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A New Modified Porcelain Adsorbent for the Removal and Preconcentration of Toxic Phenols in Wastewater

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Abstract: *A novel modified porcelain surface and its characterization as adsorbent for the removal and preconcentration of some organic pollutants was investigated. A grinded porcelain powder was treated with thewaste engine oil by using reflux method.The modified adsorbent was first used for the removal of phenol and substituted phenols from wastewater and found to dependent on some of conditions. The results revealed that the efficiency of removal was in order of: phenol >ρ-chlorophenol>ρ-aminophenol. A preliminary study has shown that Freundlich isotherm model provided a better fit with experimental data than another models. Based upon the first model, the experimental data were evaluated in which the empirical constants (K_f and n) were of 0.46, 1.38; 0.41, 1.35; and 0.38, 1.53,with high correlation coefficient R^2 of 0.9983, 0.9986 and 0.9908 for phenol, ρ-chlorophenol and ρ-aminophenol respectively, achieving that the process is exthothermic for the phenols adsorption on the surface of modified porcelain. in an attempt to extract and enrich of toxic phenol via construction of homemade cartridge made from the modified porcelain surface similar to the commercial solid phase extraction cartridge. The analytical results obtained in this study were compared with that of commercial octadecyl (C18) SPE cartridge using different polar solvents for elution of phenol under study.*

Keywords: Porcelain modified adsorbent, Adsorption, Phenolic compounds, Equilibrium isotherm, Homemade SPE cartridge.

1. Introduction

Presence of phenols and their derivatives as organic pollutants in the environment has been a serious concern especially with rapid industrialization which has created new uses for these compounds. But, the most common uses of these materials in many industries such as resins, rubber, tanning, pharmaceuticals, adhesive , petrochemicals, coal gas, steel, gasoline, plastic and paper[1,2].However, there are other sources or pathways which contribute to emanate the phenol compounds into the environment, for example, but not limited to, from exhaust gas of cars ,distillation of asphalt in coal ovens and degradation products of some pesticides [3].It is reported that the toxicity level for fish is around 9 to 25 mg L^{-1} while that for human being ranges 10-24 mg L^{-1}. Lethal blood concentration of phenol is around 150 mg/100 mL [4].Therefore, the exposure of phenol and its derivative compounds causes liver and and kidney damage, central nervous system impairment, diarrhea, and excretion of dark urine [5, 6].For this reason, and in order to protect humans and aquatic organisms from severe effect posed by phenolic compounds ,the international bodies around the world have called for setting the allowable limits for these compounds in various environmental elements especially after they were considered as priority pollutants by European Union and US Environmental Protection Agency (USEPA)[7].Due to the potential threat of phenolic compounds to human health and living organisms, the USEPA considered a concentration of less than 1 mg L^{-1} in the output of the filtered wastewater to the superficial water [8], while the World Health Organization (WHO) assess the maximum allowance of phenol in drinking water is 0.002 mg/L [9]. Accordingly, the removal of phenols from industrial effluents necessitated the development of innovative, effective and economical methods to meet the stringent standard as specified by international organizations. Many methods have been investigated for the removal of phenols and their derivative from different water sources. These include extraction[10-13],ion exchange resin [14], photodecomposition[15,16],chemical oxidation[17], electro-coagulation[18,19] , nano-filtration [20,21] , reverse osmosis[22],biological methods[23-27] and micellar enhanced ultra iltration [28,29]. Although these methods are efficient in removing phenols from waste water, adsorption methods, however, have been widely used by researchers for its efficiency, inexpensive and easy availability of adsorbent materials from industrial and agricultural wastes. Recently, the adsorption methods using various adsorbents for phenol removal by researchers are well reviewed.

In the present study, we have studied the potential of the removal of some phenol compounds from wastewater under adsorption process via exploiting the waste engine oil supported on porcelain material as an active adsorbent for the first time. A modified porcelain surface adsorbent was produced through the formation of an activated carbon coming from the waste engine oil which is supported on the porcelain surface with controllable particle sizes using reflux process. To this end, several parameters that impact on the adsorption phenomenon were investigated, due to their importance for obtaining of a high removal efficacy. Furthermore, the thermodynamic study and adsorption isotherm models were tested so that to understand the mechanism of the adsorption process and establish the adsorption capacity of the modified porcelain adsorbent. Lastly, the prepared adsorbent was also employed for the analytical purposes, in an attempt to extract and enrich of toxic phenols via construction of homemade cartridge made from the modified porcelain surface similar to the commercial solid phase extraction columns in order to find its adsorption capacity. The analytical results obtained in this study were compared with that of commercial octadecyl (C18) SPE cartridge using different polar solvents for elution of phenolic compounds under study.

2. Experimental

2.1 Chemicals and Materials

The following chemicals were purchased and used without further purification: phenol (Ph) from Lobachemie (German); ρ-chlorophenol (ρ-CPh)and ρ-aminophenol (ρ-APh) from BDH (England) andthe main physicochemical properties of these compounds are displayed in Table 1. Ethanol and acetonitrile from Sigma Aldrich (German); diethyl ether from GCC) German); hydrochloric acid and sodium hydroxide from BDH (England). Stock solutions (1000 mg L^{-1}) were prepared by dissolving 0.1 g of ph, 4-CPh and 4-APh, individually in 100 mL of double distilled water. The working solutions (1-50) mg/L was prepared by appropriate dilution of the stock solution in distilled water. A 0.1 M HCl was prepared by transferring 0.84 mL of concentred HCl (1.9 M) into 100 mL volumetric flask and dilutes to mark with distilled water, and 0.1 m NaOH was prepared by dissolving 4 g of NaOH in 500 mL volumetric flask.

2.2 Preparation of the Modified Porcelain Adsorbent

The samples of nature porcelain in the form of relatively large rocky pools were obtained from Ministryof Industry and Minerals/State Company for Geological Survey and Mining/ Iraq. The samples washed with distilled water to remove impurities and other soluble substances in water like salts, and then dried in electrical oven at 130 °C for 3hours. The samples were crushed by mechanical crusher into small pieces and ground to powders of different sizes to pass through 300, 500, and 700 µm sieves, then flooded with deionzed water for 48 hours(in order to being force water into the pores and washed as well as washing the surface) and then placed in oven at temperature of130° Cfor 10hours,to remove the physically adsorbed water, after it has been kept in tied sample bottles until use. 5 g of the above prepared porcelain powder were mixed with 10 g of the waste engine oil (as a carrier material on porcelain powder)The waste engine oil utilized in the study was collected from a

local auto repair workshop, and heated by using refluxprocessing at temperature of 235 °C for 24 hours, after, it has been filtered and then washed with organic solvent and finally with distilled water to get rid of organic solvents. The UV-Vis spectrum of the wash was recorded after each wash. The above process was repeated several times using freshsolvent each time until the absorption spectrum was identical with that of the pure washing solvent,and to make sure that no absorption peak interferes in the interested region of measurements. The modified porcelain surface was then dried for 6 hours and kept in tied sample bottle until use.

2.3 Construction homemade SPE cartridge

A homemade solid phase extraction (SPE) cartridge wasconstructed in our laboratory. The cartridge is made from moulded polyethylene “syringe-barrel body similar to those of commercial SPE columns. The cartridge is packed with 2.5 g of the modified porcelain sorbent prepared in the above section in particle size of 300 µm (50 mesh) as shown in Figure 1.

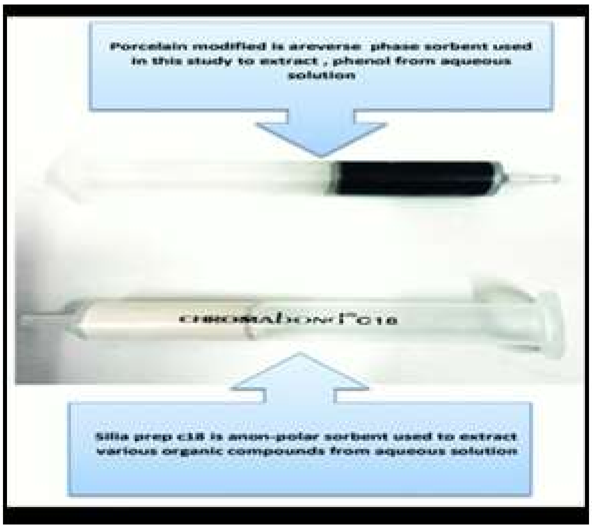


Figure 1: A homemade SPE and commercial Chromabond® C18 cartridge.

All steps involved in complete solid phase extraction procedure were carried out such as, activate to make the sorbent wet well; equilibrate to adjust the extraction strength; load sample; remove interference; wash down and collect targeted fraction. This cartridge was tested for extraction and preconcentration of target phenols and compared with the reversed phase commercial Chromabond® C_{18}(Octadecyl modified silica phase) polyethylenecartridge produced by ACHEREY-NAGEL GmbH &Co KG (Germany).

2.4 Chemical Analyses

The concentration of phenol and its derivative in the solutions before and after equilibration were determined by Varian’s Cary® 100/300 double-beam UV-Vis Spectrophotometers(USA) at each analyte respective λ_{max} .The absorption spectra of (25 mg L^{-1}) phenol, ρ-cholophenol and ρ-aminophenol against the blank reagent (distilled water) were measured and the maximum absorption wavelength were found to be of 269, 279 and 285nm, respectively. Meanwhile, the calibration curves were constructed for each target at respectiveλ_{max} and found the Beer’s law was obeyed in the range of 1-50 mg L^{-1} for Ph and 1-25 mg L^{-1} for ρ-CPh and ρ-APh. The concentration of analyte was determined by regression line. The pH of the solutions was measured using pHm 84 , Research pH meter Radiometer (Cobenhagen , Denmark).EURO. EA Elemental Analyzer Instruments and Software was used to confirm the presence of elemental C, H, N and S in the modified porcelain sorbent. Fourier Transform Infrared spectroscopy (FTIR) model 6000 Shimadzu (Kyoto, Japan) was used to identify the type of functional groups in the porcelain powderbefore after treatment with the used oil. The analysis was performed using KBr disc technique,and the spectral range varies from 4000 to 400 cm^{-1}.X-ray Diffraction Shimadzu 6000 (Japan)was used to identify the type of bonds in the porcelain powder before and after modification, that might be in vowed in the adsorption process.

2.5 Adsorption Batch Experiments

The experiments for optimization of process parameters and equilibrium and thermodynamic studied were conducted by mixing different weights of the modified porcelain adsorbent with desired concentration of Ph, ρ-CPh and ρ-APh (0.5-25 mg L^{-1}) in 250 mL conical flask. The flasks were stoppered during the equilibration period and placed on a temperature-controlled shaker (BS-11 digital, JEIO TECH, Korea, (20-185) rpm, (-10-120 $^{\circ}$C) ±0.5°)at a speed 150 rpm. The progress of each experiment was followed by periodically taking liquid samples from the flask and immediately analyzed after filtration. The final concentration of phenol and its derivatives (Ce, mg L^{-1}) in each flask were determined spectrophotometrically at each respective λ_{max}. The adsorption capacity was calculated from the following formula [30];

$$Qe = \frac{Co - Ce}{m}V$$

Where Qe is the adsorption capacity (mg g^{-1}), V the volume of phenols solution in the flask (L), *m* is the mass of adsorbent material (g), C_o is initialconcentration (mg L^{-1}) and C_e is the final concentration (mg L^{-1}). The removal percentage (RP) of phenols was calculated according to the following expression;

$$RP = \frac{Co - Ce}{Co}100$$

The efficiency of binding (Kd) for bounded to the surface of adsorbent was calculated from the following formula;

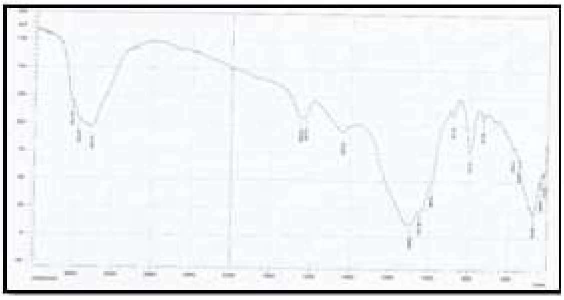
$$Kd = r_{ws}\frac{(Co - Ce)}{Ce}$$

Where r_{ws},is theratio between the volume of the adsorbate solution to the weight of adsorbent (ml/g)

3. Results and Discussion

3.1 Characterization of the Modified Adsorbent

To study and follow-up variations that have occurred on the porcelain before and after its treatment with the waste engine oil , FTIR and XRD were carried out. The FTIR spectra were shown in Figure 2 .The natural porcelain (Fig. 2a) displays the main bands , a broad absorption peak at 3612.71 cm^{-1}corresponding to the stretching vibration of the group Si(OH) and at 1093.67 and 472.38 cm^{-1}belong to the groups Si=O and Fe-O respectively. Figure 2(b) shows a remarkable change and more complex spectrum observed in modified porcelain due to the inclusion of the waste engine oil on the surface and in the pores of natural porcelain.it appears that the main difference between natural and modified porcelain in an infrared spectrum, the later displays a weak band around 3600 $cm^{-1}$of the Si(OH) group. Also, the band at 1728.85 cm^{-1} may relate to C=O stretch indicating the presence of ketones or ester in the specimen. The reason for this could be due to the fact that the waste engine oil had experienced severe oxidation under the high service temperatures and thus produced the oxidized components reflected on thecarbonyl functional group[31]. The peaks at 3119.00, 1550.82 and 1053.17 cm^{-1} which were assigned to C-H , C-C and (Si=O)respectively[32]. It is clear from this characterization that the modified porcelain adsorbent has the binding activity due the presence function groups which could explain the capacity of the adsorbent. The XRD spectra was also strongly confirmed the modification of porcelain after treatment with the waste engine oil as shown in Figure 3. The following patterns at (2Ѳ=21.85, d=4.06296 A$^{\circ}$), (2Ѳ=21065 d=4.09993 A$^{\circ}$)and (2Ѳ=30.96 d=208854 A$^{\circ}$) which were assigned to silicon dioxide, quartz and dolomite for untreated porcelain (Fig. 3(a)). Whilst the treated porcelain gave the following patternsat (2Ѳ=21.07, d=4.21269A$^{\circ}$)and(2Ѳ=26.8774, d=3.31447 A$^{\circ}$) which were assigned to Tridymite, carbon-carbon respectively.


(a)

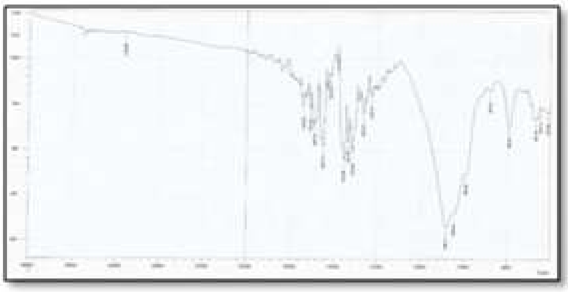

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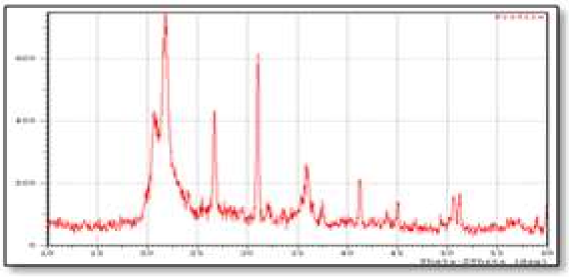
Figure 2: FTIR of porcelain powder(a) before and (b) after treatment with engine oil waste.


(a)

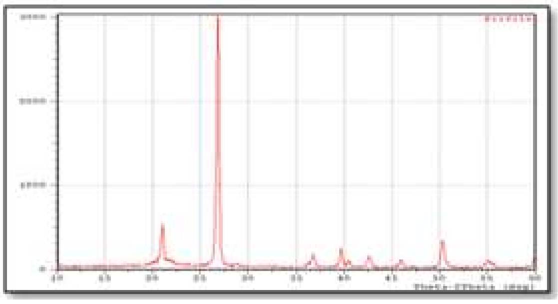

(b)

Figure 3: XRD of porcelain powder (a) before and (b) after treatment with waste engine oil

3.2 Optimization of adsorption Process Parameters

The adsorption of phenol ant its derivatives in aqueous solution on the modified porcelain adsorbent was examined by optimizing various physicochemical parameters such as; pH, contact time, and the amount of adsorbent weight , initial concentration of adsorbates and temperature by using a classical optimization (one-factor-at-a-time).

3.3 Effect of pH

The pH was considered the most important factor influencing the adsorption capacity of the phenols on the adsorbent material as it controls the electrostatic interactions between the adsorbent and the adsorbate[33].Thus,the effect of pH on the adsorption of phenolic compounds by modified porcelain was investigatedusing 50 mL of 25 mg L^{-1} of Ph, ρ-CPh and ρ-APh and 1g of adsorbent at 25 °C over pH range of 2 to 10 .The pH ofsolution was adjusted to the desired value by adding a few drops of 0.1N HCl or 0.1N NaOHsolutions to the initial solution The results were displayed in Figure.4. It can be seen that the maximum removal for all phenols was observed at pH 2 and in order of 68.48% (Ph), 60.76% (ρ-CPh) and 50.72% (ρ-APh), thereafter it gradually decreases at high pH. At very low pH , the presence of excess of H$^+$ ions inhibits the formation of phenoxide ion (i.e. The degree of ionization of phenols decreases) and thus their capacity to be adsorbed by modified porcelain increases[34]. Whilst at high pH solution , the formation of negatively charged phenoxide ion has to compete against the excess of OH$^-$ ion onto the adsorbent surface generating a repulsion between the adsorbent and adsorbates thus lowering the removal of phenols from solution[, or lead to an increase in solubility of these compounds causing high affinity of phenols molecules to persist in solution instead of being adsorbed on the adsorbent surface[35].

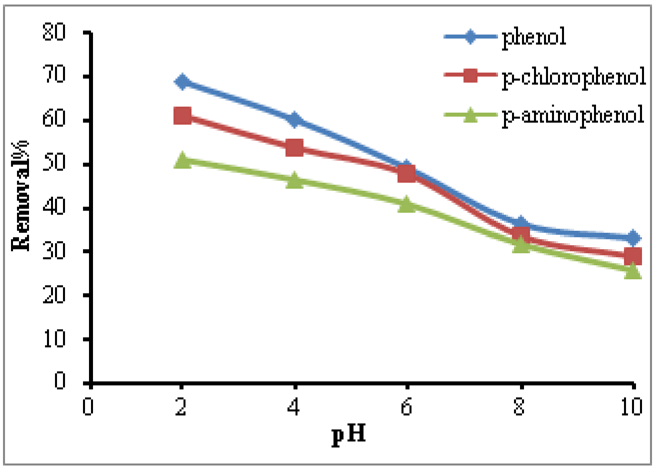


Figure 4: Effect of pH on percent removal of phenols

3.4 Effect of Contact Time

Figure 5 depicts the effectof variationof contact time on the percent removal of phenol and its derivatives at an initial concentration of 25 mg L^{-1} and 1 g of adsorbent at 25 °C and pH 2 by variation of contact time from 15 to 150 min. The relationship between contact time and percent removal of phenols is shown in Figure 5. It is evident from Fig. 5 that the time is an important factor for the adsorption of phenol onto the modified porcelain since the amount of each phenolic compound increase gradually with the increase of contact time after 30 min and reach a plateau at 90 min for Ph and 115 min for ρ-CPh and ρ-APh, resulting in removing of about 68.56% of Ph, 63.68% of ρ-CPh and 51.88% of ρ-APh. The increases in contact time after 30 min indicate that the rate of adsorption of the three phenols is quite high due to the presence of a plenty of readily accessible sites. Of at all, the equilibrium time required for the maximum adsorption as 115 min for Ph and 150 min for ρ-CPh and ρ-APh were selected as optimal for the achieving significant removal of these pollutants at initial concentration of 25 mg L^{-1}.

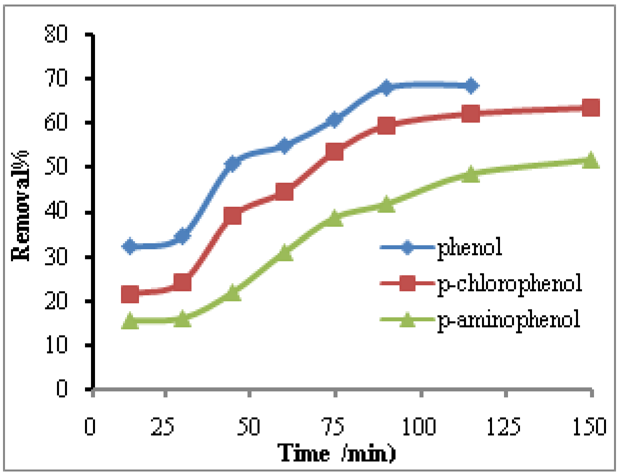


Figure 5: Effect of contact time on adsorption of phenols

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3.5 Effect of Adsorbent Quantity

It is reported that the locating ofoptimum dose is essential for optimisation of the removal process at equilibrium conditionsas this factor specifies the adsorbent capacity for a given system[36]. From Figure 5, it is explicit that the removal of phenol and its derivatives increases with an increase in the adsorbent weight up to 1 g and thereafter reach to the plateau, indicating the presence of large surface area available for adsorptionachieving , thereby a 77.20% of Ph, 68.04% of ρ-CPh and 56.52% of ρ-APhwere removedfrom the aqueous solutions at initial concentration of 25 mg L^{-1},

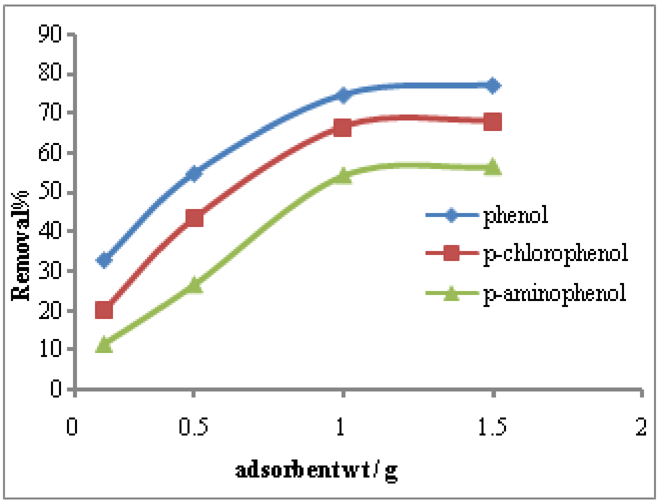

Figure 5: Effect of adsorbent weight on adsorption of phenols

their optimal pH and equilibrium time after changing in the adsorbent amount from 0.2 to 1.5 g. This is obvious, the more increasing in adsorbent weight, the high surface area and more available adsorption sites but to certain extent, thereafter it did not improve the adsorption process.This phenomenon had been reported from other researchers[37-40].Hence, in all the experiments, 1.0 g was kept as an adsorbent weight.

3.6 Effect of Initial Concentration

At previous optimized conditions and varying initial concentration of each phenol compound from 1-25 mg L^{-1} , Figure 5 depicts that the percent removal is maximum up to 3.5 mg $L^{-1}$and approached to 100% for all phenols,indicating that the adsorbent active sites are able to fully contain phenolic molecules at these initial concentration viaincreased driving force due to increased concentration gradient[41].Whilst at higher initial concentration (5-25 mg L^{-1}), a remarkable decrease in percent removal up to 60% occurs, indicating that the adsorption sites become insufficient to occupy all adsorbate molecules as seen in Fig.5 [42-43]. Nevertheless, the main reason for adopting initial adsorbate concentration at 25 mg L^{-1} as optimum in all adsorption experiments according to the highest level of toxicity of these pollutants that impact the human health and living organism.

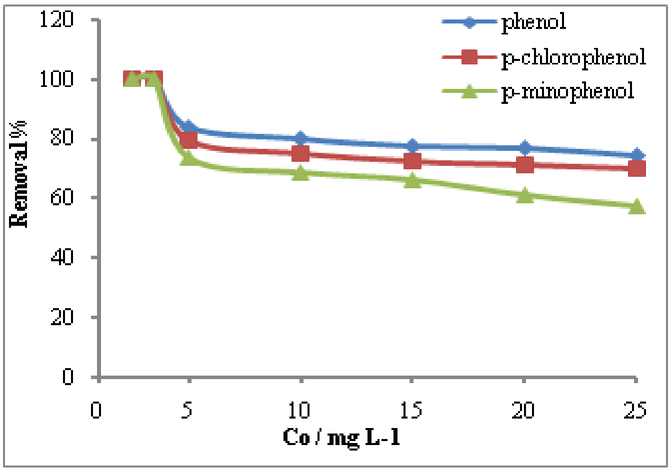

Figure 6: Effect of initial concentration of adsorbates on adsorption process

3.7 Effect of Temperature

The effect of temperature on the adsorption process for an adsorbentcan assist in understanding the type of adsorption and indicates whether the adsorption process is endothermic or exothermic. Consequently,the effect of temperature on the phenolic compounds adsorption ontothe modified porcelain surface was carried out at 25, 30, 40, 50, 60 and 70 °C and and keeping other parameters constant. The results are illustrated in Figure 7.

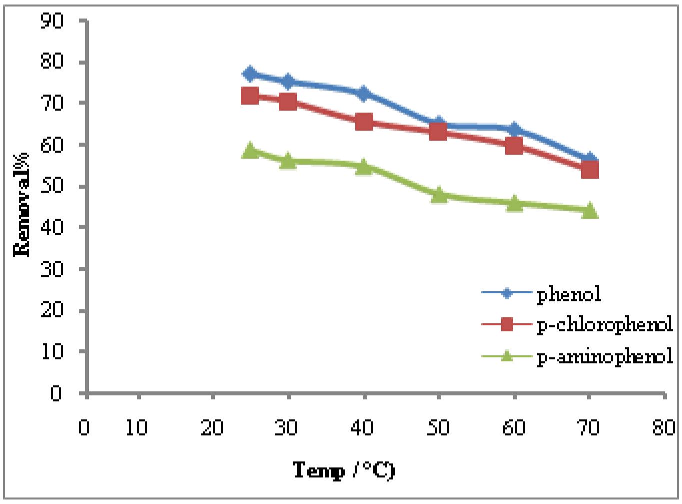

Figure 7 Effect of temperature on adsorption process of phenols

It can be seen (Fig.7) that the highest adsorption capacity took place at 25 °C and about 77.16% of Ph, 72.08% of ρ-CPh and 59.04% of ρ-APh could be removed from aqueous solution, thereafter it became at lowest. Thisdecrease in removal percentage of each phenols with increasing temperaturemight be attributed to many reasons,such as (1) the adsorbent surface can chemically change , along with the adsorption sites amount and activity (2) , the vapour pressure increases with rise in temperature making it more difficult to keep the adsorbent in its liquid state(3)the energy content increases, therefore, the adsorbent requires more energy to remain in a liquid state, thus directly affecting the adsorption balance. It can be concluded that the decrease of sorption effectiveness caused by increased temperature indicated the exothermic nature of the sorption process[44]. So the thermodynamic parameters should be determined to understand the system further.

3.8 Adsorption Isotherms

In order to express individually, the relationship between the concentration of phenol and its derivatives remaining in the solution and the amount adsorbed on the modified porcelain surface at constant temperature, some isotherm models were selected to test the experimental adsorption data, such as Langmuir, Freundlich and Temkin models. The adsorption equilibrium data of phenol, ρ-chlorophenol and ρ-aminophenol on the modified porcelain adsorbent are tabulated in Table 2.

Table 2 Adsorption equilibrium data of Ph, ρ-CPh and ρ-APh on the modified porcelain adsorbent.

adsorbent	phenol		ρ-chlorophenol		ρ-aminophenol	
C_0 (mg/l)	C_e (mg/l)	Qe mg/g	Ce (mg/l)	Qe (mg/g)	Ce (mg/l)	Qe (mg/g)
5	0.80	0.21	1.03	0.19	1.32	0.18
10	2.01	0.39	2.50	0.37	3.11	0.34
15	3.32	0.58	4.23	0.54	5.02	0.49
20	4.63	0.76	5.72	0.71	7.82	0.61
25	6.42	0.93	7.53	0.86	10.68	0.72

The preliminary investigations of the experimental adsorption c has shown that Freundlich isotherm model was better than Langm and Temkin isotherm. So, Freundlich model was adopted in study to characterize the adsorption behaviour of phenol pollutants this adsorbent at constant temperature (298 K).The Freundlich adsorption isotherm in its linearized form can be written as[45]:

$$\log Q_e = \ln K_f + 1/n \log C_e$$

Where,Q_e is the amount of adsorbate adsorbed at equilibrium,K_f 1/n are Freundlich constants and C_e is the equilibrium concentra of the adsorbate in the solution.A linear plot of log (Q_e) vs. log (gives a straight line using the Minitab® 14 statistical software. values of (1/n) and K_f are determined from the slope and intercep plots .The Freundlich adsorption isotherm data is given in Tab and shown in Figures 8, 9 and 10.

Table 3: Freundlich parameters for the adsorption of Ph, ρ-CPh and ρ-APh

parameter	phenol	ρ-chlorophenol	ρ-aminophenol
n	1.38	1.35	1.53
K_f	0.46	0.41	0.38
R^2	0.9983	0.9986	0.9908

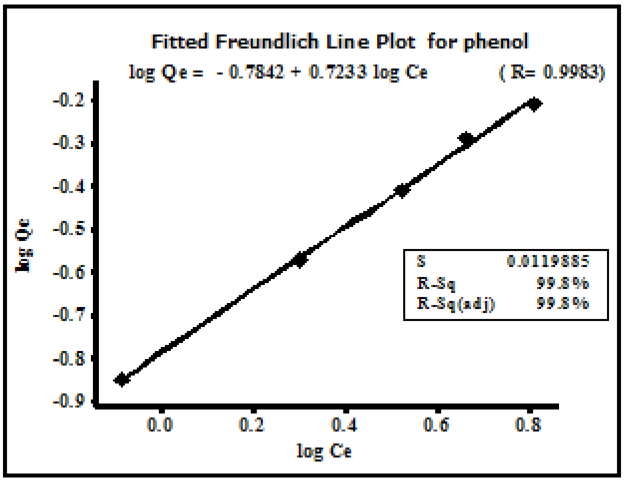

Figure 8: Freundlich adsorption isotherm of phenol

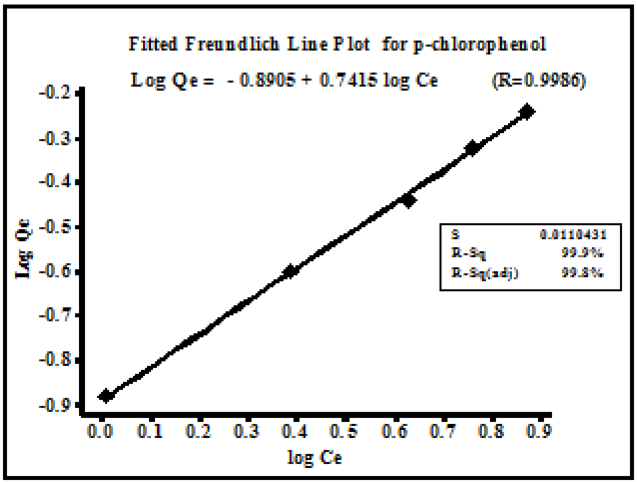

Figure 9: Freundlich adsorption isotherm of ρ-chlorophenol

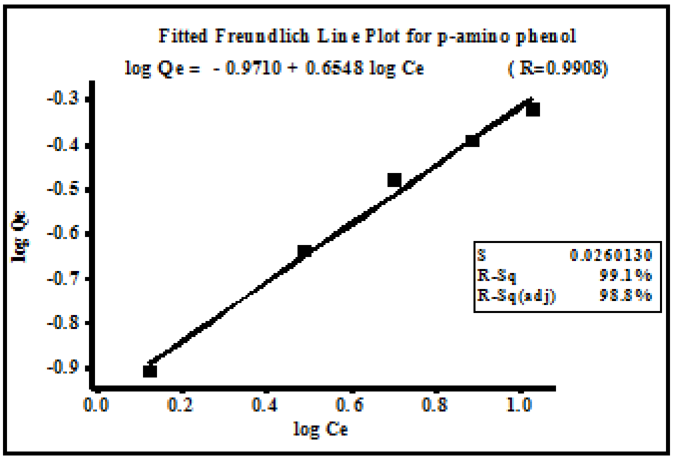

Figure 10: Freundlich adsorption isotherm of ρ-amino phenol.

As shown from Table 2 , the three plots gave a strong correlations between the ordinates which were closer to unity. On the other hand, the analysis of variance (ANOVA) also proved thelinear regression for all phenol compounds were statistically valid. Thisbecause of the ratio (MSreg/MSerror) for 1 and 4 degree of freedom (dof) , larger than critical value(F1,3= 10.13 at 95% CI),indicating that the predication based on the regressionline is satisfactory (Table 4) .Based on the R^2 values , the adsorption of all adsorbates on modified porcelain are best fitted on the Therefore The adsorption Freundlichisotherm equation.

Table 4: Analysis of Variance table of regression line for the three plots

compound	Source dof SS MS F P
Ph	Regression 1 0.257489 0.257489 1791.54 0.000 Residual Error 3 0.000431 0.000144 Total 4 0.257920
ρ-CPh	Regression 1 0.257554 0.257554 2111.98 0.000 Residual Error 30.000366 0.000122 Total 40.257920
ρ-APh	Regression 1 0.219050 0.219050 323.71 0.000 Residual3 0.002030 0.000677 Total4 0.221080

dof=degrees of freedom, SS: sum of squares, MS: mean of squares, F (Fisher F-test); p:probability

Thus, it can be concluded that the best fit of equilibrium data in theFreundlich isotherm. It can be noted (Table 2) that the value of (n: adsorption intensity) are all more than 1.00 for all phenol compounds which can be ascribed to the molecular interaction between adsorbates and adsorbent and indicating that the heterogeneity surface and adsorption favourability of the adsorbent [46].Whilst the K_f values were found to be 0.46, 0.41and 0.38 for Ph, ρ-CPh and ρ-APh respectively, indicating that the uptake of phenols on the modified adsorbent increased in the order Ph > ρ-CP > ρ-APh.

3.9 Analytical Application

A preliminary investigation was performed to exploit the prepared adsorbent for the analytical purposes in an attempt to expand the work and efficiency of this new adsorbent surface for the separation and enrichment of analytes in different mixture. At first, a study was conducted to compare the percent removal of phenol at different concentrations (1-5 μg mL^{-1}) using a home-made cartridge comparing with commercial one. The results are summed up in Table 5. It was shownthat the phenol was entirely removed at concentration of 3 μg mL^{-1} which represent the highest concentration was removed by home-made cartridge.

Table 5: The removal percentage of phenol by commercial cartridge (C18) compared with home-made cartridge

Initial conc. phenol before treatment (μg mL^{-1})	Commercial cartridge (C18)			Home-made cartridge		
	Conc . after treatment (μg mL^{-1})	Q_e (mg/g)	Removal (%)	Conc. after treatment (μg mL^{-1})	Q_e (mg/g)	Removal (%)
1	0.00	0.002	100.00	0.00	0.002	100.00
2	0.00	0.004	100.00	0.00	0.004	100.00
3	0.00	0.006	100.00	0.00	0.006	100.00
4	0.00	0.008	100.00	0.71	0.007	82.25
5	0.75	0009	71.00	1.23	0.008	47.80

A 250 mL of phenol (3 μg mL^{-1} pH 2) was eluted with 4 mL of different solvents namely ethanol, acetonitril and diethyl ether by varying elution time from 5-30 min using home-made at flow rate 17.36 mL min^{-1}of and commercial cartridges at 16.23 mL min^{-1}. The results aredepicted in Figures 11 and 12. The results were revealed that the adsorption capacity of commercial cartridge was of 1.35 fold more than our laboratory-made cartridge, but the complete recovery of phenol with ethanol and acetonitrile at elution time from 5 to 30 min was achieved in both cartridges. whilst, the recovery percentage of phenol with elution of diethyl ether was of less 100%, i.e. from 53.82-87.92% using a commercial C18 cartridge and from 41.88-86.27% with home-made cartridge. These findings have encouraged the authors in continuing to conduct more experiments for the evaluating the home-made cartridge in the separation and preconcentration of phenolic compounds in a mixture of environmental samples rather than in phenol alone , and the authors are intending to publish it as an independent work in the near future

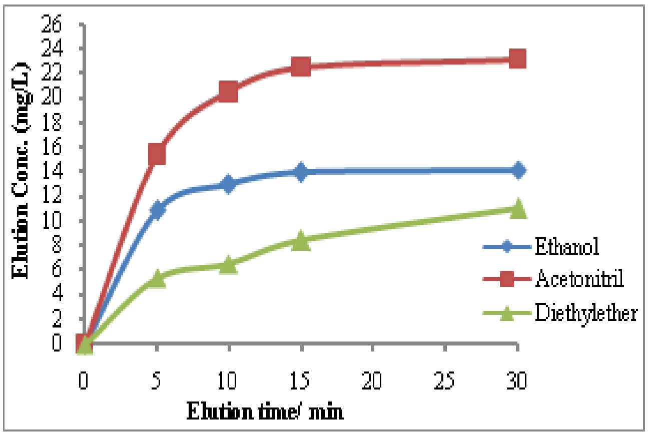

Figure 11: Effect of time on the elution concentration for the prepared cartridge with adsorbent under study

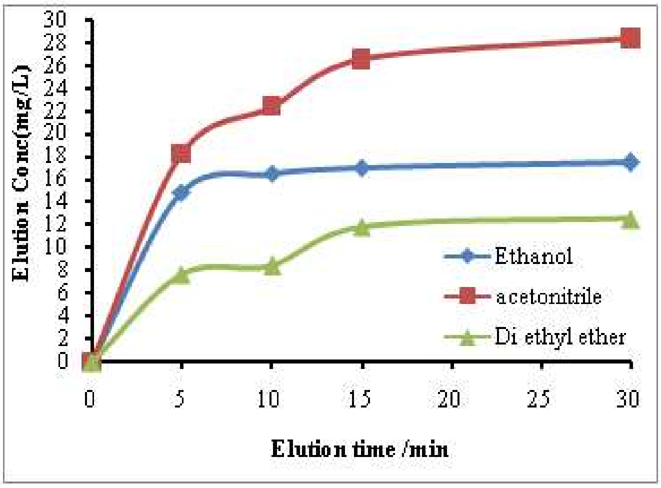

Figure 12: Effect of time on the elution concentration for a commercial C18 cartridge

4. Conclusions

In this study, the reflux method was use as new method for converting the normal phase (Porcelain surface) by loading using waste diesel oil as suitable adsorbent for removal of phenolic compounds from water. The experimental adsorption data were implemented in this direction. Such method is good preconcerated for compounds of low concentrations in contaminated water.

References

[1] M.T.Uddin, M.S. Islam, and M. Z, Abendin , " Adsorption of phenol from aqueous solution by water hyacinth ash" , j. Eng. and Appl. Sci. , 2(2) 11-17, 2007.

[2] S. , Kumar, K. Mohanty, and B. Meikap , ," Removal of phenol from dilute aqueous solutions in a multistage

bubble column adsorber using activated carbon prepared from tamarindus indica wood)" , J. of Environ. Prot. Sci., 4, 1-7, 2010.

[3] P. Chocholous,, K., D. , Satins K., R., Sladkovs Pilova, M. and P. , Solich, "Determination of pesticides fenoxcarb and permethrin by sequential injection chromatography using minlaturized monolithic columns", Talanta, 77, 566-570, 2008.

[4] K. Sunil, and K., Jayant, "Adsorption for Phenol Removal-A Review", Int.J. Sci. Eng. and Res. , 1(2) 85-96,2013.

[5] M. Sarkar,. and K.P., Acharya, " Use of fly ash for the removal of phenol and its nalogues from contaminated water", Waste Management, 26, 559-570, 2006.

[6] O. O., Olujimi, O. S., Fatoki, J. P. Odendaal, And J. O. , Okonkwo, " Endocrine isrupting chemicals (phenol and phthalates) in the South African environment: a need for more monitoring", Water SA, 36 (5), 671-682 2010.

[7] C.M., Santana, Z.S., Ferrera, M.E. Torres Padrón, and J.J., Santana Rodríguez, "Methodologies for the Extraction of Phenolic Compounds from Environmental Samples: New Approaches", Molecules 14: 298-320,2009.

[8] A. Balasubramanian, and S., Venkatesan, " Removal of phenolic compounds from aqueous solutions by emulsion liquid membrane containing ionic liquid $[BMIM]^+[PF6]^-$in tributylphosphate", Desalination, 289,27-34, 2012.

[9] X., Zeng , Y., Fan, Wu, G., C. Wang, and R., Shi, "Enhanced adsorption of phenol from water by a novel polar post-crosslinked polymeric adsorbent", J Hazard Mater,169,1022-1028, 2009.

[10] N.N., Rao, J.R. Singh, R. Mishra, and T., Nandi, "Liquid liquid extraction of phenol from simulated sebacic acid wastewater", J. Sci. and Indust. Res.,68, , 823-829, 2009.

[11] J-Q., Xu, W-H., Duan, X-Z. Zhou, and J-Z., Zhou, "Extraction of phenol in wastewater with annular centrifugal contactors" J.Hazard. Mater. ,131(1–3), 98–102,2006.

[12] M.S.A ., Palmaa, J.L. Paivab, and M., Zillic, " Batch phenol removal from methyl isobutyl ketone by liquid–liquid extraction with chemical reaction", Converti Chemical Engineering and Processing , 46 ,764–768, 2007.

[13] S.N., Jabrou, " Extraction of Phenol from Industrial Water Using Different Solvents", Res. J.Chem. Sci. , 2(4), 1-12, 2012.

[14] M., Caetano, C., Valderrama,A. Farran, and J.L., Cortina, "Phenol removal from aqueous solution by adsorption and ion exchange mechanisms onto polymeric resins" , J. Colloid. and Interface Sci., 338(2), 402–409,2009.

[15] I., Ilisz, Z. László, and A., Dombi, "Investigation of the photodecomposition of phenol in near-UV-irradiated aqueous TiO_2 suspensions. I: Effect of charge-trapping species on the degradation kinetics" , Applied Catalysis A: General , 180(1–2), 25–33, 1999.

[16] Akbal,. and Onar, N., "Photocatalytic Degradation of Phenol" Environ. Monit. and Assess., 83, (3), 295-302, 2003

[17] F, Metcalf and Eddy "Wastewater Engineering: Treatment and Reuse" (Mc. Graw Hill International Edition, Newyork, 2003.

[18] M.A, Zazouli,. and M., Taghavi, " Phenol Removal from Aqueous Solutions by Electrocoagulation Technology Using Iron Electrodes: Effect of Some Variables" Journal of Water Resource and Protection, 4, 980-983, 2012.

[19] Y.A., El-Ashtoukhy1, O. A., El-Taweel, and E.M., Nassef, " Treatment of Petrochemical Wastewater Containing Phenolic Compounds by Electro coagulation Using a Fixed Bed Electrochemical Reactor", Int. J. Electrochem. Sci., 8 ,1534 – 1550,2013.

[20] A., Bódalo, A.M., Hidalgo, E., Gómez, I., López, M Gómez,. and M.D., Murcia," Nanofiltration membranes to reduce phenol concentration in wastewater", Desalination, 246, 307-313, 2009.

[21]]H. K., Koseoglu, B. I., Harman, N.O., Nevzat ,N. Yigit, Kabay, and M., Kitis,"The impacts of operational conditions on phenol removal by nanofiltration membranes", Desalination and Water Treatment, 26, 118-123,2011.

[22] U., Ipek,"Phenol removal capacity of RO with and without pre-treatment", Filtration & Separation,41(7), 39–40, 2004.

[23] B.,Marrot , Barrios-Martinez, A., P.Moulin, and N., Roche , "Biodegradation of high phenol concentration by activated sludge in an immersed membrane bioreactor", Biochemical Engineering Journal (30) 174–183, 2006.

[24] K.M. Basha, Aravindan, A.Rajendran, and V.,Thangavelu, "Recent advances in the Biodegradation of Phenol: A review" Asian j. Exp. Biol. Sci., Vol 1 (2), 219-234, 2010.

[25] R.,Pishgar, G., Najafpour, B.N., Neya, N.Mousavi, and Bakhshi, "Anaerobic Z., Biodegradation of Phenol: Comparative study of Free and Immobilized Growth" Iranica Journal of Energy & Environment ,4, 348-355, 2011.

[26] N.V , Pradeep Anupama , U.S ,Hampannavar. "Biodegradation of Phenol using Rotating Biological Contactor" international journal of environmental sciences , 2(1),105-113, 2011

[27] A., Almasi, M. Pirsaheb, and A., Dargahi, "The efficiency of anaerobic Wastewater stabilization pond in removing phenol from Kermanshah Oil Refinery Wastewater" , Iran J. Healthe and Environ., 5(2), 21-39, 2013.

[28] A., El-Abbassi , H., Kiai , J. Jan Hoinkis, And ,A., AHafidi"Removal of phenolic compounds by micellar enhanced ultrafiltration using an anionic surfactant", J. Mater. Environ. Sci. 5 (1), 57-66, 2014.

[29] W., Zhang, G., G., Huang,, J., Wei, Li, , R. Zheng, and Y., Zhou, " Removal of phenol from synthetic waste water using Gemini micellar-enhanced ultrafiltration (GMEUF)", J Hazard Mater. 15, 235-236:128-37, 2012.

[30] S.E.E., Laigwu, L., Ausman, ,G.V.,Awolola ,G.B. Adebayo, and R.M.K., Ajayi, "Adsorption of Pb (II) from aqueous solution by Activated carbon prepared from cow Dung", Adv. In. Sci., 3(3) : 442-446 ,2009 .

[31] X., Jia, B., Huang, F. Benjamin ,B.F. Bowers, and S., Zhao, "Infrared spectra and rheological properties of asphalt cement containingwaste engine oil residues", Construction and Building Materials 50 , 683–691, 2014.

[32] E.,Pretsch ,Clem,T.,Seihl,J.,and Simon,W., "Spectra Data for structure Determination of organic Compounds", Berlm:Springer- Verlag ,1981.

[33] S.E. Agarry, and M.O., Aremu," Batch Equilibrium and Kinetic Studies of Simultaneous Adsorption and Biodegradation of Phenol by Pineapple Peels Immobilized Pseudomonas aeruginosaNCIB 950", British Biotechnology Journal 2(1), 26-48, 2012.

[34] G., Vazquez, J., ÁLvarez, M. Freire, and M.,Calvo.," Determination of the optimal conditions for adsorption of cadmium ions and phenol on chestnut (castanea sativa shell)" , Global Nest J., 11(2),196- 204 (2009).

[35] I. A. W.,Tan, B. H. Hameed, and, A. L., Ahmad "Equilibrium and Kinetic studies on basic dye adsorption by oil plam fiber activated carbon", J. Chem. Eng.,127,111-119, 2007.

[36] AA .Magda Akl, B. Magda Dawy and A .Asmaa Serage,"Efficient Removal of Phenol from Water Samples Using Sugarcane Bagasse Based Activated Carbon", J Anal Bioanal Tech, 5,1-12,2014

[37] V.C., Srivastava, M. M., Swammy, I.D., Mall, B. Prasad, and I.M. Mishra, " Adsorptive removal of Phenol by Bagasse flies ash and activated carbon: equilibrium, kinetics and thermodynamics", Colloids Surf. A Physicochem Eng. Aspects. 272: 89 – 104, 2006.

[38] S.H. Lin, and R.S.," Juang, Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: a review", J. Environ. Manag. , 90,1336-1349.2009.

[39] O.A., Ekpete, A.I., Spiff, M. Horsfall, and P., Adowei,"Adsorption of Phenol and Chlorophenol in Aqueous Solution on a Commercial Activated Carbon in Batch Sorption Systems" , Innovations in Science and Engineering 2, 72-78, 2012.

[40] Y.P., Chauhan, M., Talib, V.C., Renge, S.L. Bhagat, and S.V. Khedkar,.," Adsorption of phenol onto Chafa (Michella Champaka L.)tree leaf powder",Indian Journal of Science,1(1), 36-39, 2012.

[41] A. Gupta, M., Abdul Rafe," Removal of phenol from wastewater using Mango Peel", International Journal of Engineering and Technical Research (IJETR) 1(9), 58-62, 2013.

[42] A.T.M., Din, B.H. Hameed, and A.L. Ahmad,., " Batch adsorption of phenol onto physiochemical activated coconut shell" J. Hazard. Mater., 161(2-3), 1522-1529 ,2009.

[43] S. Mishra, and J., Bhattacharya, " Potential of leaf litter for phenol adsorption - A kinetic study", Indian J. Chem. Technol., 13(3), 298-301 ,2006.

[44] A. Sharma, and K.G., Bhattacharyya, "Azadirachtaindica (Neem) leaf powder as a biosorbent for removal of Cd (II) from aqueous medium", J. Hazard.Mater. B125, 102-112,2005.

[45] M.N., Rashed,"Organic Pollutants - Monitoring, Risk and Treatment" InTech publisher , Europe , Croatia , 1st ed. Ch7, pp. 169 2013.

[46] F.H. Frimmel, and L., Huber, "Influence of humic substances on the aquatic sorptionof heavy metals on defined minerals phases" Environment International 22,507-517, 1996.

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