ in the batch reactor. The liquid from the reactor outlet showed a PCP concentration ranging from 0.3 to $0.5\,mg\,l^{-1}$. This liquid was passed through the packed-bed reactor and no PCP was detected ($<$ $0.01\,mg\,l^{-1}$) in the liquid from the outlet of the packed-bed reactor. The release of chloride was found to be stoichiometrically equivalent.

It must be noted here that after treatment, the wood was further extracted to determine the presence of any residual PCP or other organic compounds. Analysis of effluent samples by a GC/MS showed no such compounds. *P. chrysosporium* is a proven degrader of trichlorophenols, PAHs and other aliphatic and aromatic compounds [18,23] that are normally present in treated wood. This is another advantage of utilizing this fungal culture for treating contaminated wood.

5.9. Separation of PCP and ethanol by distillation

The PCP was removed from the spent ethanol solution by a bench-top distillation unit at 78.4 °C. Approximately 95% of the ethanol was recovered from the commercial grade

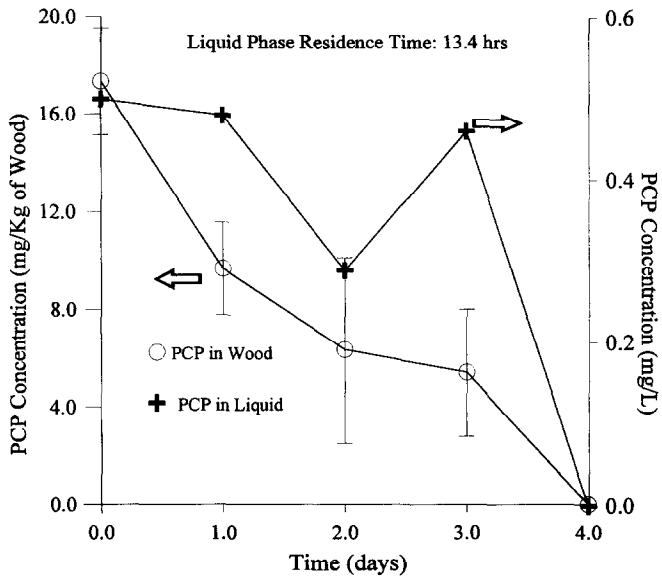

Fig. 11. Biodegradation of PCP in wood in combined reactor configuration.

Table 1
The first-order rate constant values for various reactor configurations

Reactor configuration	Nomenclature	Presence of PCP in which phase	Value of first-order biodegradation rate constant (day^{-1})
Batch	K_L	Liquid	0.272
Batch	K_W	Embedded in wood	0.088
CSTR (fixed-film)	K_L	Liquid	2.9151
Silo (semi-batch)	K_w	Embedded in wood	0.1374
Fluidized bed (semi-batch)	K_w	Embedded in wood	0.3182

ethanol and the PCP along with a very small amount of wood extractables was present as the residue.

6. Conclusion

The study shows that the combination of sonochemical extraction followed by biological treatment can successfully treat the PCP contaminated wood, which is suitable for further reuse. Approximation of first-order kinetics for degradation pattern resulted in the following values for various reactor configurations given in Table 1.

From Table 1, one can observe that the degradation rate of PCP in embedded wood is substantially slower compared to that dissolved in liquid phase. In addition, the reactor configuration significantly affects the degradation rate as evident by K_w values for various reactor configurations. Such wide variation of the first-order rate constant is due to the approximation of the enzyme mediated kinetics [18] with simple first-order kinetics. However, these approximate estimations show how the degradation rate is affected by reactor configuration. Therefore, continuous reactor configuration is a better choice for the polishing step.

These results show that, under properly controlled conditions, all products generated in this technique can be completely recycled. A number of modifications can be made to this technology on a commercial scale as described below.

During the extraction under sonication, a low power sonicator (270 W) was used and literature reveals that the extraction efficiency can be significantly increased using higher power sonicator [10]. The solvent volume requirement can be significantly reduced by performing the extraction under high power sonication with a three-step counter current process.

Separation of PCP from ethanol by pervaporation can be combined with distillation to reduce the energy cost which appears to be a feasible technique [24,25].

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