



Batch Equilibrium and Kinetic Studies of Simultaneous Adsorption and Biodegradation of Phenol by Pineapple Peels Immobilized *Pseudomonas aeruginosa* NCIB 950

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Research Article

Received 1st October 2011
Accepted 13th November 2011
Online Ready 23rd January 2012

ABSTRACT

This study was aimed to investigate the use of pineapple as a cheap, eco-friendly adsorbent and support matrix for the immobilization of microbial cell and for subsequent removal of phenol from waste water. The effects of initial phenol concentration, pH and adsorbent particle size on the simultaneous adsorption-biodegradation (SAB) of phenol were studied. The batch simultaneous adsorption and biodegradation (SAB) of phenol in simulated phenol waste water by pineapple peels immobilized *Pseudomonas aeruginosa* NCIB 950 has been studied with the use of glass bottles as bioreactors placed in a rotary mechanical shaker for 72 h. The results of the batch equilibrium adsorption-biodegradation studies showed that adsorption-biodegradation capacity decreased with increase in particle size. The equilibrium adsorption-biodegradation data were analyzed by the Langmuir, Freundlich and Redlich-Peterson models of adsorption. The results showed that the equilibrium data for phenol degradation sorbent systems were well fitted to the three adsorption models with Langmuir and Redlich-Peterson adsorption isotherms having the best fit. The adsorption-biodegradation kinetic data obtained at different initial phenol concentrations and pH showed that the adsorption-biodegradation capacity of the pineapple peels immobilized *P. aeruginosa* generally increased with increase in initial phenol concentration and pH. The kinetic data were analyzed using Lagergren pseudo-first order, pseudo second-order, Elovich and intraparticle diffusion rate equations. The rate equations fitting showed that the adsorption-biodegradation kinetic data generally fitted the four rate equations tested from which the rate constants and diffusion rate constants were estimated. However, the Lagergren pseudo first-order rate equation gave the best fit and, thus the process followed first-order rate kinetics. Therefore, pineapple peels being an

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agricultural waste product have the potential to be used as low-cost adsorbent and support matrix for microbial culture immobilization for the removal of organic pollutant from waste water.

Keywords: Adsorbent; adsorption-biodegradation; pineapple peels; phenol; P. aeruginosa; adsorption isotherms; kinetics.

1. INTRODUCTION

The ever increasing demand for water has caused considerable attention to be focused towards recovery and re-use of waste waters (Annadurai et al., 2000). More than two thousand chemical contaminants have been found in waste waters and over 600 are of organic origin (Annadurai et al., 2000). Phenols are among the most common water pollutants (Smith, 1988). Phenol and their derivatives are present in the effluent of a number of industrial processes such as oil refineries, petrochemical plants, coke oven plants, steel plants, pharmaceuticals and so on. The concentration of phenols in waste waters varies from 10 to 3000 mg/l. They impact taste and odour to water and are highly toxic to aquatic life, animal and human beings (Mahadewswamy et al., 1997, Annadurai et al., 2007).

Consequently, many treatment processes have been applied for the removal of phenols from waste waters. Some of these processes include: adsorption (Achuk et al., 2008; Mohd Din et al., 2009; Zhao et al., 2010), photo-fenton degradation (Segura et al., 2009; Parida and Pradhan, 2010; Babuponnusami and Muthukumar, 2011), photocatalytic degradation (Laoufiy et al., 2008; Devipriya and Yesodharan, 2010), and biodegradation (Agarry and Solomon, 2008; Agarry et al., 2009). Combined methods like biochemical, electrochemical, physicochemical or simultaneous adsorption and biodegradation is nowadays gaining importance. Simultaneous adsorption and biodegradation increases the life of adsorbent, as biofilm on adsorbent degrade the adsorbate (Dabhade et al., 2009).

Biodegradation is performed in the presence of microorganisms either in free or immobilized phase. There are certain species of *Pseudomonas* that can degrade phenol under very controlled conditions of pH, temperature and in the presence of some specific nutrients (Bandyopadhyay et al., 1998; Agarry et al., 2010). The immobilization of living microbial cells on a suitable adsorbent improves the removal efficiency (Mordocco et al., 1999). This improvement is due to the bio-layer formation on the adsorbent bed where adsorption and biodegradation occurs simultaneously resulting to simultaneous adsorption-biodegradation (SAB) (Thompson et al., 2001; McKay et al., 1985; McKay and Bino, 1987). Unlike adsorption, there is a continuous diffusion of adsorbate unto the solid surface and back diffusion of solute into the solution phase. The solute remaining in solution exists in dynamic equilibrium with that in the surface of bio-film (Andrews and Tien, 1981). In many natural ecosystems a combination of biological and adsorption processes is a common phenomenon. Organic pollutants discharges from industries are removed from the environment due to simultaneous adsorption and biodegradation (Orshansky and Narkis, 1997).

The recent literature on methods of phenol and its derivatives removal from waste water focuses on simultaneous adsorption and microbial degradation process (Zhong-Cheng et al., 1994; Sagar et al., 2004; Mondal and Balomajumder, 2007; Annadurai et al., 2007). This adsorption-biodegradation process using suitable adsorbent has shown high efficiency for phenol removal. The adsorption-biodegradation process involves immobilization of microbial culture on solid porous support matrix (Baoshan et al., 1994). Different adsorbents used as solid support matrix for the immobilization of microorganisms are alginate beads (Klein and Schara, 1981), polyacrylamide hydrazide gel (Bettman and Rehm, 1984; Klein et al., 1979), stintered glass (Morsen and Rehm, 1980) and activated carbon (Ehrhardt and Rehm, 1985; Morsen and Rehm, 1990; Pazarliogu and Telefoncu, 2005) have been reported in literature. Adsorbents used as solid support matrix for immobilization should be stable both physically and chemically and have a high mechanical strength or resistance (Annadurai et al., 2000). Activated carbon is most widely used as adsorbent and solid support matrix for microbial cell in the removal of heavy metals, phenols and other hazardous chemicals (Hameed, 2009) which may be found in waste waters, but its high cost and difficulty in regeneration limits its commercial application in large-scale waste water treatment (Popuri et al., 2007).

In recent years, extensive research has been undertaken to develop alternative and economic adsorbents from microbial biomass (Texier et al., 1999) and agricultural by-products which is a ubiquitous green waste in the environment and may cause some serious environmental pollution when filling at a fixed site. Some of the agricultural waste products that has been developed as adsorbents include, orange and banana peels (Annadurai et al., 2002), spent tea leaves (Hameed, 2009), tamarind fruit shell (Popuri et al., 2007), soya bean hull (Marshall et al., 2000), cotton seed hull and corn cobs (Reddad et al., 2002), rubber fruit pericarp (Agarry and Owabor, 2005). More and more interests are focused on developing these agricultural wastes as adsorbent for wastewater treatment due to their relative high sorption affinity, ubiquitous presence in the environment, and the ease of being modified to materials with higher efficiency (Li et al., 2010; Chen et al., 2011). Chung et al., (2007) found brown seaweed (*Sargassum hemiphyllum*) powder showing high phenanthrene removal efficiency at different conditions and it was viewed as a potential candidate for tackling polar organic pollutants pollutions. High sorption affinity of tea leaf powder with phenanthrene was reported (Lin et al., 2007). The characteristics of agricultural plant materials, such as polar and aromatic components, impose a significant influence on their sorptive behavior (Chen and Schnoor, 2009). Lignin is assumed to be the main storage medium of organic pollutants (Barbour et al., 2005), and sorbents with higher lignin contents show higher affinity with polar organic pollutants (Mackay and Gschwend, 2000; Crisafulli et al., 2008).

Reports from literature have shown that the composition of agricultural by-products has a strong influence on the final porous and chemical features of the solid products obtained from pyrolysis and activation (Savova et al., 2001; Cabal et al., 2009). It was observed that high contents of cellulose yield predominantly microporous materials, whereas; high content of lignin favour the development of a macroporous structure. It has also been reported from earlier works that these adsorbents obtained from agricultural by-products need further modifications to increase the active binding sites and to make them readily available for sorption. It is stated that these modifications involves pretreatment with chemicals like HCl, H₂SO₄, ZnCl₂, H₃PO₄, alkaline hydroxides and physical pretreatment using steam or carbon dioxide to remove surface impurities on the adsorbents and expose the available binding sites for pollutant adsorption (Huang and Huang, 1996; Cabuk et al., 2005; Popuri et al., 2007). Literature shows the use of activated carbon made from various low cost materials like straw, bagasse, rubber seed coat, coconut husk, oil palm shell, saw dust etc for phenol adsorption (Rengaraj et al., 2002; Vinod and Anirudhan, 2002; Hamad et al., 2011).

However, the use of raw agricultural waste adsorbent for the immobilization of cells has rarely been reported for the biodegradation of phenol.

The objective of this study is to investigate the potential of pineapple peels, an abundantly available agricultural by-product as a non-conventional adsorbent used as support matrix for *Pseudomonas aeruginosa* NCIB 950 immobilization to remove phenol from simulated phenol waste water. The effects of initial phenol concentration, pH and adsorbent particle size on the simultaneous adsorption-biodegradation (SAB) were studied. According to Mondal and Balomajumder (2009), adsorption predominates over biodegradation in SAB until adsorption equilibrium has been reached after which biodegradation predominates. Thus, the adsorption-biodegradation equilibrium data were fitted to adsorption isotherms of Langmuir, Freundlich and Redlich-Peterson models and the maximum adsorption capacity estimated. The adsorption-biodegradation kinetic data were also checked for Lagergren pseudo first-order, pseudo second-order, Elovich and intra particle diffusion kinetic model equations from which the rate constants were estimated and evaluated.

2. MATERIALS AND METHODS

2.1 Chemicals and Adsorbent

Phenol (99% pure, chemical grade) a product of Merck (Darmstadt Germany) was purchased from a chemical store, Lagos, Nigeria. All chemicals used as mineral salt medium are of analytical or biochemical grade. Pineapple peels, a waste product of pineapple pulp to be used as adsorbent and solid support matrix for microbial cell immobilization were obtained from pineapple fruits bought from a local market at Ogbomoso, Nigeria.

2.2 Synthetic Waste Water and Preparation of Inoculum

The microorganism, *Pseudomonas aeruginosa* NCIB 950 which degrades phenol was obtained from the Department of Microbiology, Obafemi Awolowo University, Ile-Ife, Nigeria. The microorganism was maintained in a standard nutrient agar medium. The synthetic waste water used in this work was composed of: K_2HPO_4 1.0 g, KH_2PO_4 0.5 g, $(NH_4)_2SO_4$ 0.5 g, NaCl 0.5 g, $CaCl_2$ 0.02 g, $MnSO_4$ 0.02 g, $CuSO_4 \cdot 5H_2O$ 0.02 g, H_3BO_3 0.01 g, $MgSO_4 \cdot 7H_2O$ 0.5 g, $FeSO_4$ 0.02 g, Molybdenum powder 0.02 g, deionized water 1000 ml.

A primary culture was prepared by transferring two loops full of microorganisms from an agar slant culture into 100 ml of feed medium containing 20 ml of mineral salt medium and 80 ml of 50 mg phenol solution in a 250 ml Erlenmeyer conical flask. This was then incubated in a New Brunswick gyratory shaker (G25-R model, New Jersey, U.S.A) for 48 h at a temperature of 30 °C and agitated with a speed of 120 rpm. Thereafter, 10 ml of the primary culture was transferred into another 100 ml of feed medium in a 250 ml Erlenmeyer conical flask and the incubation process was repeated. This was the secondary culture that was used as the inoculum for the degradation studies as this ensures that the organisms had fully adapted to growth on the phenol as sole source of carbon and energy.

2.3 Preparation and Pretreatment of Adsorbent

The pineapple peels were sundried and then reduced to small-sized particles by grinding using a serrated disk grinder. The powdered particles were sieved to obtain different desired average particle sizes (0.152 – 0.422 mm). They are washed thoroughly with sterilized de-

ionized water and dried in the oven for 2 – 3 hrs at 60°C. The physical and chemical composition of fresh and dried pineapple peels as obtained from literature (Rani and Nand, 2004) are given in Table 1. Analysis of the chemical composition showed that pineapple peels are mainly composed of cellulose, hemicelluloses, lignin and other carbohydrates. Thus, pineapple peels exhibit a combination of large quantities of cellulose and lignin which makes the material an excellent candidate for adsorbents and as well as preparation of carbons probably with well-developed micro and macro porosity.

The pretreatment of powdered pineapple peels (PPP) was carried out to increase the phenol uptake efficiency. 10 g of the pineapple peels were treated with 100 ml of 1M HCl for 24 hrs and then kept on water bath (70°C) for 30 mins. It was later cooled and neutralized with 50 ml of 1M NaOH. The filtrates were separated and dried in the oven at 60°C for 4 – 5 hrs. The pretreated powdered pineapple peels were used as adsorbent for the study.

Table 1. Physical and chemical composition of pineapple peels

Parameters	Fresh Peels	Dry Peels (% dry weight basis)
Cellulose	11.2	12
Hemi cellulose	7.0	6.5
Lignin	11.52	11.0
Pectin	6.70	7.10
Protein	3.13	3.30
Ash	3.88	4.18
Moisture	71.1	27.43
pH	4.7	4.7

2.4 Batch Adsorption Equilibrium Studies

Batch adsorption studies were carried out by adding a known volume (100 ml) of prepared inoculums of *P. aeruginosa* into a number of glass bottles containing a known amount of PPP adsorbent (2 g). Definite volume (150 ml) of synthetic waste water with different initial phenol concentration (100 – 500 mg/l) was added to each flask and the pH of the waste water was maintained at 7. The flasks were placed in a rotary mechanical shaker for 72 hrs at a speed of 180 rpm and temperature of 30°C so as to reach equilibrium. At time $t = 0$ and equilibrium, the phenol concentrations were determined using UV-spectrophotometer. The amount of adsorption at equilibrium, q_e (mg/g) was calculated according to equation (1) (Crisafully et al., 2008):

$$q_e = \frac{(C_o - C_e)V}{W} \quad \text{-----} \quad (1)$$

Where C_o and C_e (mg/l) are the initial and final (equilibrium) concentrations of phenol in waste water. V (ml) is the volume of the waste water and W (g) is the mass of dry adsorbent (PPP) used.

2.5 Batch Kinetic Studies

The procedures of kinetic studies were basically identical to those of batch equilibrium studies. The kinetic experiments were carried out at different pH (5, 7 and 9) of the waste waters. The pH was adjusted with 0.1M H₂SO₄ and 0.1M NaOH and measured by making use of digital pH meter. In every 6 hrs intervals, samples were taken to determine the amount of phenol adsorbed and degraded.

2.6 Determination of Phenol Concentration

The unadsorbed and undegraded phenol was determined quantitatively by the spectrophotometric method using 4-aminoantipyrine as the color indicator and absorbance wavelength of 510 nm (Oboirien et al., 2005; Agarry et al., 2009). The amount of phenol adsorbed and degraded at time t , q_t was calculated according to equation (2) (Xun et al., 2007):

$$q_t = \frac{(C_o - C_t)V}{W} \text{ -----} \quad (2)$$

Where C_t is the concentration of phenol in waste water at time t .

3. RESULTS AND DISCUSSION

3.1 Effect of Particle Size

Fig.1 shows the effect of particle size on the simultaneous adsorption-biodegradation of phenol by pineapple immobilized *P. aeruginosa*. It is seen that the removal of phenol increases as the particle size diameter decreases. Similar observations have been reported for simultaneous adsorption-biodegradation of phenol (Annadurai et al., 2000; Mondal and Balomajumder, 2007). Decrease in particle size increases the percentage removal due to increase in surface area as well as micro pore volume (Annadurai et al., 2000; Kumar et al., 2007).

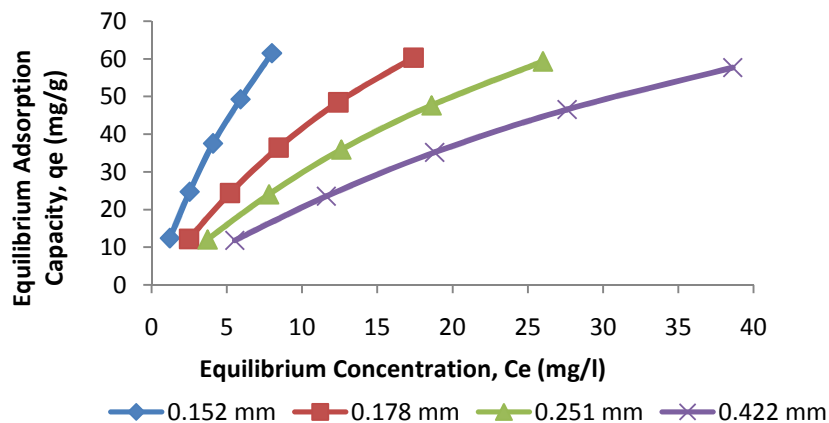


Fig. 1 Effect of particle size on the simultaneous adsorption-biodegradation of phenol by pineapple peels immobilized *P. aeruginosa*

Smaller particle size means more interior surface and micro pore volume and hence more will be the area of active sites for adsorption. Also for larger particles the diffusion resistance to mass transfer is higher and most of the internal surfaces of the particle may not be utilized for adsorption and consequently the amount of phenol adsorbed is small (Lakshmi et al., 1994; Annadurai et al., 2000; Dabhade et al., 2009). Small particles are better for phenol removal from liquid waste effluents. However, one cannot use small particle sizes in a continuous packed bed adsorber because of higher pressure drops that will be encountered (Annadurai et al., 2000).

3.2 Effect of Initial Concentration and Contact Time

The effect of initial phenol concentration and contact time on the adsorption-biodegradation of phenol is shown in Fig. 2. It could be seen that the amount of phenol adsorbed per unit mass of adsorbent increased with the increase in initial concentration and contact time until equilibrium was reached at about 48 h. However, the percent phenol removal decreased with the increase in initial concentration. A similar observation has been reported for the adsorption of phenol by activated carbon (Mondal and Balomajumder, 2007). Fig. 2 also shows rapid adsorption-biodegradation of phenol in the first 18 h for all initial concentrations, and thereafter the adsorption-biodegradation rates decreased gradually till it reached equilibrium. The higher rate of adsorption-biodegradation at the beginning was due to large available surface area of the biosorbent and after the capacity of the biosorbent gets exhausted (i.e. at equilibrium), the rate of uptake is controlled by the rate at which the sorbate is transported from the exterior to the interior sites of the biosorbent particles (Verma et al., 2006; Popuri et al., 2007).

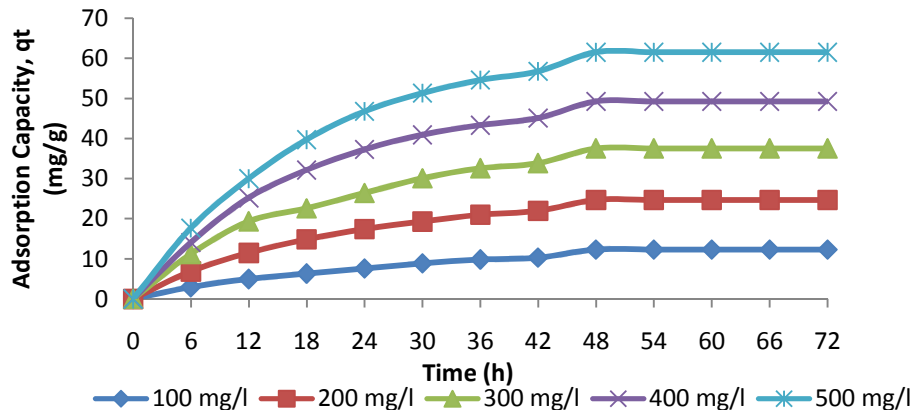


Fig. 2. Effect of initial phenol concentration and contact time on the simultaneous adsorption-biodegradation of phenol by pineapple peels immobilized *P. aeruginosa*

3.3 Effect of pH

The pH of the solution is one of the most important factors which affect phenol adsorption-biodegradation as it controls the electrostatic interactions between the biosorbent and the sorbate. The effect of solution pH on phenol adsorption-biodegradation was studied using 2 g of PPP, 100 mg/l phenol and at room temperature (30°C). Since, at very low pH bacteria can't sustain, in the present study the pH was varied between 5 and 9. According to Mondal

and Balomajumder (2009) biodegradation predominates over adsorption in SAB after the adsorption equilibrium has been reached, hence, the pH responsible for maximum growth of microbes may be the optimum value of the whole process. The results are shown in Fig. 3. It can be seen that the adsorption capacity generally increased with increase in pH. The maximum adsorption-biodegradation capacity occurred at pH 7 and above this value, it decreased. This observation agrees with the fact that at neutral pH or close to it, the specified microbes achieve maximum efficiency. A similar observation has been reported (Annadurai et al., 2000; Mondal and Balomajumder, 2007; Annadurai et al., 2009). The hydrogen ion concentration (pH) of primary sorbate and the surface properties of the biosorbent lead to alterations in the kinetic behaviour of the sorption process. From Fig. 3, it is clear that the removal rate of phenol varies with pH. The lowest phenol adsorption-biodegradation was observed at pH 5. The lower adsorption-biodegradation of phenol at acidic pH was probably due to the presence of excess H^+ ions competing with the cations group on the phenol for adsorption sites. The adsorption of cells on the surface of PPP is through extracellular polymers which are monopolysaccharides in nature. The extracellular polymers exhibit zwitter ionic characters that are highly influenced by the pH of the medium (Chitra et al., 1996).

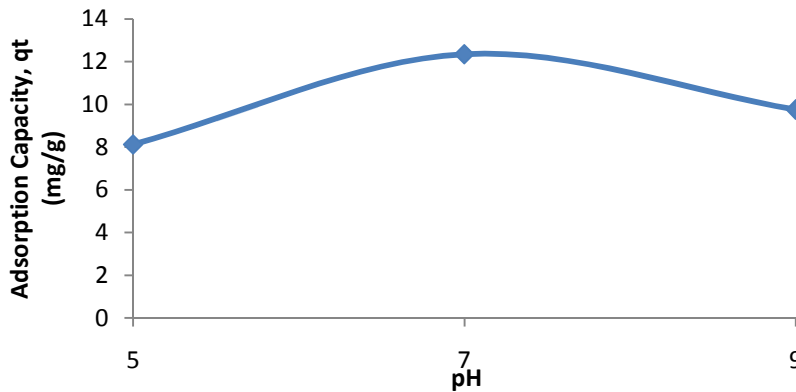


Fig. 3. Effect of pH on the simultaneous adsorption-biodegradation of phenol by pineapple peels immobilized *P. aeruginosa*

3.4 Adsorption Isotherms Studies

The equilibrium adsorption isotherm is of fundamental importance in the design of adsorption system (Annadurai et al., 2000). Adsorption and biodegradation equilibrium data can conveniently be characterized by adsorption isotherms (Annadurai et al., 2007; Mondal and Balomajumder, 2007) which are helpful in determining the adsorption capacity of an adsorbent material such as immobilized peels matrix. In order to analyze an adsorption isotherm, it is fundamental to develop an equation which accurately represents the results and which may be used for design purposes. Classical adsorption models are used to describe the equilibrium established between adsorbed component on the adsorbent and unadsorbed component in solution (represented by adsorption isotherms). Langmuir, Freundlich and Redlich-Peterson adsorption models were used to analyze the equilibrium data for adsorption and biodegradation of phenol by pineapple peel-immobilized *P. aeruginosa*.

The Langmuir model is as given in equation (3):

$$q_e = \frac{KaC_e}{1 + aC_e} \text{-----} \quad (3)$$

Where K and a are isotherm constants. Langmuir constant (K) is a measure of the amount of phenol adsorbed per unit weight of adsorbent, when saturation is attained. Langmuir constant (a) is related to energy of adsorption (i.e. affinity of the binding sites). Langmuir equation is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the sorbent surface (Popuri et al., 2006). The basic assumption of Langmuir model is that sorption takes place at specific sites within the adsorbent. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place. The essential characteristics of Langmuir isotherms can be described by a separation factor (Hall et al., 1966; Annadurai et al., 1997; Annadurai et al., 2007) which is defined in equation (4) as:

$$R_L = \frac{1}{(1 + aC_e)} \text{-----} \quad (4)$$

The separation factor (R_L) indicates the isotherm shape as follows: $R_L < 1$ unfavourable, $R_L > 1$ unfavourable, $R_L = 1$ linear, $0 < R_L < 1$ favourable and $R_L = 0$ irreversible.

The data obtained from the batch equilibrium adsorption-biodegradation experiment (plot of q_e vs C_e) (Fig. 4) were fitted to equation (3) (Langmuir isotherm) using the non-linear fitting routine of MATLAB 7.0 software package. The Langmuir constants (K and a) values estimated from the plot are presented in Table 2. The results in Table 2 showed that the adsorption-biodegradation capacity due to monolayer (K) decreased with increase in particle size. This could be due to substantial decrease in surface area and pore volume. A similar observation has been reported (Annadurai et al., 2000; Agarry and Owabor, 2005; Annadurai et al., 2007). The values of K in this work ranges from 153.5 to 193.3 mg/g and the corresponding values of ' a ' from 0.0157 to 0.0583. The value of K in other studies were 155.38 mg/g (Juang et al., 1996), 30.78 mg/g (Mondal and Balmojumder, 2007), 146.16 mg/g (Vinod and Anirudhan, 2002), 165.80 mg/g (Kumar et al., 2007), 133 mg/g (Dabhade et al., 2009). The corresponding value of a was 0.0425, 0.03, 0.0182, 0.04 and 0.00539 respectively. Therefore the constants obtained in this work are comparable with those in published literature. The difference could be due to different range of concentration, different type of material used and their properties like functional groups present on the surface, surface area, pore structure, pH and temperature of the solution (Kumar et al., 2007).

For this experiment, the values of R_L are less than 1, indicating a favourable adsorption as given in Table 3. It is also clear from the shape of the adsorption-biodegradation isotherm that it belongs to the L_2 category of isotherm, which indicates the normal or Langmuir type of adsorption (Stephen et al., 1989; Annadurai et al., 1997). This type of isotherms is often encountered when the adsorbate has a strong intermolecular attraction for the surface of the adsorbent. The L_2 shape of isotherm observed in the present case clearly suggests that phenol molecules must be strongly attached to pineapple peels (PPP).

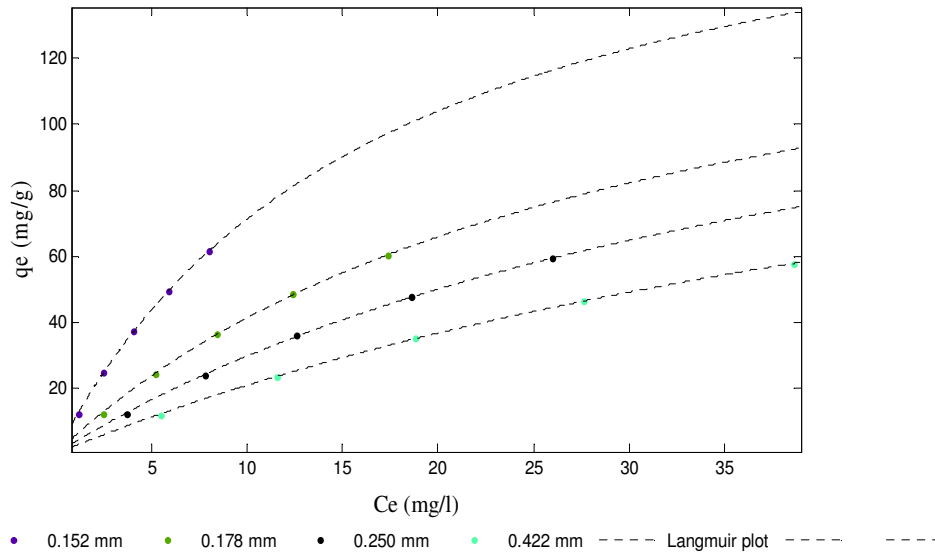


Fig. 4. Langmuir isotherm model fitted to simultaneous adsorption-biodegradation equilibrium data of phenol by pineapple peels immobilized *P. areuginosa* at different particle sizes

The Freundlich isotherm model is given in equation (5):

$$q_e = K_f C_e^{1/n} \text{ -----} \tag{5}$$

Where K_f and n are Freundlich constants. K_f is roughly an indicator of the adsorption capacity and n is the adsorption intensity.

The Freundlich isotherm is used for heterogeneous surface energy systems (Annadurai et al., 2000). It suggests that binding sites are not equivalent and/or independent. McKay et al., (1982) and Annadurai et al., (1997) have stated that the magnitude of the exponent $1/n$ gives an indication of the favourability and capacity of the adsorbent/adsorbate system. Values $n > 1$ represent favourable adsorption conditions according to Treybal (1988). In most cases, the exponent between $1 < n < 10$ shows beneficial adsorption.

The data obtained from the adsorption-biodegradation equilibrium experiment (plot of q_e vs C_e) (Fig. 5) was fitted to equation (5) (Freundlich isotherm) using the non-linear fitting routine of MATLAB 7.0 software package. The values of the Freundlich constants estimated from the plot are also given in Table 2. The high value of the correlation coefficient as shown in Table 1 indicated that the data conform well to the Freundlich equation (i.e. a good agreement between the parameters).

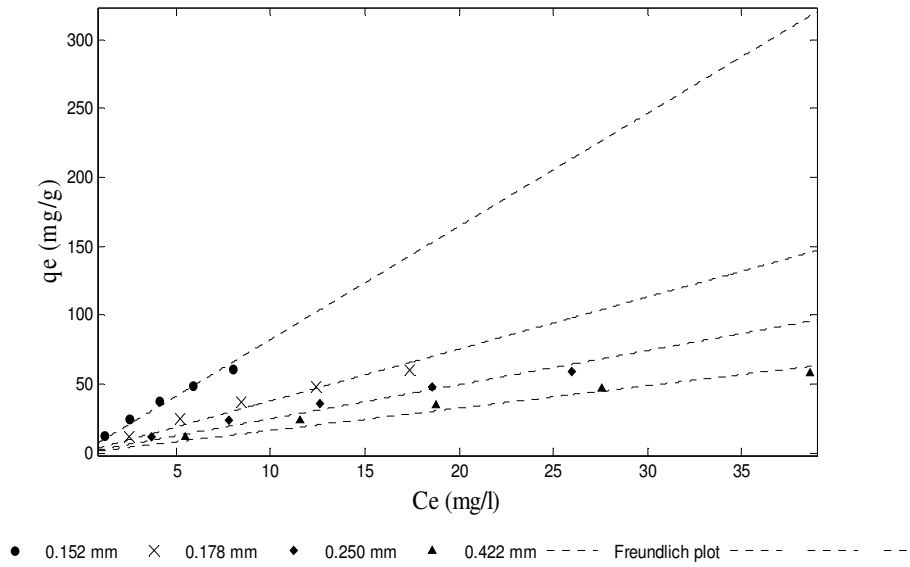


Fig. 5. Freundlich isotherm model fitted to simultaneous adsorption-biodegradation equilibrium data of phenol by pineapple peels immobilized *P. aeruginosa* at different particle sizes

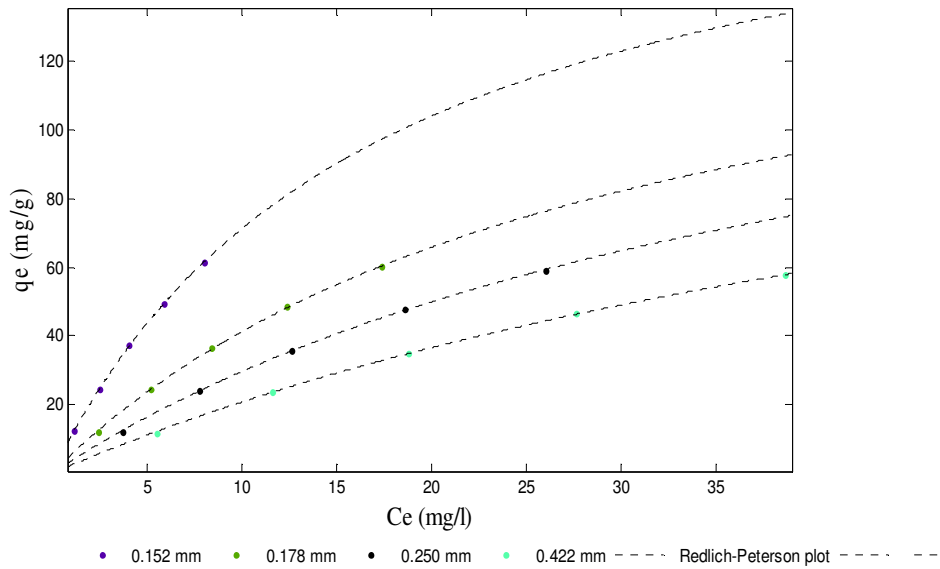


Fig 6. Redlich-Peterson isotherm model fitted to simultaneous adsorption-biodegradation equilibrium data of phenol by immobilized *P. aeruginosa* at different particle sizes

Table 2. Langmuir, Freundlich and Redlich-Peterson constants at different particle sizes

Particle size (mm)	Langmuir			Freundlich			Redlich-Peterson			
	K (mg/g)	a	R^2	K_f	n	R^2	K	a_R	b	R^2
0.152	193.3	0.0583	0.9998	8.23	1.00	0.9623	11.3	0.0583	1.0	0.9998
0.178	163.3	0.0338	0.9998	4.51	1.20	0.9424	5.52	0.0338	1.0	0.9998
0.251	159.5	0.0228	0.9998	2.58	1.04	0.9416	3.64	0.0228	1.0	0.9998
0.422	153.5	0.0157	0.9998	1.58	0.97	0.9395	2.41	0.0157	1.0	0.9998

Table 3. Langmuir isotherm with separation factor (R_L) at different particle size

Initial phenol concentration (mg/l)	R_L values			
	Particle sizes (mm)			
	0.152	0.178	0.251	0.422
100	0.9346	0.9225	0.9217	0.9200
200	0.8719	0.8503	0.8489	0.8460
300	0.8084	0.7782	0.7770	0.7722
400	0.7440	0.7047	0.7022	0.6978
500	0.6821	0.6297	0.6277	0.6227

From Table 1, it is seen that the sorption capacity (K_f) decreased with increase in particle size. A similar observation has been reported (Annadurai et al., 2000). However, Annadurai et al., (2007) have reported that K_f increases with particle size for chitin used as adsorbent. In general, as shown in Table 1, n values (0.97-1.20) are less than 1.5, indicating that $1/n$ values are less than or equal to unity. This suggests that the surface of the adsorbent is heterogeneous in nature (Lynbchik et al., 2004; Popuri et al., 2006). In the present study, K_f values ranges from 1.58 to 8.23. The literature shows the parameter values of $1/n$ and K_f as 0.508, 13.37 (Mondal and Balomajumder, 2007); 0.5077, 8.11 (Vinod and Anirudhan, 1996); 0.245, 36.51(Kumar et al., 2007); 0.7269, 1.681(Dabhade et al., 2009).

The Redlich-Peterson isotherm equation contains three parameters and incorporated the features of the Langmuir and Freundlich isotherm (Redlich and Peterson, 1959; McKay and Ho, 1999). This isotherm equation is as given in equation (6):

$$q_e = \frac{KC_e}{1 + a_R C_e^b} \text{-----} \quad (6)$$

The Redlich-Peterson isotherm is as shown in Fig. 6. The isotherm constants are given in Table 2. Generally, the high value of the correlation coefficient (R^2) indicated that the Langmuir, Freundlich and Redlich-Peterson isotherm equations gave a better fit to the experimental data.

3.5 Kinetics of Simultaneous Adsorption-Biodegradation

The kinetics of adsorption-biodegradation was studied for its possible importance in the treatment of phenol containing industrial effluents. Numerous kinetic models have been proposed to elucidate the mechanism by which pollutants are adsorbed. To investigate the mechanism of the phenol adsorption-biodegradation, four kinetic model equations, that is, Lagergren pseudo first-order, pseudo second-order, Elovich and intra particle diffusion equations were considered to interpret the experimental data.

The Lagergren pseudo first-order kinetic model equation (Lagergren, 1898; McKay and Ho, 1999) is represented in an integral form as given in equation (7):

$$\ln(q_e - q_t) = \ln q_e - k_{ad}t \text{-----} \quad (7)$$

The pseudo second-order kinetic model (McKay and Ho, 1999) is expressed as given in equation (8):

$$\frac{t}{q_t} = \frac{1}{k_{ad_2} q_m^2} + \frac{1}{q_m} t \text{-----} \quad (8)$$

The initial adsorption rate, h (mg/g min), as $t \rightarrow 0$ can be defined as (equation 9):

$$h = k_{ad_2} q_m^2 \text{ -----} \quad (9)$$

Where k_{ad_2} is the second-order rate constant ($\text{gmg}^{-1}\text{min}^{-1}$) and q_m is the maximum adsorption capacity (mg/g). The second-order rate parameters can be determined experimentally from the slope and intercept of the plot of $\frac{t}{q_t}$ vs. t .

The Elovich equation (Low, 1960; Gok et al., 2008) is generally expressed as presented in equation (10):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \text{ -----} \quad (10)$$

To simplify Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta t \gg 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$. Equation (10) becomes (Sparks, 1999):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \text{ -----} \quad (11)$$

Where α is the initial adsorption rate (mg/g min) and β is the desorption constant (g/mg).

The intra particle diffusion kinetic model (Weber and Morris, 1963) can be written as presented in equation (12):

$$q_t = K_p t^{1/2} \text{ -----} \quad (12)$$

Where K_p is the intra particle diffusion rate constant ($\text{mg/g min}^{-1/2}$)

The plots of $\ln(q_e - q_t)$ vs. t for Lagergren first-order model (Fig.7a and b), t/q_t vs. t for the pseudo second-order model (Fig.8a and b) and, the plots of q_t vs. $\ln t$ for the Elovich model (Fig.9a and b) have been represented at different parameters of initial phenol concentrations and pH, respectively. A linear relationship was observed for each of the plots indicating the applicability of Lagergren pseudo first-order, pseudo second-order and Elovich equations respectively.

The kinetic parameters of phenol under different conditions of initial concentration and pH were calculated from these plots and are given in Table 4. It is observed from the Table that the rate constant (k_{ad}) values for Lagergren pseudo first-order increased with increase in initial phenol concentration and pH. For pseudo second-order model, the estimated average value of the rate constant k_{ad_2} decreased with increase in initial phenol concentration and generally increased with increase in pH. The correlation coefficients (R^2) for the Lagergren first-order kinetic model are between 0.993 and 0.998, the correlation coefficients (R^2) for pseudo second-order kinetic model are between 0.959 and 0.995 and the correlation coefficients (R^2) for the Elovich kinetic model are between 0.950 and 0.995. These high R^2 values indicate a good fit of the three kinetic models to the experimental kinetic data.

The adsorption steps include the transport of adsorbate in bulk phase and in solid phase. The properties of adsorbate, adsorbent, solution phase decide the uptake rate. The initial transport of adsorbate to macropore is fast, then transport to mesopore is medium and finally there is slow diffusion into micropores. In general, intra particle diffusion transport is considered as rate limiting step in case of adsorption on porous solid adsorbent from aqueous solution, if system is well mixed. In adsorption of phenol using PPP, there is the possibility of intra particle diffusion. It can be described by three consecutive steps, (i) the transport of sorbate from bulk solution to outer surface of the sorbent by molecular diffusion known as external or film diffusion, (ii) internal diffusion, the transport of sorbate from the particles surface into interior sites, (iii) the sorption of the solute particles from the active sites into the interior surface of the pores (Binary and Narendra, 1994; Annadurai and Krishnan, 1997).

The Lagergren first-order, pseudo second- order and Elovich kinetic models cannot identify the diffusion mechanisms and the kinetic results were then subjected to analysis by the intra particle diffusion model of Weber and Moris (1963), and it may be the rate- controlling step.

If this occurs, then the plot of sorption Q_t vs square root of time ($t^{1/2}$) should be linear and if it passes through the origin then the intra particle diffusion will be the sole rate-limiting process (Bhattacharyya and Sharma, 2004; Ozcan and Ozcan, 2005). The intra particle diffusion plots may presents multilinearity indicating that two or more steps take place. The first sharper portion is the instantaneous adsorption stage or external surface adsorption. The second portion is the gradual adsorption stage where intra particle diffusion is rate-limiting. The third portion is the final equilibrium stage where intra particle diffusion slows down due to extremely sorbate concentration left in the solution. The double nature of these plots, as initial curve portions and final linear portions may be explained by the facts that the initial curved portions are boundary layer diffusion effects (Annadurai and Krishnan, 1997). The final portion is as a result of intra particle diffusion effect.

In the present study, it was found that the plots of Q_t vs. square root of time ($t^{1/2}$) exhibited an initial linear portion followed by a plateau which occurred after more 50 h (Fig. 10a and 10b).

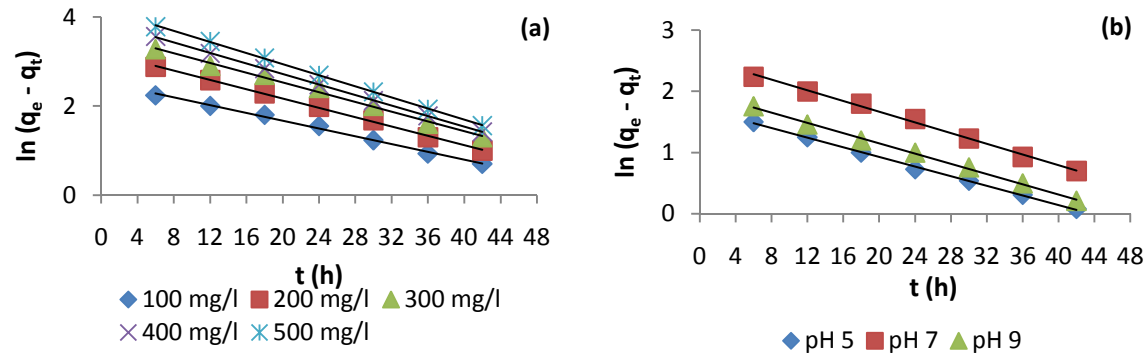


Fig. 7: Lagergren first-order model fitted to the simultaneous adsorption – biodegradation of phenol by pineapple peels immobilized *P. aeruginosa* at (a) initial phenol concentration (b) pH

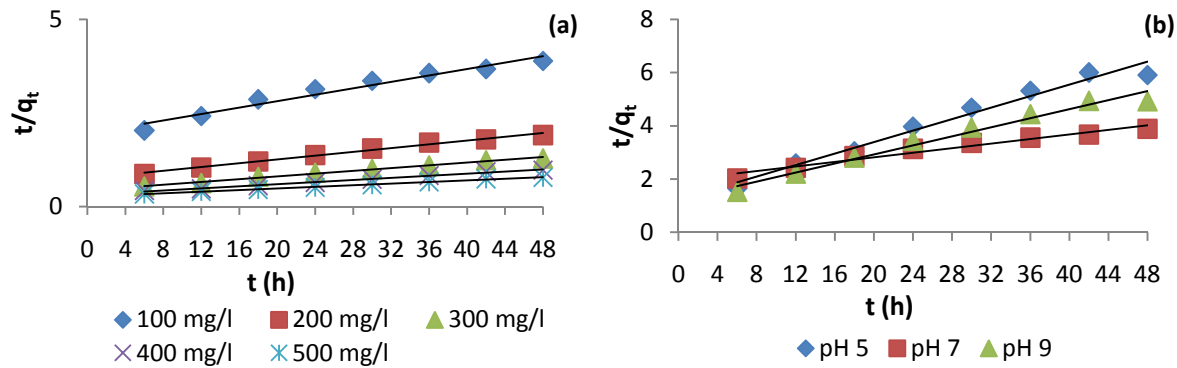


Fig. 8: Pseudo second-order kinetic model fitted to simultaneous adsorption – biodegradation of phenol by pineapple peels immobilized *P. aeruginosa* at (a) initial phenol concentration (b) pH

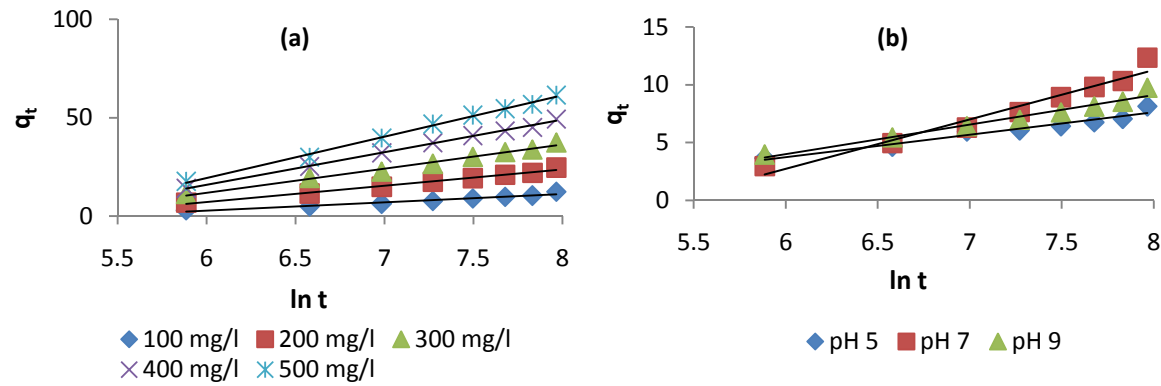


Fig. 9: Elovich kinetic model fitted to simultaneous adsorption - biodegradation of phenol by pineapple peels immobilized *P. aeruginosa* at (a) initial phenol concentration (b) pH

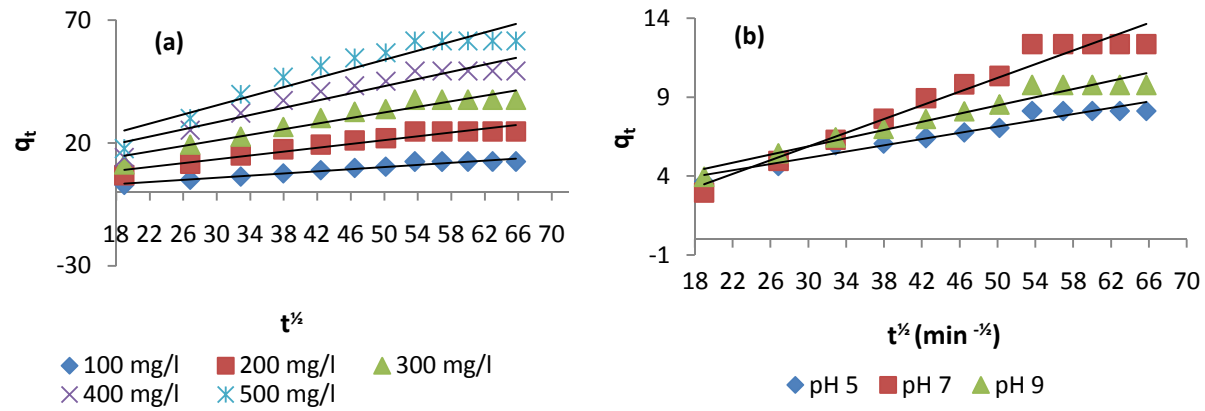


Fig. 10: Intra particle diffusion model fitted to simultaneous adsorption - biodegradation of phenol by pineapple peels immobilized *P. aeruginosa* at (a) initial phenol concentration (b) pH

Table 4. Kinetic constant parameters for the adsorption-biodegradation of phenol by *P. aeruginosa* NCIB 950 immobilized in pineapple peels for various initial concentration and pH

Kinetic models	Initial phenol concentration					pH		
	100	200	300	400	500	5	7	9
Lagergren								
k_{ad} (h ⁻¹)	0.043	0.052	0.054	0.059	0.062	0.038	0.043	0.041
q_m (mg/g)	12.68	24.88	37.52	49.50	65.43	5.50	12.68	7.28
R ²	0.995	0.998	0.993	0.999	0.999	0.996	0.996	0.997
Pseudo second-order								
k_{ad2} (g/mg/h)	91.6	22.62	10.60	7.91	6.96	13.77	91.6	17.92
q_m (mg/g)	0.51	1.33	2.29	3.12	3.79	0.82	0.51	0.81
R ²	0.959	0.990	0.982	0.993	0.995	0.972	0.959	0.973
Elovich								
α (mg/g/min)	0.020	0.049	0.079	0.108	0.132	0.032	0.020	0.030
β (g/mg)	0.234	0.120	0.082	0.060	0.047	0.515	0.234	0.390
R ²	0.957	0.989	0.988	0.997	0.996	0.950	0.957	0.967
Intra particle diffusion								
K_p (mg/g/min ^{-1/2})	0.217	0.390	0.568	0.732	0.926	0.098	0.217	0.129
R ²	0.958	0.938	0.934	0.909	0.906	0.958	0.944	0.956

The curved portion of the plots seems to be due to the boundary layer diffusion and the linear portion as a result of intra particle diffusion with the plateau corresponding to the equilibrium (Chen et al., 2003; Gok et al., 2008). However, none of the plots passed through the origin. This indicates that although intra particle diffusion was involved in the adsorption-biodegradation process, it was not the rate-controlling step. Values of the intra particle diffusion constant, k_p , were obtained from the slopes of the linear portions of the plots and are presented in Table 4. The correlation coefficients (R^2) for the intra particle diffusion model were between 0.995 and 0.990. These values indicate that the sorption of phenol into PPP may be followed by the intra particle diffusion up to more 50 h. It is seen that from Table 4 that the intra particle diffusion constant, k_p , increased as initial phenol concentration increases, while k_p was higher at pH 7 than at pH 5 or 9.

4. CONCLUSION

The adsorption-biodegradation of phenol from synthetic waste water using pineapple peels-immobilized with *P. aeruginosa* NCIB 950 has been investigated under different reaction conditions in batch and equilibrium mode. The monolayer adsorption capacity determined was reasonably high (193.3 mg/g) at phenol concentration of 100 – 500 mg/l, pH 7 and particle size (0.152 mm) for adsorption-biodegradation of phenol respectively. The values of rate constant and intra particle diffusion constant varied with initial phenol concentration and pH. Pineapple peels showed competitive properties for bacterial biomass immobilization and may have potential in process application because of its relatively high biomass loading and good chemical and physical stabilities. The kinetics of phenol adsorption-biodegradation nicely followed Lagergren first-order rate expression and demonstrated that intra particle diffusion plays a significant role in the adsorption-biodegradation mechanism. Langmuir, Freundlich and Redlich-Peterson adsorption isotherms could be used to describe phenol sorption equilibrium and the kinetic data of pineapple peels immobilized *P. aeruginosa* also gave a better fit. The treatment is simple and economic. The reaction kinetics data thus generated may be used for designing an economically viable treatment plant for phenol effluents using batch or stirred tank reactors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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