

# REMOVAL OF PHENOL USING POLYMER COATED MAGNETIC NANOPARTICULAR ACTIVATED CARBON

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## Abstract

Phenol is a toxic organic pollutant which is present in many industrial effluent streams originating from petrochemical industry, ceramic production process, wood plants and resin manufacturing plants. Phenol is difficult to remove from most wastewater effluent streams. In the presented study, phenol removal from wastewater sample was investigated using the adsorption method. The experiments were conducted to investigate the adsorption performance of activated carbon (AC), magnetic activated carbon (MagAC), styrene-butadiene styrene magnetic activated carbon (SBS/MagAC) and poly charbonat magnetic activated carbon (PC/MagAC) samples. The effects of various parameters, for example, temperature, solid-liquid ratio, adsorbent type, initial phenol concentrations and solution pH were investigated under similar experimental conditions. The results showed that the maximum adsorption of 98-99% was achieved at low pH values with the use of both AC and MagAC adsorbent materials. It was also found that the polymer coated magnetic materials did not perform very well at high pH values. The experimental data also showed that MagAC and SBS/MagAC were more effective than AC and PC/MagAC to remove phenol. In conclusion, we found that phenol can be removed more easily from the aqueous medium by using both magnetic and polymeric materials.

**Keywords:** Activated carbon, adsorption, magnetic adsorbent, phenol, isotherm

## 1. INTRODUCTION

Phenol is a toxic organic pollutant which is present in many industrial effluent streams originating from petrochemical industry, ceramic production process, wood plants and resin manufacturing plants. Phenol is difficult to remove from most wastewater effluent streams as it does not readily degrade and form stable complexes with any metallic ions in aqueous solutions. Currently, there are many methods which can be used to remove or degrade many

organic pollutants from wastewater including extraction-separation, adsorption, oxidation, air flotation and biological methods (Zazo et al., 2006, Zeng et al., 2013; Ahmaruzzaman et al., 2005). The use of nanomaterials is predominantly used in wastewater treatment due to their high surface area. In addition, the presence of a high porous structure increases the adsorption efficiency. The most difficult and undesirable situation in the adsorption process is the removal and separation of nano-based materials from different systems at the end of the adsorption process. It is reported that this difficulty can easily be solved by using magnetic nanoscale materials, as adsorbents, and then exposing them to the external magnetic fields. This simple and effective way can be used to remove organic pollutant and also recycling, recover and reuse adsorbent materials (Shaker et al., 2016, Ghaedi et al., 2016). Our literature review revealed that iron-based magnetic nano-powders are most widely used and preferred as material candidates due to their distinctive properties and characteristics (Davarnajad and Panahi 2016, Akin et al., 2015). If magnetic materials are used with adsorbents to remove environmental contamination, it is highly desirable to remove and recycle the adsorbent after adsorption. The samples of activated carbon (AC) coated with magnetically iron-containing iron components ( $\text{FeO}$ ,  $\gamma\text{-Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ ) have recently been used to remove toxic organic (Bagheri et al., 2017, Bhatia et al., 2018), Cr(VI) (Gong et al., 2018), different heavy metals (Zhnag et al., 2018), antibiotics (Badi et al., 2018) and As(V) (Wen et al., 2017) to purify effluent streams using adsorption method. These novel adsorbents materials can also be used for different purposes after being treated with certain polymeric materials. In literature studies, effective mercury removal has been tried by using polymer coated activated carbon. In one study, polysulfide-rubber (PSR) polymer, a sulphur-rich compound, was treated to increase the affinity for mercury removal with activated carbon. Hg-Cl and Hg-S interactions of the chemical bond with mercury on the active carbon surface are reported (Kim et al., 2011).

The presented study was designed to easily remove the adsorbents from the environment first for this purpose, polymer-modified magnetic nanoparticles were synthesized and their characterization and other structural properties were investigated. Then AC, MagAC, SBS/MagAC and PC/MagAC were synthesized and used as adsorbents. In phenol adsorption experiments, temperature, solid-liquid ratio, adsorbent type, initial concentrations and solution pH were selected as parameters and experiments were carried out on a constant shaker. As a result of the studies. the performances of the synthesized materials were compared with adsorption kinetics and thermodynamic parameters.

## 2. MATERIALS AND METHODS

### 2.1. Materials and Preparation of Adsorbents

#### 2.1.1 Activated carbon (AC)

The activated carbon samples used in the study were obtained commercially, Sigma-Aldrich, 242276. Other iron samples were also obtained commercially (ZAG, ZK.100380.1000) and prepared according to literature studies (Fard et al., 2017).

#### 2.1.2. Magnetic activated carbon (MagAC)

$\text{FeCl}_3$  (1.08 g) and  $\text{FeCl}_2$  (2.40 g) were added to 150 ml of distilled water and shaken at 60-65 °C for 1 hour. Then, 5.0 g of activated carbon was added to these samples and shaken at the same temperature for 2 hours. In the final step 5.0 g of NaOH was added and stirring for 1 h and aged at overnight. After washing several times with distilled water the sample was dried in an oven to a constant weight.

#### 2.1.3. Styrene-butadiene styrene magnetic activated carbon (SBS/MagAC)

Styrene-butadiene styrene (SBS) 1.0g + tetrahydrofuran (THF) and dimetilformamid (DMF), THF/DMF 50ml (30:20) samples were prepared and stirred at 60-65°C for 2 hours. Then 5.0 g of activated carbon was added to the same temperature for one hour. To this mixture was added FeCl<sub>3</sub> (1.08 g) + FeCl<sub>2</sub> (2.40 g) and the mixture and it was stirred at 60-65°C for 2 hours. In the final step, 5.0 g of NaOH was added to the samples stirred for 1 hour and allowed to stand overnight. These samples were washed several times with distilled water, filtered and dried to a constant weight in the oven.

#### 2.1.4. Poly carbonate magnetic activated carbon (PC/MagAC)

Poly carbonate (PC) 1.0g and tetrahydrofuran (THF) and dimetilformamid (DMF), THF/DMF 50 ml (30:20) samples were taken and stirred at 60-65°C for 2 h. 5.0g of AC was added and stirred at the same temperature for one hour. FeCl<sub>3</sub> (1.08 g) + FeCl<sub>2</sub> (2.40 g) was then added and the mixture was stirred for 2 hours at 60-65°C. In the final step, 5.0 g of NaOH was added and the mixture was allowed to stand for 1 hour with stirring. After washing several times with distilled water, the filtered samples were dried to a constant weight in the oven.

#### 2.2. Adsorption Studies

Before the experiments; a solution of 250 mg/L was prepared by stirring 0.4 g of phenol in 100 ml of purified water (Stock solution). 12.5 ml of stock solution was completed to 200 ml of water. Adsorption experiments were performed with this mixture. Changes in phenol concentration were determined before and after adsorption by UV/vis spectrophotometer at 278 nm and determined by calibration curve. Commercially activated granular activated carbon (AC), MagAC, SBS/MagAC and PC/MagAC magnetic adsorbents were used in the experimental study. All adsorption experiments (except experiments where the pH effect was examined) were performed at natural pH. Temperature, solid-liquid ratio, adsorbent type, initial concentrations and solution pH were selected as parameters. In the experiments in which the pH effect was examined, the pH of the solution was adjusted using dilute HCl and NaOH solutions using a pH meter (WTW-Germany. pH 330i). Adsorption experiments were carried out on a constant shaker with cooling effect. All synthesized materials and the adsorption experiment apparatus are shown in Fig 1

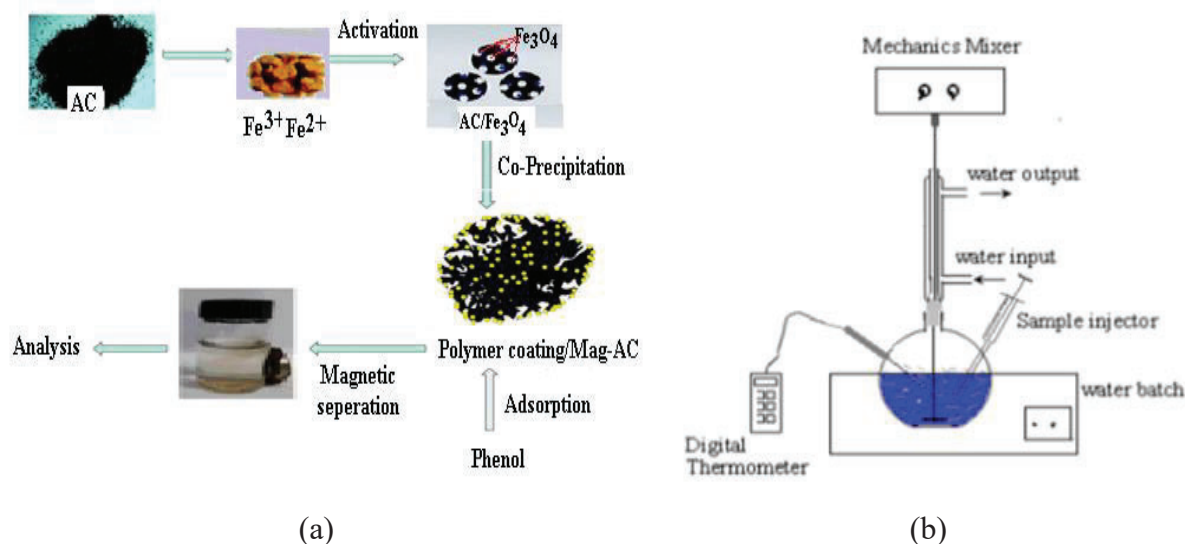


Fig 1. Synthesis of magnetic materials and general flow chart of experimental design (a) Adsorption experiment setup (b)

### 3. DISCUSSION AND CONCLUSION

#### 3.1. Adsorption Results

Magnetic and polymer coated adsorbents were synthesized on the basis of AC-based material. Solid-liquid ratio, initial concentration, suspension pH and temperature effects were investigated. The variation of the adsorbed amount per gram weight of adsorbents over time was evaluated separately for each parameter.

##### 3.1.1. Effect of solid-liquid ratio

To investigate the effect of solid/liquid ratio, the removal rates of phenol using adsorbent materials were plotted in Fig.2.

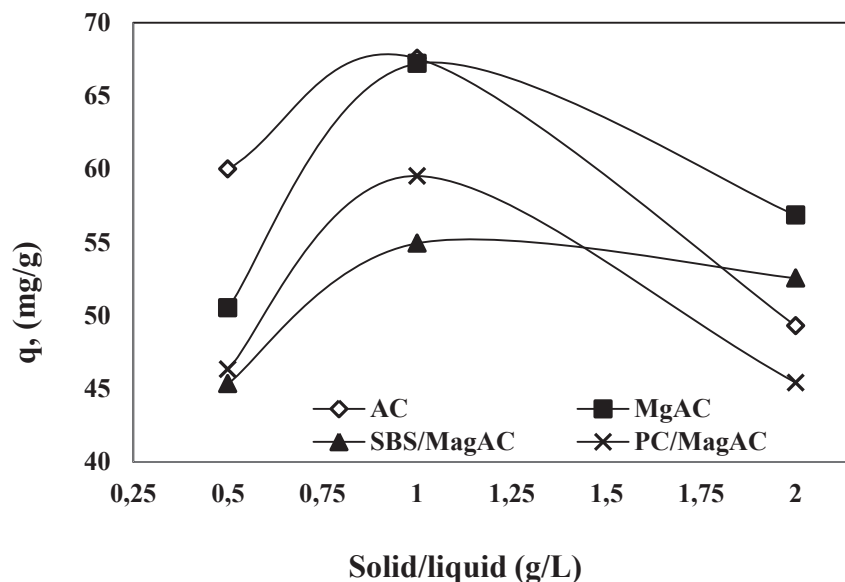


Fig. 2: Amount of phenol adsorbed per gram of adsorbent depending on solid-liquid ratio (Time 120 min., 250 mg/L. natural pH. constant mixing speed. 298K)

In Fig 2, it is seen that adsorption in per gram generally decreases with increase of solid-liquid ratios. However, as the amount of adsorbent is increased, the amount of substances adsorbed on the adsorbent materials also increased in total. In addition, it is seen that the best performance is achieved by using both AC and MagAC adsorbents samples. Other adsorbents are thought to have partially reduced elimination which possibly due to reduced surface areas. The maximum adsorption capacity was found to be 55,00 and 67.33 mg/g.

##### 3.1.2. Temperature effect

In order to investigate the effect of temperature, the removal values of phenol using adsorbent materials are shown in Fig 3.

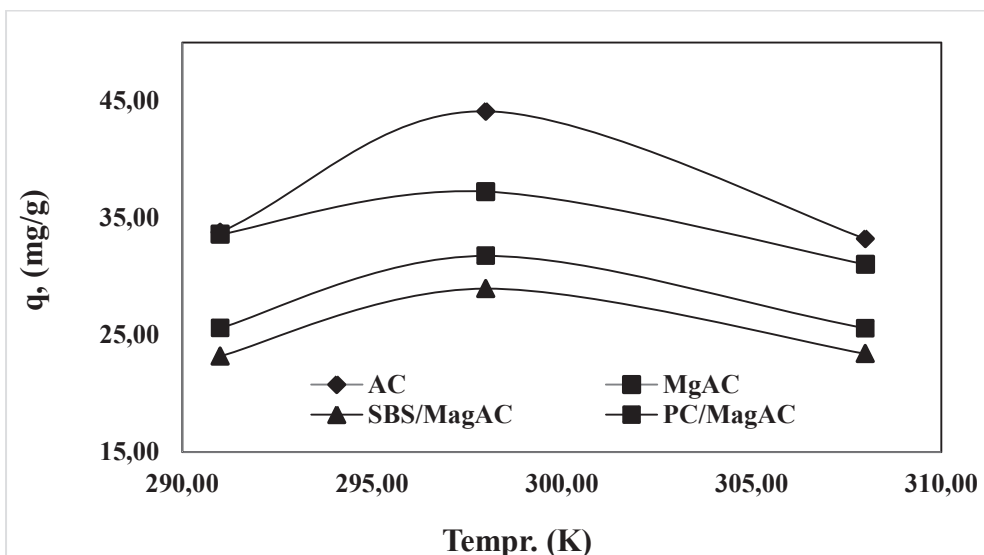


Fig. 3: Amount of phenol adsorbed per gram of adsorbent depending on temperature effect rates. (time: 120 min., 125 mg/L, natural pH, constant mixing speed, 1g/L).

When the effect of temperature was examined, it was found that removal was higher at 298K. It is seen that less removal occurs with increasing temperature and adsorption reaches equilibrium in a very short time. It is seen that adsorption is better in AC and MagAC samples. Furthermore, the partial reduction of removal as the temperature increases can be associated with the exothermic nature of adsorption (Mohammed et al., 2019).

### 3.1.3. The Effect of initial concentration

To examine the initial concentration effect, changes in the amount of phenol adsorbed per gram using adsorbent materials are plotted in Fig.4.

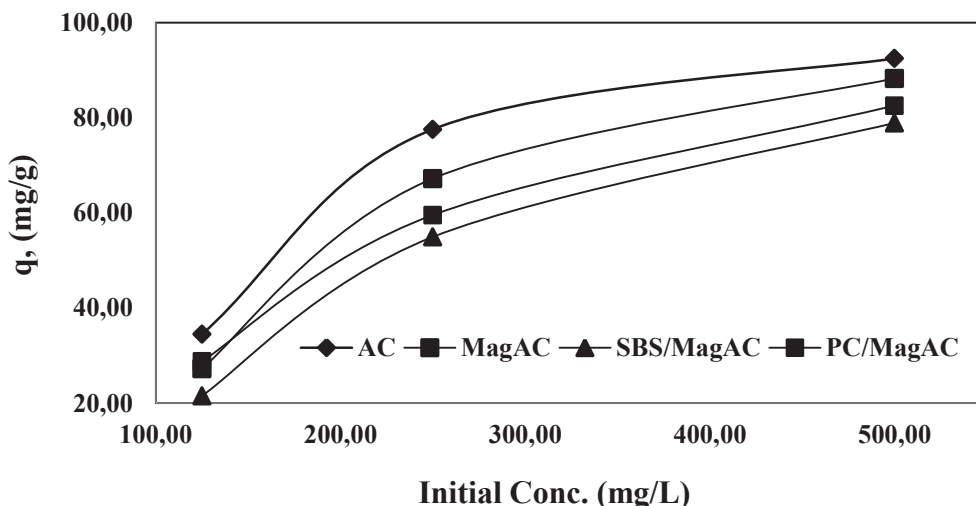


Fig. 4: The amount of phenol adsorbed per gram of adsorbent depending on the concentration effect ratios (Time: 120 min., natural pH, constant mixing rate, 298K, 1g/L).

Fig 4 is examined in different initial concentrations and fixed adsorbent using the study realized. the higher the removal of phenol concentration is seen to be more. In general, all samples show similar trends. This is especially noticeable at a concentration of 500 mg/L. The adsorption efficiency was increased by significant changes in high concentration. In addition, due to the greater reach of active and unsaturated regions on sample surfaces, the initial

concentration was increased while adsorption capacity also increased (Karimipour et al., 2019)

### 3.1.4. The Effect of pH

In order to investigate the effect of pH, the changes that occur due to suspension pH in phenol adsorption using AC and synthesized magnetic adsorbents are given in Fig.5. When the adsorption values of phenol removal are examined depending on the pH change, it is seen that the removal is high in pH: 5.0 and pH: 7.0 and the minimum removal is at pH 9.0 (Fig 5). In addition, more adsorption was observed in AC and PC/MagAC samples. Particularly high adsorption at low pH may be related to the fact that the surface may be caused by adsorption of phenol to protons and the resulting positive charges. In literature research, it is reported that in acidic solutions, phenol is preferably more adsorbed than basic solutions. At high pH, phenol can convert into phenolate ions ( $C_6H_5O^-$ ) and it is thought that electrostatic repulsion occurs between negatively charged adsorbents and phenolate ions, thereby greatly reducing its adsorption capacity (Caetano et al., 2009, Cañizares et al., 2006).

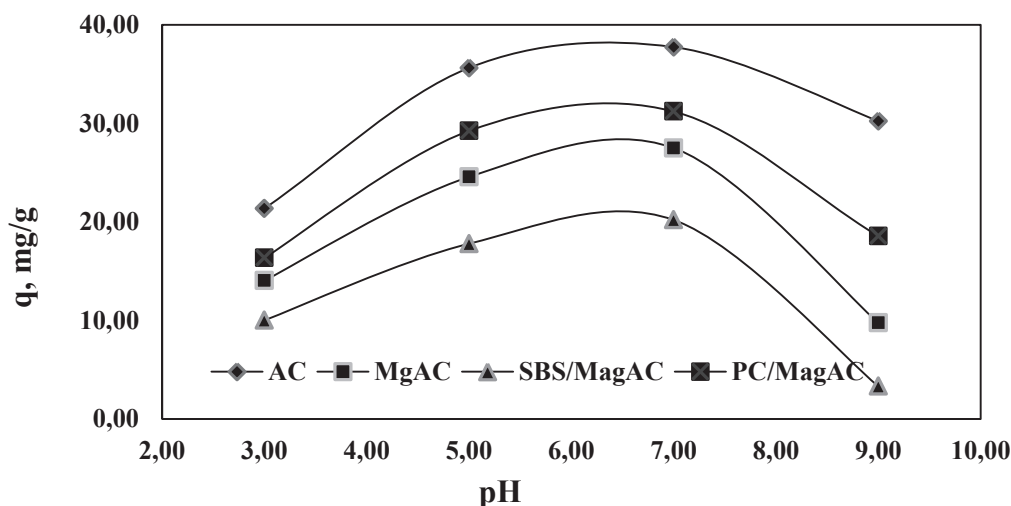


Fig. 5: The amount of phenol adsorbed per gram of adsorbent depending on the pH effect rates (condition: 120 min., 125 mg/L, constant mixing rate, 298K, 1g/L).

### 3.1.5 Adsorption isotherms

Adsorption isotherms are vital and very important tools in describing how phenol interacts with all adsorbents, which is of great importance in characterizing the adsorption process (He et al., 2019). Herein, the adsorption behaviour of phenol onto adsorbents were evaluated by the most frequently used isotherm models. Monolayer surface coverage and the equal availability of adsorption sites and no transmigration of adsorbates in the plane of the surface are the idealized assumptions associated with the Langmuir adsorption model (Li et al., 2019). On the other hand, the Freundlich isotherm is an empirical model that assumes the presence of the interaction between the molecules of the adsorbate. all surface sites are different and the multilayer adsorption (Luo et al., 2015). Obviously, it is apparent from the results reported in Table 1 that the adsorption of phenol onto adsorbents at all temperatures is well described by the Langmuir isotherm model ( $R^2$  value of 0.95). The goodness of Langmuir model suggests monolayer adsorption of phenol at the outer surface of adsorbents at all temperatures (Miyah et al., 2018). The b values were found to range from 0 to 1 implying that the adsorption on the zeolite was a favourable process (Hamdaoui et al., 2007).

The relatively highest  $R^2$  value of the Freundlich isotherm probably indicates a heterogeneous surface adsorption. The values of n are greater than 2 which suggests a good adsorption

capacity of phenol onto adsorbents (Konicki et al., 2017). The values of  $g$  at all temperatures were closer to 1 which confirm again the suitability of the Langmuir model (He et al., 2019).

Table1: Freundlich and Langmuir values for AC, MagAC, SBS/MagAC and PC/MagAC

Adsorbents	Freundlich			Langmuire		
	n	$K_f$	$R^2$	$bx10^{-2}$	$Q_0$	$R^2$
AC	1.882	6.85	0.82	0.67	208	0.95
MagAC	1.511	3.23	0.83	3.66	26.31	0.98
SBS/MagAC	0.784	2.03	0.84	4.49	17.24	0.95
PC/MagAC	2.666	7.84	0.80	1.89	70.92	0.97

### 3.1.6 Adsorption thermodynamics

Thermodynamic parameters of phenol adsorption on different temperatures and adsorbents are given in Table 3. The  $\Delta G$  values were calculated using Eq.(7) and were found to the temperature range of 291–308K which indicated the spontaneously nature of the adsorption process. The change in the enthalpy was found to be  $-5.456$  and  $-11.553$  kJ/mol for all adsorbents. The negative value of  $\Delta H$  indicated that the adsorption was exothermic and suggested that adsorption was physical in nature involving weak forces of attraction. The positive value of  $\Delta S$  indicated good affinity of the material with dye molecules and showed an increase in the degree of freedom of the adsorbed species (Bouchra, 2019).

Table 3: Thermodynamic parameters of phenol adsorption on different temperatures and adsorbents

Adsorbents	T (K)	$\Delta G^0(kJmol^{-1})$	$\Delta H^0(kJmol^{-1})$	$\Delta S^0(Jmol^{-1})$	$R^2$
AC	291	-2.273	-11.553	35.49	0.87
	298	-0.833			
	308	-0.685			
MagAC	291	-1.042	-5.456	16.38	0.92
	298	-0.448			
	308	-0.454			
SBS/MagAC	291	-1.212	-9.876	36.33	0.95
	298	-0.673			
	308	-1.051			
PC/MagAC	291	-0.190	-6.917	24.19	0.98
	298	-0.411			
	308	-0.610			

Using the kinetic, adsorption and thermodynamic data, it was concluded that physical adsorption in the polymer network and chemical interaction of the phenol molecules via ion-exchange were both involved in the adsorption process.

## 4. CONCLUSION

In the presented study, adsorption isotherms, kinetic and thermodynamic calculations were made to investigate the adsorption potential of all adsorbents for the removal of phenol from aqueous solution. It was seen that adsorption is affected by various parameters. The kinetic models indicated that the adsorption process of phenol onto adsorbents at all temperatures obeyed pseudo-second-order and intra-particle diffusion models rather than the pseudo-first-order kinetic model ( $R^2$ : 0.98-1.00). The Langmuir isotherm model was found to be more suitable for predicting the adsorption of phenol ( $R^2$ : 0.95-0.98). It was observed that adsorption efficiency was generally better  $AC \geq MgAC \geq PC/MagAC \geq SBS/MagAC$  samples, respectively, in the parameters examined. As a results, although higher efficiency is obtained with AC, it is seen that phenol can be removed from the aqueous environment more easily,

especially when magnetic and polymeric materials are used to remove the adsorbent from the environment more easily.

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