Removal of Phenol from Aqueous Solutions using Potato Peel

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ABSTRACT

Background: Phenols that discharge from many industries constitute large group of very toxic and difficult to degrade contaminant. Objective: The aim of this paper is to study the potential of Potato Peel (PP) to remove of phenol from simulated synthetic aqueous solutions (SSAS) using immobilized enzyme and adsorption process. Poly Phenol Oxidize (PPO) enzyme was extracted from PP, loaded on the biocatalyst (zeolite) prepared from rice husk and tested for phenol removal. Results: Results show high ability of biocatalyst to remove of phenol and the efficiency was 99%. The residual of Potato Peel (PP) was tested as an adsorbent media for phenol removal in adsorption unit. Results show that maximum removal efficiency of phenol was 95.37%. Statistical models were achieved to describe the behavior of removal efficiency with all operating parameters used. The Potato Peel (PP) waste remaining from adsorption process shows good results when used as rodenticide. Conclusion: The percentage removal of phenol was increased with any decrease in the flow rate of SSAS, and in the initial concentration of phenol while the percentage removal was decreased with any increase in the pH, treatment time and the height of adsorbent material of PP. Thus it can discard more type of wastes in eco-friendly method.

INTRODUCTION

Recently most of water resources (surface water or ground water) suffer from many problems and the most important problem is the contamination. Different kinds of industrial and agricultural pollutants is discharged to water resources. One of the most dangerous water contaminants is phenols. Phenol which classified as very toxic contaminant is discharged to water sources from many industries such as explosives, adhesives, fertilizers, rubber, textiles, drugs, paints, wood preservatives, soap and paper. Beside the toxic effects, phenolic compounds create an oxygen demand in receiving waters, and impart taste and odor to water with minute concentrations of their chlorinated compounds. Surface and ground waters are contaminated by phenolics as a result of the continuous release of these compounds. Therefore, the wastewaters containing phenolic compounds must be treated before release to the water resources. Considerable wizards were developed to solve the problem of water pollution with phenols. Currently there are many methods or techniques used for this purpose but these methods included many problems during and after treatment e.g. decreases the efficiency of remediation and long time for treatment in addition to high cost for operation, perpetuate and removal the waste remaining in safe way, Abbas and Abbas, 2013; Abbas and Abbas, 2013. Adsorption method is a better method to wastewater treatment. It is easy, efficient, economic, suitable for most types of contaminated water and can utilize in different routes from the waste remaining after the end of remediation process, LiZ et al., 2000. Activated carbon is the famous adsorbent material in most adsorption process for its activity and efficacy, however due to high price and needed to periodically regeneration make the researches turned to other alternative materials for adsorption process. An alternative material is agricultural wastes (such as rice husk, banana peel, orange peel, potato peel, bean peel, eggplant peel, peanut husks, coconut shell, date seed, etc.) which have several properties like available, cheap, good efficiency, do not need high cost for using it in adsorption process, re-use many times and profitiering from its residual after treatment. Many types of agricultural waste are used in adsorption process of different pollutants e.g. heavy metals, toxic materials, organic matters, dyes and radioactive substances, Abbas, 2013; Abbas, 2013. Potato Peel (PP) is one type of agricultural waste that lags about 80-100 gram from every 1kg of potato crop. It has many uses and can be used in adsorption of contaminants from aqueous solutions and wastewaters. Potato Peel (PP) contains a poly phenol oxidize enzyme (PPO) which has ability to remove the phenol and dyes compounds using enzyme immobilization method which is an excellent technique to treat huge amount of waste. The first objective of the present work is to extract the PPO enzyme
from PP and use it as a biosorbent of high concentration phenol. The second objective is to study the possibilities of PP waste (remaining from PPO extraction process) as low cost adsorbent material for removing phenol from SSAS and finally to investigate the usability of PP residual (PP loaded with phenol) as cheap rodenticide.

MATERIAL AND METHODS

2.1 Potato Peel (adsorbent media):
Mature potato with brown peel, was collected from local market in Baghdad city. Potato Peel (PP) was washed three times with excess double distilled water and boiled to remove dust, impurities and other fine dirt particles that may be attached to the PP. The washed PP was cut into small pieces (0.5-1 cm) and then dried at 50°C for 24 hours.

2.2 Preparation of Crude Poly Phenol Oxidase (PPO) Enzyme:
Weight of 100g from PP was cut into small pieces and homogenized by using 200ml of pre-chilled 4°C containing 0.1M sodium phosphate buffer extraction buffer pH 6.5, Poly vinyl pyrolidone (PVP) and Triton X-100 using blender for 1 minute at maximum speed. The slurry was centrifuged at 9000 rpm at 4°C for 15 minutes. The supernatant obtained was filtered under vacuum from a buncher funnel containing Whatman® No. 1 filter paper and the filtrate was collected in a conical flask. Then, 100ml of the filtrate was pipette drop by drop into 200ml of cold acetone (− 20°C) for the formation of the precipitates. The crude PPO precipitates separated by centrifugation at 10000 rpm at 4°C for 15 minutes. The resultant light brown colored acetone precipitates was dried overnight at room temperature. The acetone powder that obtained was stored at − 20°C. The enzyme extraction from acetone powder was conducted by mixing 0.1g acetone powder, 15ml of pre-chilled 0.1M sodium phosphate buffer, pH 6.5 and stirring for 1 hour at 4°C with a magnetic stirrer. The temperature was maintained by covering the beaker with aluminium foil and was enclosed with ice surrounding the beaker. The obtained crude extract was filtered through cheese cloth and the filtrate was centrifuged at 10000 rpm for 30 min. The supernatant was discarded and used as crude PPO, Yapar et al., 2012; Manohan and Wai, 2012.

2.2.1 Enzyme Assay:
The assay solution was prepared by mixing 1ml of 20mM substrate (L-DOPA), 1ml 0.2M sodium phosphate buffer, 0.9ml H2O and 0.1ml of enzyme solution. Enzyme activity was measured spectrophotometrically at 475nm against a blank containing no enzyme. One unit of enzyme activity is defined as the amount of enzyme that transforms 1μmole of substrate Levodopa (L-DOPA) (L-3,4-dihydroxyphenyl-alanine) per minute under assay conditions, Manohan and Wai, 2012.

2.2.2 Preparation of Zeolite from Rice Husk as a Carrier for PPO:
Rice husk (which was a raw material for zeolite type Y catalyst synthesis) firstly treated with 10% phosphoric acid (H3PO4) for 24 hours. Then they were washed with double distilled water, filtered, dried in air, and calcined at 750°C for 6 hours. A 12g of calcined rice husk were subjected for dissolution in sodium hydroxide NaOH (4M) followed by refluxing at 90°C for 12 hours. Then, concentrated hydrochloric acid (37%) was added to the aforementioned base dissolved rice husk for complete precipitation. Rice husks were filtered, washed with excess distilled water to be freeing from chloride ions and finally dried in an oven at 120°C for 6 hours. Zeolite type Y was synthesized using prepared rice husk above as a silica source in the following method. A 500ml Teflon beaker containing a magnetic stirrer was washed with deionised water. Sodium hydroxide of 1.6616g was added slowly to deionised water and stir until clear and homogenous solution appeared for about 5 minutes. The aqueous solution of sodium hydroxide was ready for the preparation of seed gel. The gel was prepared from the following molar chemical composition: 10.67 Na2O: Al2O3: 10 SiO2: 180 H2O. A 2ml of aqueous solution of sodium hydroxide was added to 0.7515g sodium aluminate oxide until a homogenous mixture was formed. A 1.5361g of prepared rice husk above was added separately to 5.5 ml sodium hydroxide aqueous until mixed homogenously. Both of the preparations were heated under vigorous stirring to obtain a homogenous mixture. The sample was aged for 24 hours at a room temperature in the Teflon bottle. Aluminate and silicate solutions were mixed together in the polypropylene beaker, subsequently stirred for 2 hours with the purpose of making it completely homogenized. This combined solution was used as the feed stock gel. The synthesized zeolite type Y which was in sodium (Na+) powder form. In order to make a promoted HY-zeolite catalyst ready for test in any process, hydrogen zeolite (HY-zeolite) form must be prepared. The HY-zeolite was prepared by exchanging Na+ ions in the sodium form zeolite type Y with ammonium chloride solution NH4Cl. In order to obtain ideal degree of ion exchange, the technique of multi-steps (three times repeating) was used. Thus, the first step is 2N of ammonium chloride solution (26.75g of NH4Cl in 250 ml of distilled water) contacted with 90g of prepared NaY-zeolite with stirring for 2 hours. In the second step, the procedure in the
first step was repeated under the same conditions but on about 60g of zeolite, which was taken from the total zeolite amount produced in the first step. Finally, in the third step, the procedure under the same conditions was repeated again but on about 3g of zeolite, which was taken from the total zeolite amount produced in the second step. The exchanged ammonia zeolite were filtered off, washed with deionized water to be free of chloride ions dried overnight at 120°C and then calcined initially at 150°C for two hours. The temperature was increased 75°C per hour until it reached 550°C and it was held constant for 5 hours at this temperature. During calcinations, ammonia and water were liberated and HY-zeolite was formed, Akcay, 2004.

2.2.3 PPO Immobilization in Zeolite Type Y: A 25g of prepared HY-zeolite powder (prepared in section 7.2 above) was used for the immobilization of PPO in HY-zeolite. Immobilization solution of PPO was achieved by adding 10mg of NaY-Zeolite carrier to 10ml 0.05M sodium phosphate buffer (pH 7.0) and mixing with 40mg of crude PPO enzyme prepared. Mixture was left over night on shaker at 600 rpm at 4°C. Biocatalyst (enzyme and support) was taken out from solution, centrifuge at 10000 rpm and washed six times in 20ml 0.05M sodium phosphate buffer to remove free PPO enzyme. The removed biocatalyst was finally stored in 0°C, Lončar et al., 2011; Roostaei and Tezel, 2004.

2.3 Stock Solutions: In order to avoid interference with other elements in wastewater, the experiments in this study were carried out using simulated synthetic aqueous solution (SSAS) of different phenol concentrations. 1000 mg/l stock solution of phenol was prepared by dissolving known weight of phenol C6H5OH in one litre of double distilled water, all solutions using in the experiments were prepared by diluting the stock solution with double distilled water to the desired concentrations for the experimental work of this investigation. The phenol concentrations were measured using spectrophotometer method using spectrophotometer thermo – genesys 10 UV, USA.

2.4 Application of Immobilized PPO (biocatalyst) Using Sorption Unit: Adsorption unit shown in Fig. 1 was used to study the potential of immobilized PPO (biocatalyst) to remove of phenol from simulated synthetic aqueous solutions (SSAS). The operating conditions used in this study were temperature, pH, flow rates of SSAS of phenol, initial feed concentration and height of biocatalyst bed. Values of these parameters are 25°C for the temperature, 7 for pH, 5 ml/min for flow rates of SSAS of phenol and 1m for height of biocatalyst bed. Initial feed concentrations of SSAS are varied between (50-100) mg/l. Outlet samples after treatment in each experiment were collected every 10 minutes from the bottom of packed column and the remaining phenol concentration in SSAS was detected by spectrophotometer. The results show the ability of prepared biocatalyst to remove of phenol from SSAS in different concentrations, and the removal efficiency reach to 99% and 86% for initial concentration 50 mg/l and 100 mg/l respectively as shown in Fig. 2.

2.5 Sorption Unit: Fixed bed column of continuous mode experiments were conducted in order to examine phenol removal by treated SSAS of phenol at desired concentration with various bed heights of the waste PP as an adsorbent media (PP waste remaining from extraction of PPO enzyme) using different flow rates of SSAS of phenol at various pH. The pH value was adjusted using 0.1N NaOHand0.1NHCl solutions. As schematic representation of the sorption unit is shown in Fig. 2 where the flow direction is downward by gravity. The sorption unit consists of two glass container for SSAS of phenol one for inlet feed and another for outlet each of (1 liter) capacity. Glass column has 2.54cm ID and 150cm height. The sorption column packed with adsorbent media to a height of (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 cm) supported from the top and the bottom by glass hollow cylinder layer, each cylinder have (0.5cm ID, 0.1cm thickness and 1cm long). Before starting the runs, the packed bed sorption column was rinsed by double distilled water down flow through the column. The adsorbent media is packed in the column to the desired depth, and it was fed by mixing PP with distilled water in order to avoid the formation of air bubbles inside the media. After the packed bed sorption column was accommodation and putting the required amount of PP, the adsorption process started by allowing the phenol SSAS of required concentration and pH down flow through the sorption column from inlet container by gravity at a precise flow rate in experiment which is adjusted by rotameter. To determine the best operational conditions, the experiments were carried out at a temperature between (5-45°C), various pH values between (1-8) and initial feed concentrations of SSAS which are between (1-100) mg/l and at different flow rates which are between (5-100) ml/min for SSAS of phenol. Outlet samples after treatment in each experiment were collected every 10 minutes from the bottom of packed column and the unadsorbed concentration of phenol in SSAS was analyzed by spectrophotometer.
RESULTS AND DISCUSSION

The ability of Potato Peel (PP) to remove the phenol from SSAS in fixed bed column of continuous mode at various parameters which are pH of SSAS of phenol (pH), height bed of adsorbent media of PP (l), flow rates of SSAS (F), SSAS temperature (T feed) and time of treatment (t) was investigated. The experiments were achieved by varying all above parameters for different initial concentrations (Co) of SSAS of phenol. Thus, the results obtained are explained below.

3.1 Effect of Initial Concentration:

The results showed that the percentage removal of phenol decreases when the initial concentration (Co) of SSAS of phenol increases at a constant of other variables, as shown in Fig. 3. This can be explained by the fact that the initial concentration of phenol had a restricted effect on phenol removal capacity, simultaneously, the adsorbent media had a limited number of active sites for adsorption which would have become saturated at a certain concentration. This lead to an increase in the number of phenol molecules competing for the available functions groups on the surface of adsorbent material. Since the solution of lower concentration has a small amount of phenol than the solution of higher concentration of it, so the percentage removal was decreased with increasing initial concentration of phenol. For adsorbent media, higher percent removal was 95.37% for phenol at initial phenol concentration of 1 mg/l, so adsorbent material was found to be efficient to phenol removal from SSAS and wastewater.
3.2 Effect of pH:

The effect of pH of SSAS is illustrated in Fig. 4. It can be found that, the percentage removal of phenol increases with any decrease in the pH of SSAS of phenol at a constant of other variables. The adsorption of phenol from aqueous solution is dependent on the pH of the solution, which affects the surface charge of the adsorbent, and the degree of ionization and speciation of the adsorbate species. This can be attributed to the depending of phenol ionization on the pH value. Phenol which is a weak acid pKa=10 will be adsorbed to a lesser extent at higher pH values due to the repulsive force prevailing at higher pH value. Also, at higher pH range phenol forms salts, which readily ionize leaving negative charge on the phenolic group. At the same time, the presence of OH- ions on the adsorbent prevents the uptake of phenolate ions. pH also affects the surface properties of the sorbent. At very low pH values, the surface of the sorbent would also be surrounded by the hydronium ions, which enhance the phenol interaction with binding site of the sorbent by greater attractive forces, hence its uptake on polar adsorbent is reduced, LiZ et al., 2000.

3.3 Effect of Adsorbent Bed Height of the Media:

The results elucidated that when the adsorbent media bed height increases, the percentage removal of phenol increases at a constant of other variables, as shown in Fig. 5. The increase of bed height meaning increase in the amount of adsorbent media of PP. Thus increase the surface area of adsorbent material, hence increase the number of active sites in the adsorbent material surface i.e. increase the availability of binding sites for adsorption and consequently increase phenol removal capacity on PP. This lead to an increase in the ability of adsorbent media to absorb greater amount of phenol from SSAS at different initial concentrations and ultimately the percent removal of phenol increases.
3.4 Effect of Flow Rate:

From Fig. 6, it can be shown that when the flow rate of SSAS of phenol increases, the percentage removal of phenol decreases at a constant of other variables. This may be due to the fact that when the flow of SSAS of phenol increases, the velocity of SSAS in the column packed with the adsorbent media of PP also increases. Then the solution spends shorter time than that spend in the column while at low flow rate, and the SSAS of phenol resides in the column for a longer time, therefore undergoes more treatment with the adsorbent media, thus the adsorbent media uptake low amount of phenol from SSAS of phenol for high flow rate, therefore the percent removal of phenol decreases with any increase in the flow rates.

3.5 Effect of Feed Temperature:

The results demonstrated that when the feed temperature increases, the percentage removal of phenol increases at a constant of other variables, as shown in Fig. 7. The effect of temperature is fairly common and increasing the mobility of the acidic ion. Furthermore, increasing temperatures may produce a swelling effect within the internal structure of the adsorbent media enabling phenol ions to penetrate further. It was indicated that phenol adsorption capacity was increased at any increase in the feed temperature (5 to 45°C). This effect may be due to the fact that at higher temperature an increase in active sites occurs due to bond rupture.

![Graph showing effect of adsorbent media bed height on percent removal of phenol](image1)

**Fig. 5:** Effect of adsorbent media bed height (l) on the percent removal of phenol @ C_l = 1 mg/l, pH=1, T_f =55°C, t=60 min and F=5 ml/min

![Graph showing effect of SSAS flow rate on percent removal of phenol](image2)

**Fig. 6:** Effect of SSAS flow rate (F) on the percent removal of phenol @ C_l = 1 mg/l, pH=1, T_f =55°C, l = 1 m and t=60 min
3.6 Effect of Treatment Time:

The percentage removal of phenol increases with any increase in the treatment time of SSAS of phenol as shown in Fig.8. This may be due to the fact that when the treatment time of phenol SSAS increases and the velocity of SSAS in the column packed with the adsorbent material was remaining constant, the solution spend longer time than that spend it when the time of treatment decreases, so the adsorbent material uptake more amount of phenol from SSAS, therefore the percentage removal of phenol from SSAS increases.

Statistical model:

A statistical model was carried out to the experimental results obtained from this study. Regression analysis and π Theorem was adopted to maintain a relation between the percentage removal of phenol and the feed temperature, flow rate, pressure, pH of feed solution, initial concentration of phenol, adsorbent media of PP bed height, treatment time, column diameter and other parameters. These relations are shown in equation (1) below, which has a correlation coefficient ($R^2$) 0.9983.

$$\%R = 3.317 \times 10^7 \left( \frac{\rho_{sol}}{C_0} \right)^{0.3054} \times \left( \frac{l}{d} \right)^{0.1878} \times \left( \frac{T_f \cdot C_{P_{sol}} \cdot t}{\eta} \right)^{0.1475} \times \left( \frac{K_{sol} \cdot T_f}{\gamma \cdot \mu} \right)^{0.0259} \times \left( \frac{1}{pH} \right)$$  \hspace{1cm} (1)

Where:

- $\%R$: Percentage removal of phenol from SSAS,
- $\rho_{sol}$: Density of SSAS (kg/m$^3$)
- $C_0$: Initial concentration of phenol (kg/m$^3$)
- $l$: Adsorbent material bed height (m)
- $d$: Initial diameter of sorption column (m)
- $T_f$: Feed temperature (K)
- $C_{P_{sol}}$: Heat capacity of SSAS (kJ/kg.K)
- $t$: Treatment time (s)
- $\eta$: Kinematic viscosity (m$^2$/s)
- $K_{sol}$: Thermal conductivity of SSAS (W/m.K)
- $\gamma$: Surface tension ((N/m))
- $\mu$: Velocity of SSAS (m/s)
Utilization of Potato Peel Residual after uses:

Huge amount of PP was lingered after using it to phenol removal from SSAS as explained above. Utilization of PP can be achieved as a promoter of zeolite catalyst follows: Potato peel (PP) waste which were adsorbed phenol from SSAS at different operating conditions were segregated and classified according to its contain of phenol and utilization from these remaining samples as a rodenticide without any treatment. The samples give different ratios of phenol to PP (0.1 to 1 wt %). Before the treated PP wastes with phenol, give to the rats. The rats were left for one week and nurtured with normal feed to make sure that it’s were not suffer from anything leading to death. Then, the rats nurtured with treated PP wastes with phenol, the results were fate the rats in a different periods as shown in Table 1.

Table 1: Hours lead to kill rat when it nurtured with treated potato peel waste

<table>
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<th>Phenol to Potato Peel Ratio (wt %)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
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<td>14</td>
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</table>

Conclusion:

The objective of this paper is to study the potential of Potato Peel (PP) to remove of phenol from simulated synthetic aqueous solutions (SSAS) using immobilized enzyme and adsorption process. Results show that high concentrations of phenol (between 50-100 mg/l) is removed by extract PPO enzyme from Potato Peel (PP) and loaded it on the prepared biocatalyst (zeolite type Y) and treated the wastewater containing phenol. Waste of PP remaining from PPO extraction showed a good ability to remove of phenol from SSAS using fixed bed adsorption unit. Higher percent removal was 95.37% for phenol at initial concentration of 1 mg/l. Also, waste of PP adsorbent material was found to be efficient to remove of phenol from SSAS and wastewater. The percentage removal of phenol was increased with any decrease in the flow rate of SSAS, and in the initial concentration of phenol while the percentage removal was decreased with any increase in the pH, treatment time and the height of adsorbent material of PP. It can be utilized from the residual samples of Potato Peel that adsorb phenol from SSAS as arodenticide for rodent control.

REFERENCES


