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Solid phase extraction of phenol from wastewater by magnetic iron oxide nanoparticles

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Abstract: This study present a new removal method of phenol from wastewater by iron oxide nanoparticles (IONPs) modified with active carbon as solid adsorbent. The novel magnetic nanoparticles (nano-adsorbent) is quite efficient for removing phenol. Different parameters such as pH, agitation times, and amount of nanoparticles were optimized. In an aqueous solution of phenol, the adsorption data could be fitted by langmuir equation. The desorption conditions such as different composition percentage of ethanol solutions and pH were optimized. The phenol concentration was measured by spectrophotometric method based on ASTM D1783-01 at λ_{max} = 510 nm. The phenol in an aqueous solution removed up to 98% and was successfully applied for Fajr petrochemical wastewater samples.

Keywords: Iron oxide nanoparticles, solid phase extraction, and phenol removal.

1. Introduction

Many industrial wastes contain organics which are difficult or impossible to remove by conventional biological treatment processes. Phenols as a class of organics are similar in structure to the more common herbicides and insecticides in that they are resistant to biodegradation. Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for epoxy resins, adhesives and polyamide for various applications [1]. Phenol is also formed from the breaking of “bisphenol A” which is used as a monomer for production of polycarbonate and epoxy resins [2]. In the presence of chlorine in drinking water, phenol form chlorophenol, which has a medicinal taste and is quite objectionable [3]. Phenolic constitute the 11th of 126 chemicals which have been designated as priority pollutants by the United States Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to less than 1mg L^{-1} [4]. There are many methods such as oxidation with ozone/hydrogen peroxide [5], ion exchange [6], electrochemical oxidation [7], reverse osmosis [8], photo-catalytic degradation [9] and adsorption [10] which have been used for the removal of phenols. The treatment with active carbon is considered to be an effective method for phenol removal from wastewater because of its large surface area, micro-porous nature, high adsorption capacity, high purity and availability. However, activated carbons are notoriously difficult to separate from solutions and thus magnetic separation is an attractive alternative to filtration or centrifugation or coagulation. Because of this disadvantage, it is necessary to develop new solid phase extraction methods. Recently, a unique magnetic carrier technology (MCT) has been reported by several research groups. Attractive property of MCT is that magnetic particles can readily be isolated from sample solutions by the application of an external magnetic field. These particles are super paramagnetic, which means that they can readily be attracted by a magnet but do not retain magnetism after the field is removed. Therefore, suspended super paramagnetic particles tagged with organic contaminant (phenol) can be removed from the matrix by applying a magnetic field, but they do not agglomerate after removal of the field. Hence, the particles may be reused or recycled. To achieve this purpose we synthesize the solid phase from iron oxide nanoparticles and active carbon to remove phenol from Fajr petrochemical[1] wastewater up to 98 %.

2. Experimental

2.1. Instrumentation

The spectrophotometric measurements were carried out with a (perkin elmer lambada 25) UV/Vis spectrometer. A pH meter (691 metrohm, herisau Switzerland), a Nd-Fe-B magnet (1.2T, 5×4×2Cm), a balance (Sartorius, BL 210S, d=0.1mg), a Jar test stirrer (VELP® made in Italy), an oven (memmert) were used.

2.2. Reagents

All reagents and standards were of analytical grade and all dilutions have been carried out with demineralized (DM) water. pH adjustments were performed with 0.1 mol L^{-1} HCl (37%) and NaOH from Merck (Darmstadt, Germany). $FeCl_3.6H_2O$, $FeSO_4.7H_2O$, $K_3Fe(CN)_6$[2], 4- aminoantipyrine[3], ammonia solution (25%), ammonium chloride, powdered activated carbon were also prepared from Merck (Darmstadt, Germany).

2.3. Magnetization of Activated Carbon (MAC)[4] With Iron Oxide Nanoparticles

Activated carbon was magnetized by coprecipitation of a stoichiometric mixture of ferrous sulfate (1.2 g $FeSO_4.7H_2O$) and ferric chloride (2.7 g $FeCl_3.6H_2O$). At first 1 g of powdered activated carbon and 100 mL sodium hydroxide (49%) were mixed and stirred for 2 houres by a magnetic stirrer and then it was filtered to remove the excess amount of concentrate sodium hydroxide. Then 2.7 g $FeCl_3.6H_2O$ and 1.2 g $FeSO_4.7H_2O$ were mixed in 300 mL DM water which was deoxygenized by N_2 gas and its temperature was 60-70^{0}C. Finally alkalized active carbon was added to ferrous sulfate and ferric chloride solution little by little with vigorous agitation that can be influenced to decrease the size of nanoparticles which was deposited on the active carbon. This composite was collected by a strong magnet and thoroughly washed with DM water to remove excess amount of sodium hydroxide. After several times of washing it was dried in oven at 80^{0}C temperature for 1 hour.

2.4. Investigation of the magnetic property and phenol removal capability of MAC

To achieve a composite with high phenol removal capability and magnetic property, we synthesized different composite with changing the amount of active carbon (0.5, 1, 1.5, 2 g) which was added to the ferrous sulfate and ferric chloride solution. For testing of their phenol removal capability, 0.05 g of different prepared MAC was added to 10 mg L^{-1} phenol standard solution at pH=7.0 and it was stirred by a Jar test stirrer for 2 hours. After that the result was compared with 0.05 g active carbon and Fe_3O_4 separately. In spite of low phenol removal efficiency of composite No. 3 it was recognized as an ideal composite that is because of the highest magnetic property and it was used in the following tests. (Figure. 1) shows the result.

2.4. SPE procedure

The extraction procedure was carried out in a batch mode. 0.05 g MAC was added to 100 mL phenol standard solution with 10 mg L^{-1} concentration and it was stirred by a Jar test stirrer at RPM=200 for 2 hours in a 1000 mL beaker after pH adjustment. The beaker was placed on the strong magnet and the MAC was collected at the bottom of the beaker after 5 minutes. 50 mL from the supernatant was pipeted to a 100 mL Erlenmeyer and the residue of phenol concentrate on was determined.

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[1] - Fajr petrochemical company is located in Iran-Mahshar (Imam Khomeini port), pet zone, site 4

[2] - potassium hexacyano ferrate (III)

[3] -4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one

[4] - Magnetic Activated Carbon

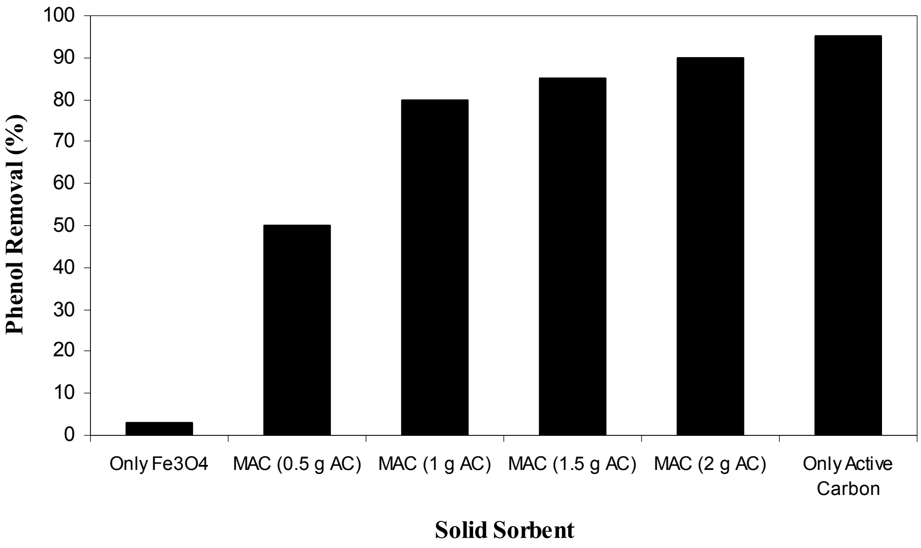

Figure 1. The effect of different solid sorbent in the removal of phenol.

2.5. Spectrophotometric Determination

The residue of phenol concentration in the supernatant solution was determined by spectrophotometric method based on ASTM D1783-01 [11] at $\lambda_{max} = 510$ nm. In this test method phenol form a reddish complex with 4-aminoantipyrine and $K_3Fe(CN)_6$ in the presence of ammonia/ammonium chloride buffer solution. A blank solution was also run without adding the analyte.

The percentage of phenol adsorption was calculated from below equation:

$$Phenol\,Removal(\%) = \frac{Ai - Af}{Ai} \times 100 \qquad (1)$$

A_i = the absorbance of initial solution at λ_{max}=510 nm
A_f = the absorbance of final solution after phenol removal at λ_{max}=510 nm

2.6. Method Validation

The spectrophotometric method was validated for linearity, precision, accuracy according to ASTM D1783-01[4]. The calibration curve of phenol was plotted by using of standard sample solution at seven concentrations in the range of 0.1-5 mg L^{-1} with regression coefficient R^2=0.9994. The LOD[5] with K=3 was obtained 1.3×10^{-3} and RSD[6] 1% and 0.46% was calculated for two standard solution (1, 5 mg L^{-1}), respectively.

The SPE procedure was also validated for reproducibility result by retesting two groups of eight phenol standard solutions with same concentration and calculating the relative standard deviation. RSD=2.7 % was achieved for 10 mg L^{-1} phenol standard solution and RSD=6.9% for 5 mg L^{-1} phenol standard solution.

3. Results and Discussion

3.1. Effect of pH

The adsorption of phenol by MAC was studied at various pH values. HCl and NaOH 0.1 mol L^{-1} were used for pH adjustment. For this test 0.05 g MAC was mixed by 100 mL phenol standard solution of 10 mg L^{-1} concentration and it was stirred for 2 hours with RPM=200 of Jar test stirrer. The highest adsorption of phenol by MAC was obtained at pH=7.0 but in the range of pH=5.0 to pH=7.0 the differences was negligible, therefore this range of pH is an optimum one, the lowest phenol removal was observed at pH=12. It is because of the dependency of phenol ionization and the formation of phenolate ion. At this alkali pH the presence of OH-ions on the MAC prevent the uptake of phenolate ions. The ionic fraction of phenolate ion (φ_{ions}) can be calculated from [1]:

$$\varphi_{ions} = \frac{1}{[1 + 10^{(pKa - pH)}]} \qquad (2)$$

Obviously, φ_{ions} increases as the pH value increase. Accordingly, phenol which is a weak acid (pK_a=10), will be adsorbed to a lesser extent at higher pH values due to the repulsive forces prevailing at higher pH values. Figure. 2 show the results.

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[5] - Limit Of Detection
[6] - Relative Standard Deviation

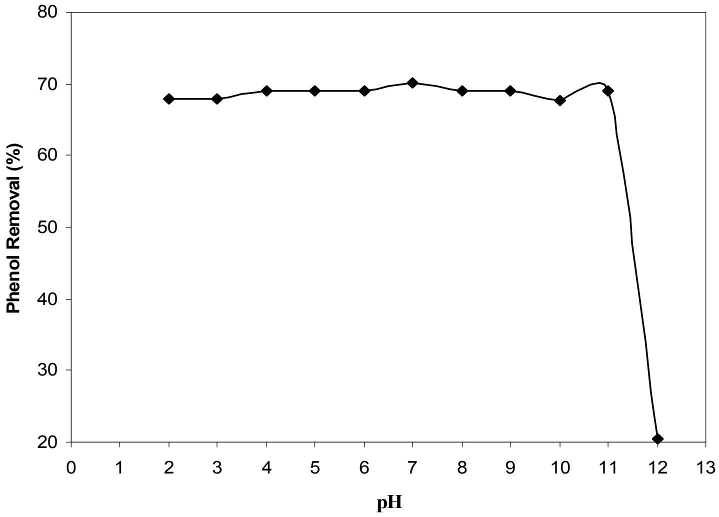

Fig 2. The effect of pH on the removal of 10 mg L^{-1} of phenol.

3.2. Effect of Contact Time

The results in figure. 3 show that the equilibrium time required for the adsorption of phenol on the MAC is 2 hours. For this test 0.05 g MAC was mixed by 100 mL standard solution of 10 mg L^{-1} phenol and pH was adjusted at 7.0 with RPM=200 of Jar test stirrer. At the first half an hour, the adsorption was increased sharply and after that the adsorption was increased slowly up to 2 hours.

3.3. Effect of The amount of MAC

The figure. 4 shows the removal of phenol as a function of the amount of MAC in the solution at pH=7.0. In this test 100 mL phenol standard solution of 10 mg L^{-1} concentration was mixed with a range of 0.05-0.4 g MAC as a solid phase and it was stirred for 2 hours with RPM=200 of Jar test stirrer. For 98 % adsorption of phenol 0.3 g of MAC is an optimum amount. The results also clearly indicate that the removal efficiency increases up to the optimum amount beyond which the removal efficiency is negligible.

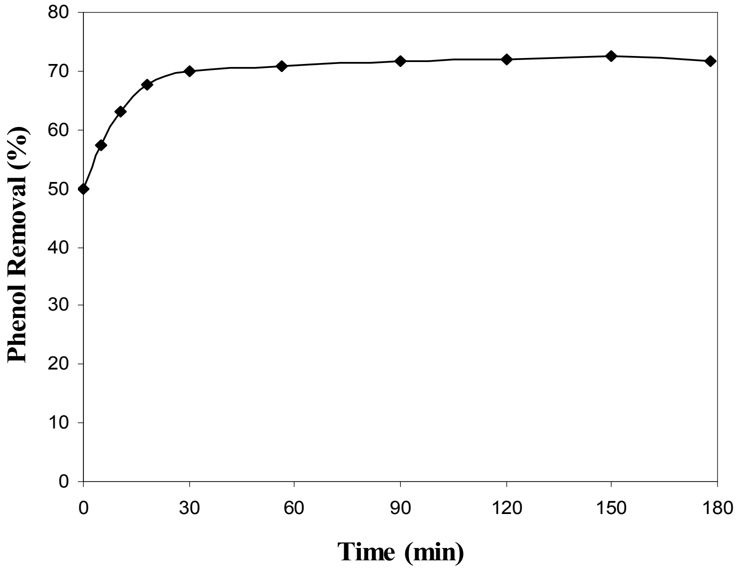

Fig. 3. The effect of Contact Time on the removal of 10 mg L^{-1} of phenol at pH 7.0.

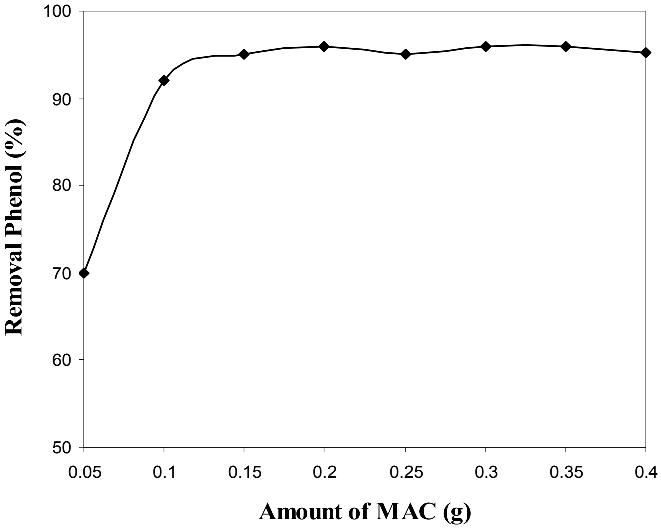

Fig. 4. The effect of the amount of MAC on the removal of 10 mg L^{-1} of phenol.

3.4. Effect of the Volume of Phenol Solution

In this stage the maximum volume of phenol standard solution that can be adsorbed and separated by MAC, was studied. In this test different volumes and concentrations from phenol standard solutions were prepared and 0.3 g MAC was added and the mixture was stirred by Jar test stirrer for 2 hours while the pH=7.0 (figure. 5). The MAC was agglomerated by the strong magnet for 5 minutes. The absorbance was measured in respect to the blank solution at $\lambda_{max} = 510$ nm and the phenol removal were calculated.

3.6. Adsorption isotherm

For calculating the maximum amount of phenol adsorption on the surface of 0.05 g MAC from Langmuir Equation was used.

$$\frac{C}{q} = \frac{1}{Kq_m} + \frac{C}{q_m} \qquad (3)$$

C (mg L^{-1}): the equilibrium concentration of phenol (the residue concentration of phenol in the solution that MAC could not adsorb it anymore)
q (mg mg^{-1}): adsorbed phenol on the MAC
K(L mg^{-1}): equilibrium coefficient of Langmuir adsorption
q_m (mg mg^{-1}): maximum amount of phenol that can be adsorbed on the MAC

in below curve, the maximum amount of phenol that was adsorbed on the MAC was obtained approximately 0.3 mg mg^{-1}.

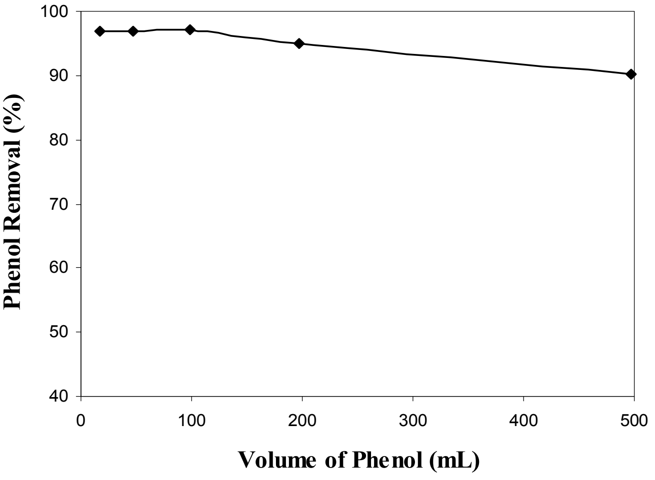

Fig. 5. Effect of the volume of phenol solution on its removal by MAC.

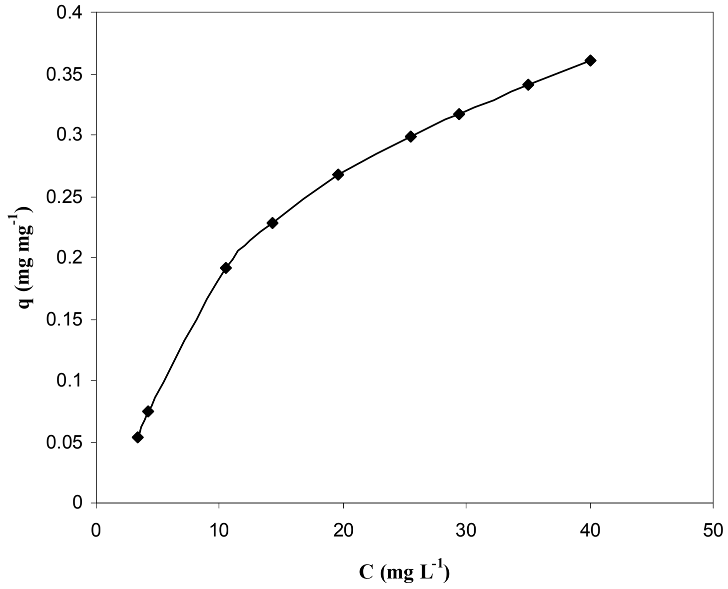

Fig. 6. Adsorption isotherm for phenol.

For exact determination of maximum amount of phenol that was adsorbed on the MAC surface the Langmuir adsorption isotherm was plotted for phenol in the optimum condition with regression coefficient R =0.9862 which is a measure of goodness-to-fit and q_m was obtained 0.59 mg mg^{-1} and K=0.06.

3.7. Desorption and reuse condition

Seven samples of 0.05 g MAC after phenol adsorbing at pH=4.0 were desorbed by different percentage of 100 mL ethanol solution and then the collected MAC was reused and the removal of phenol was tested again. As shown in table. 1 the desorption condition was changed through pH adjustment.

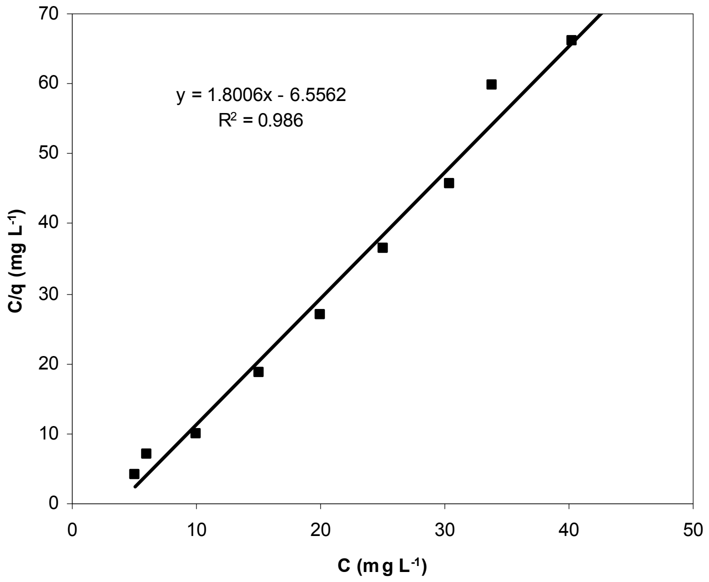

Fig. 7. Langmuir adsorption isotherm for phenol solution.

Table. 1. The results of phenol removal in desorption condition and the reuse of MAC

No.	**A_i**	**A_f**	**Phenol removal after first adsorption**	**Desorption Condition**	**A_f after desorption**	**A_f after reuse**	**Phenol removal after reuse**
1	1.194	0.322	72.9 %	Ethanol 10 % (pH=4.5)	0.455	0.626	47.5 %
2	1.194	0.337	71.7 %	Ethanol 25 % (pH=5)	0.642	0.546	53.9 %
3	1.194	0.329	72.4 %	Ethanol 50 % (pH=5)	0.937	0.449	62.0 %
4	1.185	0.345	70.8 %	DM water (pH=12)	0.642	0.449	57.9 %
5	1.185	0.340	71.2 %	Ethanol 10 % (pH=12)	0.745	0.449	62.0 %
6	1.185	0.330	72.1 %	Ethanol 25 % (pH=12)	0.875	0.425	64.0 %
7	1.185	0.333	71.9 %	Ethanol 50 % (pH=12)	0.960	0.473	60.0 %

Concentrated ethanol solutions can desorbed phenol from MAC surface better than diluted ones. For achieving better results in diluted solutions, the pH of solutions should be adjusted at pH=12. Therefore best result for reuse of MAC was obtained by ethanol 25% solution and pH=12.

3. 8 Application of the method

A 500 mL sample of Fajr wastewater that the initial phenol concentration was 37.5 mg L^{-1} was collected and it was divided to 4 samples with 100 mL volume. For removing phenol up to 98% different amount of MAC was added to them. The pH was adjusted at 7.0 and they were stirred for 2 hours by Jar test stirrer. Finally the solid phase was agglomerated by a strong magnet. The residue phenol concentration was tested based on the standard method ASTM D1783-01[11] with respect to the blank solution (Figure. 8). It is obvious that by increasing the amount of MAC the quantity of phenol removal increases. The recovery of tested samples was acceptable, thus we can suggest the presented method for the determination of phenol in different real samples.

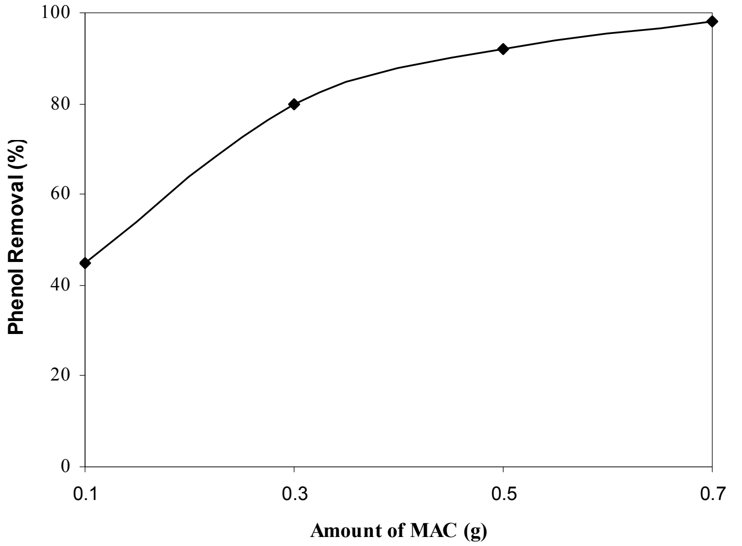

Fig. 8. Phenol removal up to 98% from Fajr wastewater by increasing the amount of MAC.

4. Conclusion

This work has demonstrated the developed SPE method based on adsorption of phenol on Magnetization of Activated Carbon (MAC) prior to their spectrophotometric determinations. For exact determination of maximum amount of phenol that was adsorbed on the MAC surface the Langmuir adsorption isotherm was plotted for phenol and q_m was obtained 0.59 mg mg^{-1}. The method was simple, easy and also rapidly applied for wastewater samples. The results show that the MAC has high analytical potential for removing phenol from water samples.

Acknowledgments

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