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Removal of Phenol Compounds from Aqueous Solution Using Coated Sand Filter Media

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Abstract

Coated sand (CS) filter media was investigated to remove phenol and 4-nitrophenol from aqueous solutions in batch experiments. Local sand was subjected to surface modification as impregnated with iron. The influence of process variables represented by solution pH value, contact time, initial concentration and adsorbent dosage on removal efficiency of phenol and 4-nitrophenol onto CS was studied. Batch studies were performed to evaluate the adsorption process, and it was found that the Langmuir isotherm effectively fits the experimental data for the adsorbates better than the Freundlich model with the CS highest adsorption capacity of 0.45 mg/g for 4-nitrophenol and 0.25 mg/g for phenol. The CS was found to adsorb 85% of 4-nitrophenol and 65% for phenol at an initial concentration of 25 mg/ℓ.

Key Words: coated sand, phenol, 4-nitrophenol, adsorption, batch study.

Introduction

Wastewaters containing phenolic compounds are serious environmental problem , and cannot simply be released into the environment without treatment .

Several methods are currently used for the removal of phenol and its derivatives from wastewater , e.g. microbial degradation [1] ,chemical oxidation [2] , incineration [3] , solvent extraction [4] and irradiation [5] . However, by far the most frequently used technology is adsorption by solid phase . Several different adsorbent solids such as activated carbon [6, 7, 8, 9], silica [10] , glass powder [11] , polymeric resins [12,13] , fly ash [14, 15, 16, 17, 18, 19, 20], peat [21, 19], kaolinite [22] and zeolites [23, 24] have all

been proposed to remove phenolic pollutants from wastewaters .

Recent studies have shown that metal oxides (such as iron oxides, aluminum oxides or manganese oxides) have relatively high surface area and surface charge, and can be applied to the removal of heavy metals and organic matters from water and wastewater [25, 26, 27, 28]. However , most of metal oxides are available only as fine powders or are generated in separation. Beside, due to their low conductivity, the aqueous solutions as hydroxide floc or gel. Therefore, they are limited to reactor configurations incorporating with large sedimentation basins or filtration units because of the difficulty in solid/liquid metal oxides alone are not suitable as filter media [29].

Recently, some researchers have developed techniques for coating metal oxides onto sand surface in order to overcome the above problems of using metal oxides powders in water treatment process . In this study kind of iron-oxide-coated sand was prepared by coating process and the phenol and 4-nitro phenol adsorption from aqueous solution was investigated by batch experiments in order to get available CS filter media for effective removal of phenol and its derivatives.

Experimental Procedure
Adsorbent Material

To prepare CS filter media, natural quartz sand (QS), with a particle size ranging from 0.5 to 0.8 mm, was used as the supporting material for iron oxide. Firstly , the sand was pre-washed several times with tap water until run-off was clear . After the sand was dried at 110ºC, it was soaked in 0.1M HCI solution for 24h. Then the sand was rinsed to remove impurities, dried at 110ºC and finally stored in capped bottles.

Stock solution of 2.5 M Fe (III) was prepared by dissolving FeCl3·6H$_2$O in deionized water. CS was prepared with the following coating processes: The solution containing a mixture of 400 mL of 2.5 M Fe (III) and 1 mL of 10 M NaOH was pourd over 800 mL dried sand placed in a heat-resistant dish . after gentle agitation , the mixture was heated for 96 h at 110ºC and then at 200ºC until it appeared to be dry. After cooling , the coated sand was washed with tap water until run-off was clear , then the coated sand was dried at 110ºC . After above coating step was finished , the sand was coated again according to the same step , and stored in polystyrene bottles for further use [30] .

Adsorbate Material

The stock solution was prepared by diluting the required quantities of phenol or 4-nitrophenol with distilled water to obtain adsorbate solution of various initial concentrations.

The effect of pH, contact time and (CS) loading was studied using 25 mg/ℓ of phenol or 4-nitrophenol and 5 gm of CS was adjusted with either dilute HCl or NaOH solution to a constant value. All the pH measurements were done with a pH meter (827 pH Lab, Metrohm). Each flask was capped and inverted 3 times to mix the contents thoroughly and then allowed to stabilize for 10 to 15 min . The effect of CS loading at 307 K were conducted by contacting initial phenol and 4-nitrophenol concentrations of 20 mg/l with varying quantities of CS (1 to 7) g in a series of 25 ml Pyrex conical flasks at a pH of 3.12 ± 0.10 . The effect of initial concentration of phenol and 4-nitrophenol was studied using different initial concentrations of (20, 40, 60, 80, 100 mg/l) with 1 g of CS, stirred at 180 rpm for 3 hours. The concentration changes of the individual compounds in the solutions were determined by means of UV-VIS spectrophotometry (SQ-4802 Double Beam). The maximum absorbance for each solute from the highest standard solution prepared were found using scanning spectrophotometry at the respective wavelength maxima λ . The λse used were 270 nm and 320 nm for phenol and 4-nitrophenol respectively. The calibration plot of absorbance vs. concentration for all the standards showed a linear working range up to 30 mg/l with correlation coefficient $\geq$ 0.99. the supernatant solutions obtained after adsorption

were also analysed using the same wavelengths .

Adsorption Kinetics

Kinetic tests using a mixture of phenol or 4-nitrophenol were performed in a batch fashion . The initial solutes mix was analyzed to determine the initial concentration of the solutes before mixing with the CS. For each adsorption data point , a 25 ml aliquot of the adsorb ate solution having an initial phenol or 4-nitrophenol concentration of 20 mg/l , constant CS loading of 5 g at temperature of 307 K were introduced into a series of 25 ml Pyrex conical flasks for different contact times and at a pH of about 3. The conical flasks were placed and shaken in a Labcon platform shaking incubator (Model FSIM-SPO16) where the last sample was collected after 300 min of contact time and at a constant stirring speed of 200 rpm . The samples were covered throughout the experiment and the supernatant solution filtered through whatman micro-fiber filters of 0.45 μm to determine the concentration of each solute left after different time intervals of agitation (15,30,60,….,300 min) .The flasks were shaken in a Labcon platform shaking incubator (Model FSIM-SPO16) to attain equilibrium after about 22 h of contact time and at a constant stirring speed of 200 rpm.

Adsorption Isotherms

The ability of the prepared CS to remove the phenol or 4- nitro phenol from aqueous solutions was determined under batch mode conditions. The equilibrium isotherms were determined by mixing 5 gram of CS with different concentrations (20, 40, 60, 80 and 100 mg/l) of each solution of phenol or 4- nitro phenol in conical flasks. Flasks were shaken at 200rpm overnight to assure that equilibrium was reached. The residual concentration was analyzed using Atomic Absorption Spectrophotometer. Data obtained from the adsorption isotherm tests were used to determine the adsorption capacity of CS . The equilibrium adsorption uptake and percentage removal of phenol from the aqueous solution q_e (mg/g) was determined using the following relationship :

Amount adsorbed $q_e = \frac{(Co-Ce)V}{w}$ ...(1)
(mg of adsorb ate / g of adsorbent)

and, % removal $= \frac{100(Co-Ce)}{Co}$ …(2)

Where:
C_o is the initial sorbet concentration (mg/ℓ)
C_e is the equilibrium sorbet concentration (mg/ℓ)
V is the volume of solution (ℓ)
w is the mass of the adsorbent (g)

Results and Discussions
Characterization of CS Filter Media

QS and CS surface photographs are shown in Fig.1. Magnification by SEM of 2000 and 25000x is made to show the morphology of the surfaces. It can be seen that the deposition had changed the smooth surface of sand. New cracks occurred on the surface with new microspores appeared between the new crystals or cubes deposited of iron oxide. It can be concluded that the coating step changed the morphology of natural sand. The amount of iron ox hydroxide deposits onto sand was determined to be about 30 mg-Fe/g-sand Jianbo et al [30] had used the same coating procedure and analyzed this amount to be 31.13mg-Fe/g-sand.

(a) QS   (b) CS

(c) QS   (d) CS
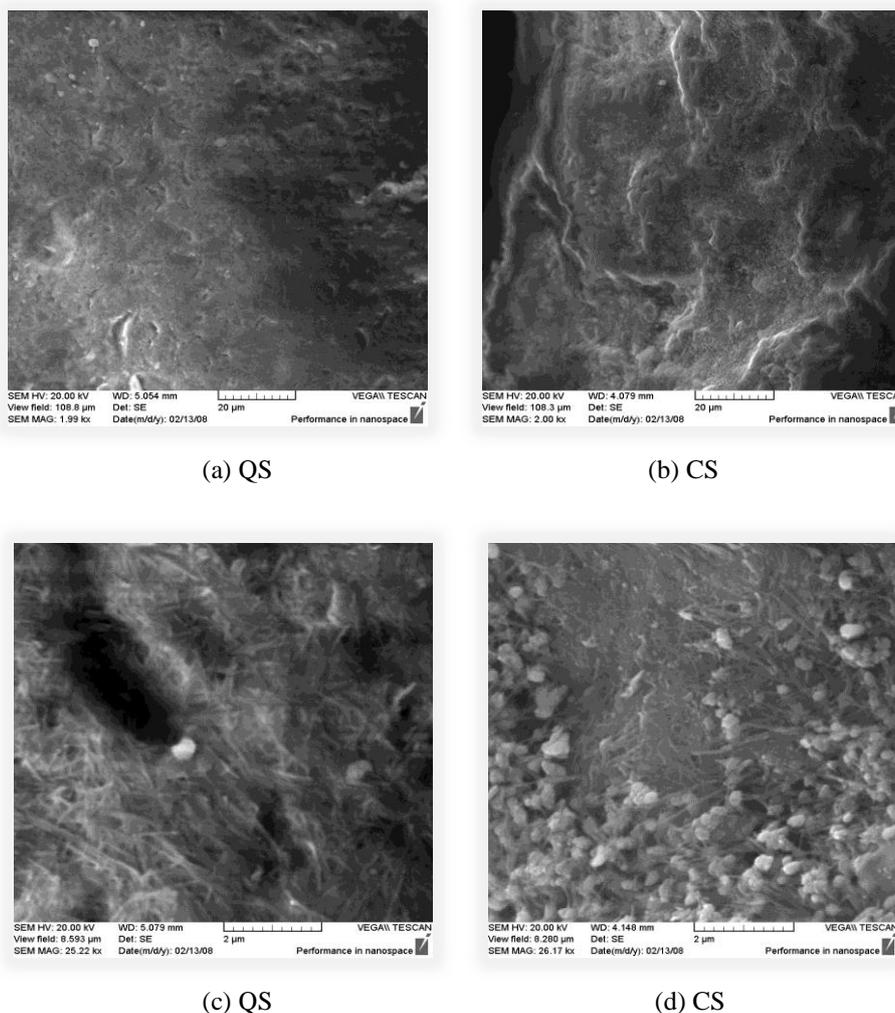
Fig.1, SEM for natural sand QS (a and c) and the prepared CS (b and d). (a) and(b) at 2000 magnification. (c) and (d) at 25000 magnification

Adsorption Time

Fig. (2) Represents the results for the effect of contact time on the removal of phenol and 4-nitrophenol from aqueous solution at an initial concentration of 20 mg/ℓ.

It can be seen that the amount of all the adsorbents adsorbed onto CS increases with time and about 65%, 70% of phenol and 4-nitrophenol had been removed within the first 15 min of agitation, respectively, after which the process approaches equilibrium. The time profile for adsorbents is a single, smooth, and continuous curve leading to saturation, which suggests possible monolayer coverage of the adsorbents on the surface of the CS.
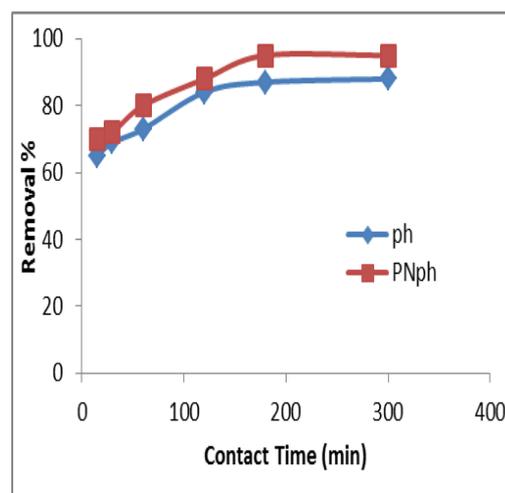
Fig. 2, Effect of contact time on percentage removal

Adsorption Isotherms

The analysis of the adsorption isotherms is important for design

purpose. Therefore, experimental data were analyzed with well-known two-parameter adsorption isotherm models including the Langmuir, Freundlich isotherms.
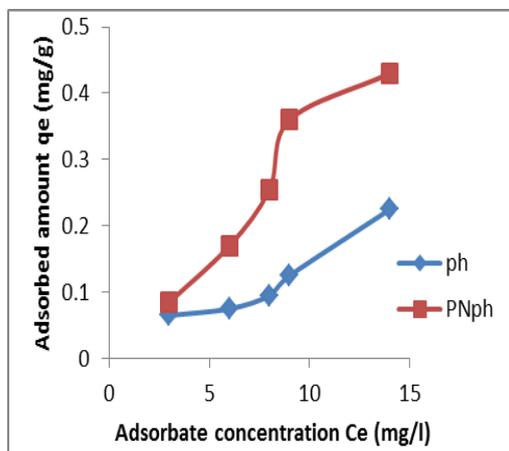
Fig. 3, Adsorption isotherms of phenol and 4-nitrophenol on CS

Phenol and 4-nitrophenol adsorption isotherms obtained for CS are shown in Fig.3. Ttese isotherms represent the adsorption behavior of phenolic compounds at various temperatures as a function of equilibrium aqueous concentration, for a contact time of 24 h.

The rearranged Langmuir isotherm can be described as:

$$\frac{1}{Q} = \frac{1}{Q_\infty} + \left(\frac{1}{\beta Q_\infty}\right)\left(\frac{1}{C_e}\right) \qquad \dots(3)$$

Where:
β is an adsorption equilibrium constant related to the binding energy

The Langmuir adsorption isotherm is based on the concept that solid surfaces have finite adsorption sites. When all the adsorption sites are filled, the surface will no longer be able to adsorb solute from the solution. The maximum amount of solute (Q_m) adsorbed in a particular system can be estimated from the isotherm parameters. The plot of $\frac{1}{Q}$ vs. $\frac{1}{C_e}$

should yield a straight line. The slope is $\frac{1}{Q}$ and the intercept is $\frac{1}{Q_m}$. The freundlich adsorption isotherm can be written in the form:

$$\text{Log } Q = \log K_f + \frac{1}{n} \log C_e \qquad \dots(4)$$

The freundlich isotherm predicts that the adsorb ate concentration on the surface of an adsorbent will increase when there is an increase in the initial adsorb ate concentration in the aqueous solution. The experimental data obtained are plotted as log Q_e versus log C_e, to obtain the constants K and $\frac{1}{n}$. The constant K_f is a comparative measure of the adsorption capacity of the adsorbent, while n is an empirical constant. The magnitude of n gives an indication of the favorability of adsorbent/adsobate system. Values of n > 1 signify that the solute has a low affinity for the adsorbent at low concentration. Likewise, a value of n < 1 is an indication of favorable adsorption and a high affinity between the solute and solid phase. The freundlich (K_f and $\frac{1}{n}$) and Langmuir constant (β and Q_m) determined from the adsorption isotherm for phenol and 4-nitrophenol depicted in figs. 3 and 4 are summarized in Table 1.

The correlation coefficient values determined for each of the adsorption isotherm indicates that the Langmuir model effectively fits the experimental data better than the Freundlich model. The adsorption capacity for phenol and 4-nitrophenol at the maximum residual concentration was calculated using the Langmuir constant β at an initial concentration of 20 mg/l for all the adsorbents and the values obtained were 3.779 mg/g, 3.679 mg/g for phenol and 4-nitrophenol, respectively.

Table 1, Adsorption isotherm models for phenol and 4-nitrophenol on CS

Model	Parameter	ph	PNph
Langmuir $Q_e = \dfrac{Q_m \beta C_e}{1 + \beta C_e}$	Q_m	3.779	3.679
	β	0.784	1.115
	R^2	0.837	0.962
Freundlich $q_e = K_f C_e^{1/n}$	K_f	4.265	0.728
	n	37.07	37.53
	R^2	0.764	0.998
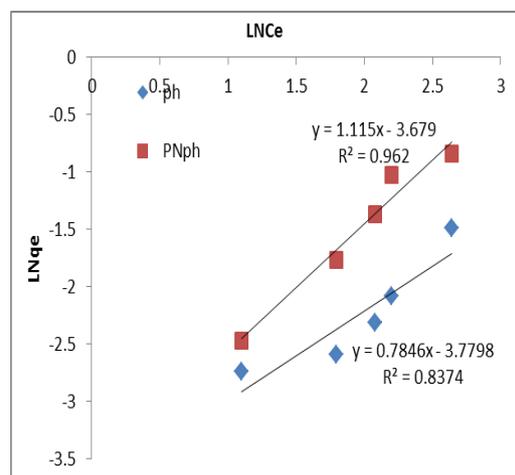
Fig. 3, The linearized Freundlich adsorption isotherm for phenol and 4-nitrophenol mixtures onto CS
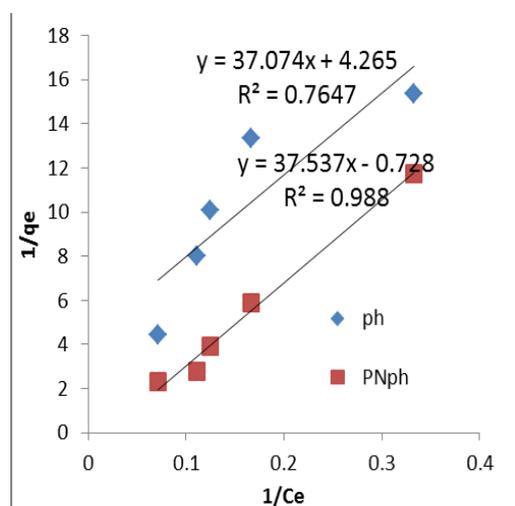
Fig. 4, The linearized Langmuir adsorption isotherm for phenol and 4-nitrophenol mixtures onto CS

Effect of Initial pH

The pH of the aqueous is an important variable that influences the adsorption at the solid-liquid interface. The effect of variation of the initial solution pH (3,4,5,6,7,8,9,10,11,12,13) on the adsorption of phenol and 4-nitro phenol is illustrated in Fig.5. for CS, the adsorption removal percentage decreases with an increase in pH from 3.6 to 10.2 and from 3.5 to 8 for phenol and 4-nitrophenol respectively. Fig.5 also shows that 70% maximum removal percentage of phenol is achieved at pH value of 3.6.While for 4-nitrophenol, a maximum removal percentage of 97% is obtainedat pH of 3.5.Therefore, the values of 3 6 and 3.5 are considered to be the best pH for removal of phenol and 4-nitrophenol, respectively.
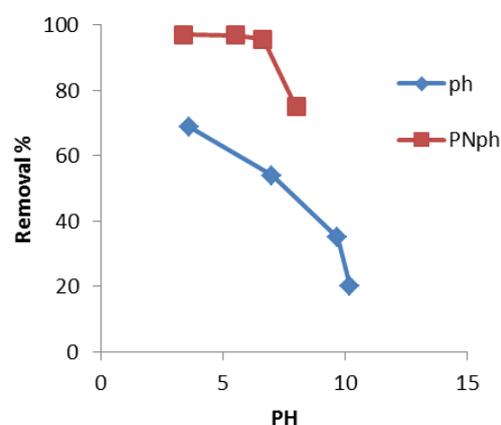
Fig. 5, Effect of solution pH on percentage removal

Effect of Initial Concentration

The effect of initial concentration of phenol and 4-nitrophenol was studied using different initial concentrations of (20, 40, 60, 80, and 100) with 1 g of each CS, stirred at 180 rpm for 3 hours. This effect is shown in Fig.6. Increasing initial concentration of phenol and 4-nitrophenol decreases the removal efficiency as can be seen in Fig. 6, especially for phenol. This can

be due to the absence of adsorption sites for the extra molecules at a constant amount of the adsorbent, while for the adsorption of 4-nitrophenol, which have smaller radius, it slightly different is high for all concentrations.
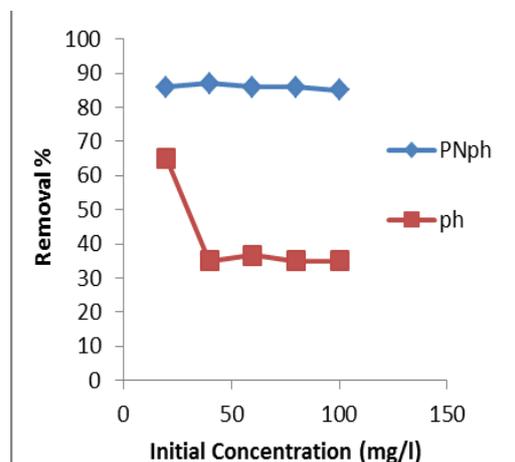
Fig. 6, Effect of initial concentration on the removal efficiency

Effect of Adsorbent Loading

The effect of adsorbent loading is studied using 25 ml of solution of initial concentration of 20 mg/ℓ using (1, 2, 5 and 7g) of CS, stirred at constant speed of 200 rpm for 3 hours. The removal efficiency increased as the amount of CS increased as it appears in Fig.7. The increase in the efficiency can be explained by the increasing surface area or binding sites where the adsorption takes place with the increasing of CS dosage.
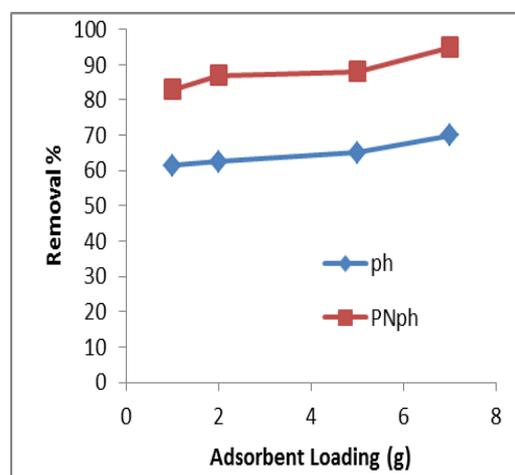
Fig. 7, Effect of adsorbent loading on the removal efficiency

Conclusions

1. A maximum 4-nitrophenol removal percentage of 97% were obtained at 3.5 solution pH and 300 min contact time, and a maximum 4- nitro phenol removal percentage of 87% at 20 mg/ℓ initial concentration solution stirred at 180 rpm for 3 hours.
2. The adsorption process obeys first-order kinetics. The Langmuir isotherm fits and describes the adsorption mechanism better than the Freundlich one for the two phenol derivatives.
3. The prepared coated sand CS was found to have good adsorption properties and can provide an effective technology based on adsorption/ filtration using CS filter media for phenol derivatives removal from water and wastewater.

References

1- Munaf E., Zein R., Kurnidi R. and Kurnidi I. (1997), The use of rice husk for removal of phenol from waste water as studied using 4-aminoantipyrine spectrophotometric method. Environ. Technol. 18(3) 355-358.
2- Bertoncini C., Raffaelli J., Fassino L., Odetti HS and Botani EJ. (2003), Phenol adsorption on porous and non-porous carbons. Carbon 41 (6) 1101-1111.
3- Khalid M., Joly G., Renaud A. and Magnoux P., (2004). Removal of phenol from water by adsorption using zeolites. Ind. Eng. Chem. Res. 43, 5275-5280.
4- Aksu Z. (2005). Application of biosorption for the removal of organic pollutants: Areview. Process Biochem. 40, 997-1026.
5- Denilzi A., Cihanger N., Tuzmen N. and Alsancak G. (2005). Removal of chlorophenols from aquatic

systems using the dried and dead fungus Pleurotus sajor caju. Bioresour. Technol. 96, 59-62.

6- Garcia-Araya JF, Beltran FJ, Alvarez P. and Masa FJ. (2003). Activated carbon adsorption of some phenolic compounds present in agro industrial wastewater. Adsorption 9 (1), 107-115.

7- Nouri S., Haghsersht F., and Maxlu GQ. (2002). Comparison of adsorption capacity of p-Cresol and p- Nitrophenol by activated carbon in single and double solute. Adsorption 8, (3), 215-223.

8- Abbas H. Sulaymon and Kawther W. Ahmed (2008). Competitive adsorption of furfural and phenolic compounds onto activated carbon in fixed bed column. Environmental Science and Technology, 42(2), 392-397.

9- Abbas. H. Sulaymon, Dheyaa W. Abbood and Ahmed H. Ali (2012). Removal of phenol and lead from synthetic wastewater by adsorption onto granular activated carbon in fixed bed adsorbers: prediction of breakthrough curves. Desalination and water treatment, 40, Issue 1-3, 244-253.

10- Hanna K., Beurroies I., Denoyerl R., Desplantiergiscard D., Galarneu A., and Direnzo F. (2002). Sorption of hydrophobic molecules by organic/inorganic mesostructures J. Colloid Interface Sci. , 252, 276-283.

11- Atun G. (1992). The adsorption of nitrophenols on a special adsorbent prepared from glass powder. Spectrosc.Lett. 1992, 25, (5), 741-756.

12- Wagner K. and Schultz S. (2001). Adsorption of phenol, chlorophenols, and dihydroxybenzens onto unfunctionalized polymeric resins at temperatures from 294.15 K to 318.15 K. J. Chem. Eng. Data 46,322-330.

13- Abburi K.(2003). Adsorption phenol and p-chlorophenol from their single and biosolute aqueous solutions on Amberlite XAD-16 resin. J. Hazard. Mater. 105, 143-156.

14- Akgerman A. and Zardkoohi M. (1996). Adsorption of phenolic compounds on fly ash. J. Chem. Eng. Data. 41, 185-187.

15- Kao PN., Tzeng JH. And Huang TL. (2000). Removal of chlorophenols from aqueous solution by fly ash. J. Hazard. Mater. 76, 237-249.

16- Sarkar M., Acharya KP. And Bhattacharya B. (2005). Removal characteristics of some priority organic pollutants from water in a fixed bed fly ash column. J. Chem. Technol. Biotechnol. 80, 1349-1355.

17- Sarkar M. and Acharya KP. (2006). Use of fly ash for the removal of phenol and its analogues from contaminated water. Waste Manage. 26, 559-570.

18- Srivastava Vc., Swamy Mm., Mall Id., Prasad B. and Mishra Im.(2006). Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, Kinetics and thermodynamics. Colloids Surf. A. 272, 89-104.

19- Viraraghavan T. and Alfaro F. (1998). A by peat, fly ash and bentonite. J. Mater. 57, 59-70.

20- JH Potgieter et. Al. (2009). Adsorptive removal of various phenols from water by South African coal fly ash. Water SA (on line), Vol.35, No. 1, 89-96.

21- Allen Sj. (1987). Equilibrium adsorption isotherms for peat. Fuel 66, 1169-1175. *Appl. Sci. 1 (4) 321-326.*

22- Barhoumi M., Beurroies I., Denoyel R., Said H. and Hanna K.

(2003). Co-adsorption of alkylphenols and nonionic surfactants onto kaolinite. Colloids surf. A. 219, 25-33.

23- Koh S. and Dixon JB. (2001). Preparation and application of organominerals as adsorbents of phenol,benzene and toluene. Appl. Clay Sci. 18, 111-122.

24- Sismanoglu T. and Pura S. (2001). Adsorption of aqueous nitrophenols on clinoptilolite. Colloids Surf. A. 180, 1-2.

25- Mark M. Benjamin, Ronald S. Sletten, et al. (1996). Sorption and filtration of metals using iron-oxide-coated sand. Water research, 30, 11, 2609- 2620.

26- G. Villasenor Nano, T.J. Strathmann (2006). Ferrous iron sorption by hydrous metal oxides. Journal of Colloid and Interface Science, 297,443-454.

27- A.H. Sulaymon, W.M.S. Kassim and Mohsin J. Nasir (2012). Competitive adsorption of organic pollutants from wastewater onto organoclay in batch adsorber. International Journal of Environment and Development.

28- Nada S. Ahmedzeki (2013). Adsorption filteration technology using iron-coated sand for removal of lead and cadmium dsorption of phenol from wastewater ions from aquatic solutions. Desalination and water treatment, 11 Feb.

29- Theis, T.L. and Iyer, R., et al. (1992). Evaluating a new granular iron oxide for removing lead from drinking water. J. Am. Water works Assoc., 84, 101-105.

30- Jianbo L., Liping S., Xinhua Z., Bin l., Yinlei L., Lei Z., (2009). Removal of Phosphate from Aqueous Solution Using Iron-oxid-coated Sand Filter Media: Batch Studies, 2009. International Conference on Environmental Science and Information Application Technology.