

# Selective Adsorption of Phenol and Resorcinol from Aqueous Solution by Pectin/Poly (Acrylamide–Co-2-Acrylamido-2-Methyl–1-Propanesulfonic Acid) Chelating (PPAA) Hydrogels: Equilibrium, Kinetics, and Modeling

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## ABSTRACT

In this work, Pectin/Poly (acrylamide–co-2-acrylamido-2-methyl–1-propanesulfonic acid) chelating (PPAA) hydrogels, a novel adsorbent was used for the adsorption of phenol and resorcinol systematically. Batch experiment studies showed that the removal efficiency of phenol and resorcinol by PPAA was influenced by pH, adsorbent dose, contact time and the concentrations of phenol and resorcinol solutions. Kinetics and isotherms at different concentrations were performed to evaluate the adsorption capacity. The PPAA adsorption capacity towards resorcinol was greater than phenol. The adsorbent was characterized by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). The adsorption capacity of PPAA hydrogels calculated from the Langmuir model was found to be 80.64 mg/g and 86.20 mg/g for phenol and resorcinol respectively.

**Keywords:** Adsorption; PPAA hydrogels; Phenol; Resorcinol; Isotherms; Kinetics.

## 1. INTRODUCTION

In the present scenario, one of the greatest problems that the world is facing today is that of environmental pollution. This has become increasingly serious, posing a great threat to human beings and sustainable environment. In fact aquatic sources, such as river water and lake water, were easily polluted by typical environmental pollutants. These pollutants include phenolic compounds, *i.e.*, phenol, resorcinol, cresol, etc. They are discharged from various industries like pesticides, dye manufacturing, coal conversion process, pharmaceuticals, petrochemical industries (Ramarao *et al.* 2017; Aghav *et al.* 2011; Qiang *et al.* 2014; R.J *et al.* 2012; Yuri *et al.* 2013; Jianming *et al.* 2011). Agricultural runoff and domestic waste may be also one of the main reasons that phenolic compounds come into the environment (Gaofeng *et al.* 2008; Ayca *et al.* 2013). Day by day increases of industries as well as increases of discharges of phenolic compounds lead to the increases of their toxicity in the natural and aquatic ecosystem (Hany *et al.* 2007; Siti *et al.* 2004). According to Environmental Protection Agency (EPA), phenolic compounds like phenol and resorcinol are identified as hazardous pollutants. They are released into the air, water and soil (Chagmai *et al.* 2017). The tolerance limit of the phenol contents in the drinking water is not very high, and the concentration should not exceed 0.002 mg/lit (Usha Soni *et al.* 2017). The health effects of exposure repeated

to low levels of phenol in water include mouth ulcers, diarrhea, damage of liver and dark urine. Resorcinol is one of the hazardous chemical substances, the health effects of resorcinol is abdominal pain, unconsciousness, nausea, immune system dysfunction (Swarnima *et al.* 2017; Singh *et al.* 2008). A lot of efforts have been made to remove organic pollutants from water, such as adsorption, osmosis, electro chemical process, reverse osmosis, membrane separation, solvent extraction, ion exchange process, precipitation, photolysis, oxidation etc (Thakur *et al.* 2009; Moreira *et al.* 2017; Naghmeh *et al.* 2018; Sibani *et al.* 2018; Anamika *et al.* 2018). The adsorption is one of the most widely used conventional methods, for it is an economically feasible, simple, effective and environmentally friendly method in practice (Bernabel *et al.* 2008, Raja kumar *et al.* 2020).

A number of commercial adsorbents like zeolite, activated carbon, activated bentonites, biomass and fly ash are normally used to remove phenolic compounds. In recent years, there has been a considerable interest in the use of biological materials. For example, algae and fungi and eco-friendly low cost bio polymers have been commonly used for the removal of phenolic compounds, such as phenol, resorcinol, etc. (Wen *et al.* 2016; Muhammad *et al.* 2017).

The focus of the present work is on the potential use of Pectin, and it is a poly saccharine composed of ( $\alpha$  (1-4)-linked d-galacturonic acid. It is water soluble and a naturally occurring substance. Commercial pectin is extracted from peels of citrus and apple pulp (Sivagangi reddy *et al.* 2015; Risi *et al.* 2019; Sourbh *et al.* 2019; Sapna *et al.* 2019; Sergey *et al.* 2019). Pectin is used in pharmaceutical products, food products and gelling agents. We synthesized Pectin with 2-acrylamido -2-methyl -1-propane sulphonic acid (AMPS) and Acrylamide (Am) based hydrogels for the adsorption of phenol and resorcinol. The adsorbent was characterized by Fourier Transform Infrared Spec-

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troscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDX). Also, the parameters such as pH, initial concentration of phenolic compound, adsorbent dosage and effect of contact time were investigated. The adsorption kinetics was examined, and the Lagergren's first order, pseudo-second order and Weber Morris models were fitted. In the same way, the Langmuir and Freundlich isotherm models were employed to evaluate the sorption process.

## 2. EXPERIMENTAL

### 2.1 Materials

Synthetic grade 2-acrylamido-2-methyl-1-propanesulphonic acid (AMPS) was purchased from Sigma –Aldrich Chemicals, USA. Synthetic grade pectin was purchased from Lab Chem. Potassium persulphate (KPS), acrylamide (Am), and HCl, NaOH were purchased from Merck, Mumbai, India. Analytical grade Phenol, Resorcinol, Acetic acid and Synthetic grade reagents of N, N-methylene- bis-acrylamide (MBA) were purchased from S.D. Fine Chemicals, Mumbai, India. Double-distilled water were used throughout the experiment.

### 2.2 Preparation of 4% pectin solution

The solution (4% w/v) of pectin was prepared by dissolving 2.0 g of pectin powder into 50 mL of double distilled water and was stirred vigorously up to 08 hours to obtain a homogeneous solution.

### 2.3 Preparation of Pectin – based hydrogels (PPAA-hydrogel)

The PPAA hydrogels were synthesized from pectin with acrylamide (Am), 2-acrylamido -2-methyl -1-propane sulphonic acid (AMPS) and N,N-methylene- bis- acrylamide (MBA) by a

free radical polymerization in the presence of potassium persulphate as an initiator. This initiator was reduced to anion radical  $[(SO_4)^{-1}]$ . These could extract hydrogen from the Am, AMPS and cross linker MBA to not only form vinyl radicals but also undergo polymerization to produce PPAA hydrogels.

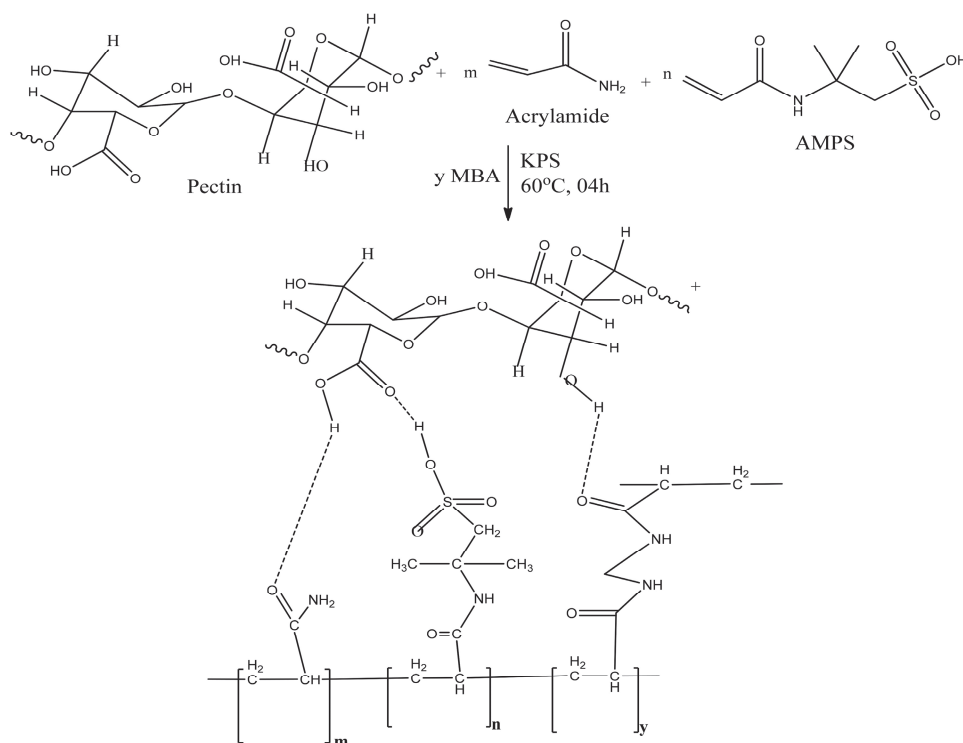
The composition of Pectin – based hydrogels is given in Table 1, and Pectin serves as a guest polymer. The structure of synthesized PPAA hydrogels is illustrated in Fig. 1.

**Table 1 Different Formulations & Compositions of PPAA Hydrogels**

Formulation Code	Pectin (4%) mL	Am (g)	AMPS (g)	MBA (3%) mL	KPS (10%) mL
A	5.0	0.5	0.5	3.0	1.0
B	5.0	0.5	0.5	4.0	1.0
C	5.0	0.5	0.5	5.0	1.0
D	5.0	0.5	0.75	4.0	1.0
E	5.0	0.5	1.0	4.0	1.0

At first 5.0 mL of pectin solution (4%) was taken in a 100 mL beakers [5–formulations] and added 0.5 g of monomer Am in each beaker. Another monomer AMPS of certain weights were dissolved in 2.0 mL of distilled water, and certain values of cross-linking agent MBA (3%) aqueous solution and 1.0 mL of initiator KPS (10% ) aqueous solution were added in each beaker and stirred to obtain a homogeneous solution.

The resulting homogeneous solution [5–formulations] was kept at 60°C for 4h to complete the formation of hydrogels. After kept in double - distilled water up to one week by rapidly changing the water for removing of KPS and the unreacted monomers. The formed hydrogels were kept in a vacuum oven at 60°C for the purpose of drying, and the dried hydrogel was used as the adsorbent to remove phenol and resorcinol.



**Fig. 1 Schematic Representation of PPAA Hydrogels**

## 2.4 Swelling studies

The following procedure was developed for analyzing the swelling characteristics of the PPAA hydrogels. At first, different formulations of PPAA hydrogels were dried to acquire dry gels; these were used for swelling studies. The amount of dried PPAA hydrogels were weighed and then immersed in 50 mL of double distilled water at 25°C.

The weights of swollen hydrogels were weighed after the removal of excess of water on the surface of hydrogels at certain intervals of time. This process was repeated until no significant change of weights was observed.

The Swelling ratio ( $Q_s$ ) is calculated from the following equation (1)

$$Q_s = \frac{W_s - W_d}{W_d} \quad (1)$$

where  $W_s$  and  $W_d$  are swollen and dried PPAA hydrogels weight, respectively.

## 2.5 Preparation of Phenol and Resorcinol standards

The stock solutions (1,000 mg/L) of Phenol and Resorcinol were prepared by dissolving 1.0 g of phenol or resorcinol into 1L of distilled water. The experimental solutions of desired concentrations were prepared by diluting stock solution with distilled water. The concentrations of Phenol and Resorcinol were measured by UV-Visible spectrophotometer (LAB INDIA, Model UV-3092). The pH of solutions was adjusted with 0.1M NaOH and HCl, using a pH meter (Thermo Scientific Model).

## 2.6 Characterization

The PPAA hydrogels used for the present study were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

FTIR measurements were performed with PPAA hydrogels, Phenol sorbed PPAA hydrogels and resorcinol sorbed PPAA hydrogels by using Perkin Elmer FTIR Spectrometer (Beaconsfield, UK). The sample pellets were developed by grinding finely PPAA hydrogels with KBr and pressing them under the hydraulic pressure of 600 dynes/cm<sup>2</sup>. The spectra were obtained between 4,000 to 500 cm<sup>-1</sup>. The FTIR spectra were used to analyze the presence of functional groups of PPAA hydrogels before and after cross linking. The PPAA hydrogels were evaluated by Scanning Electron Microscopy (SEM). This was for the study of surface morphology.

## 2.7 Batch adsorption experiments

The batch adsorption studies were carried out to explore the effects of pH (1-10), initial phenolic compounds of phenol and resorcinol with a concentration of 100 ~ 300 mg/L, a contact time of 30 ~ 300 min, the adsorbent doses from 0.05 ~ 0.6g on the adsorption performance of PPAA hydrogels agitated in an electrical thermostatic shaker at 200 rpm, after each adsorption process the samples were filtered, using Whatman No. 42 filter paper and analyzed for remaining phenolic concentration by UV-visible spectrophotometer observing the changes in the absorbance values at 270 and 313 nm for phenol and resorcinol respectively.

The amount of phenol and resorcinol adsorbed on the PPAA

hydrogels,  $q$  (mg/g) was obtained by the following equation (2)

$$q = \frac{C_o - C_e}{M} \times V \quad (2)$$

where  $C_o$  and  $C_e$ , initial and equilibrium concentration of phenol and resorcinol;  $V$  (L), volume of phenol and resorcinol,  $M$  (g) mass of the adsorbent dose.

## 3. RESULTS AND DISCUSSION

### 3.1 FTIR analysis

The FTIR spectral analysis of the Pectin/Poly (acrylamide–co-2-acrylamido-2-methyl–1-propanesulfonicacid) chelating (PPAA) hydrogels before and after adsorption are depicted in Fig. 2. The FTIR spectra of the PPAA hydrogels before adsorption (Fig. 2(a)) show a absorption peak 3,435 cm<sup>-1</sup> corresponding to the –OH stretching vibrations of the hydroxyl group and -NH stretching vibrations of the NH<sub>2</sub> groups. The peak at 2,924 cm<sup>-1</sup> was observed to correspond to the typical –C–H stretching vibrations. The peak at 1,640 cm<sup>-1</sup> resulted from the –C = O stretching vibrations of Amide group. The peaks at 1,384 cm<sup>-1</sup> and 1044 cm<sup>-1</sup> indicated in plane bending vibrations of –CH group (or) stretching vibrations of sulphur group and S–O of SO<sub>3</sub>H.

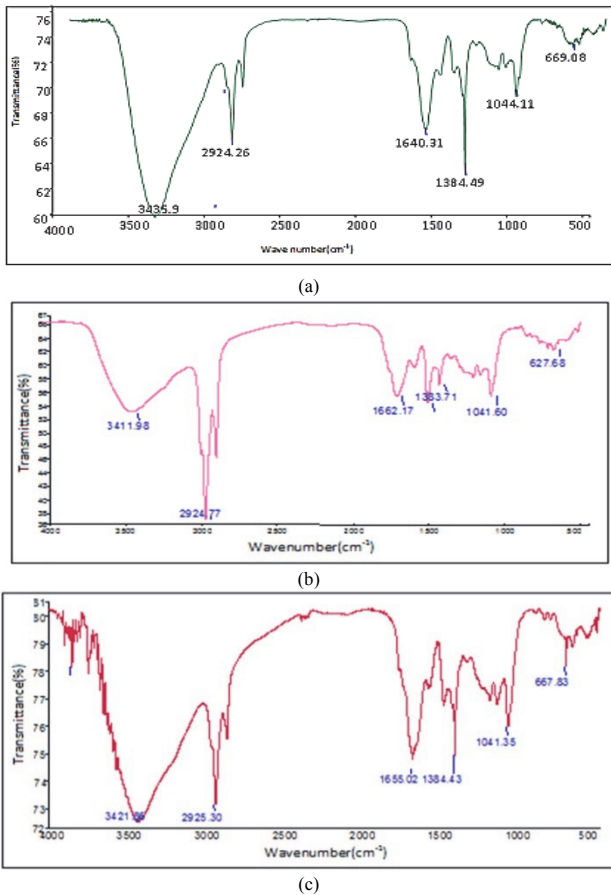
Figs. 2(b) and 2(c) show phenol and resorcinol loaded PPAA hydrogels. The broad peaks observed at 3,411 cm<sup>-1</sup> and 3,421 cm<sup>-1</sup> for phenol and resorcinol loaded hydrogels were caused by the –OH stretching vibrations of the hydroxyl group and -NH stretching vibrations of the NH<sub>2</sub> groups. The two groups were involved in the process of adsorption. The peaks at 1,662 cm<sup>-1</sup> and 1,655 cm<sup>-1</sup> in case of phenol and resorcinol loaded hydrogels indicate N–H deformation. Two sharp peaks were observed at 1,383 cm<sup>-1</sup> and 1,384 cm<sup>-1</sup> for phenol and resorcinol loaded hydrogels. This indicates that the PPAA hydrogels have higher adsorption capacity for phenol and resorcinol. These results confirm that the participation of amino, carboxylic, hydroxyl and sulphur groups of PPAA hydrogels served as potential active binding sites for adsorption of phenol and resorcinol compounds.

### 3.2 Scanning Electron Microscopy (SEM) analysis

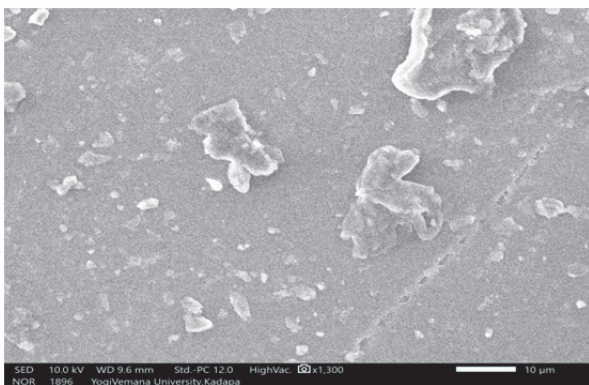
The SEM was used to examine the changes in the surface morphology of the PPAA hydrogels. It was carried out on the PPAA hydrogels to study its surface texture before and after its adsorption (Fig. 3). The adsorption capacity of an adsorbent depend upon its surface area. In other words, when the surface area increases, more binding sites are available for the adsorbate to be adsorbed. The surface morphology of PPAA hydrogels before and after phenolic compounds capture was analyzed by scanning electron microscopy (SEM).

Figure 3 (a-d) shows SEM images of dried pure PPAA hydrogel, EDX of PPAA hydrogels, phenol and resorcinol adsorption of PPAA hydrogels. SEM images of pure hydrogels showed the embroiled network of hydrogels with pores. In the solution of phenolic compounds, the gels started swelling which facilitates the functional groups to come closure of phenolic compounds and thus adsorption takes place.

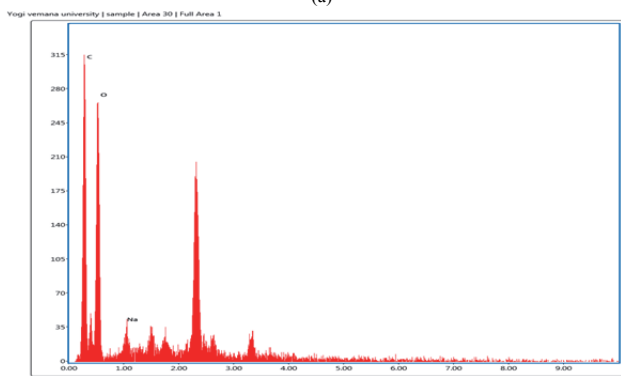
It is therefore clear that PPAA hydrogels have numbers of layers of pores where there is a good possibility for phenolic compounds to be adsorbed



**Fig. 2 FTIR Spectra of (a) Pure PPAA hydrogels (b) PPAA hydrogels loaded with phenol(c) PPAA hydrogels loaded with resorcinol**



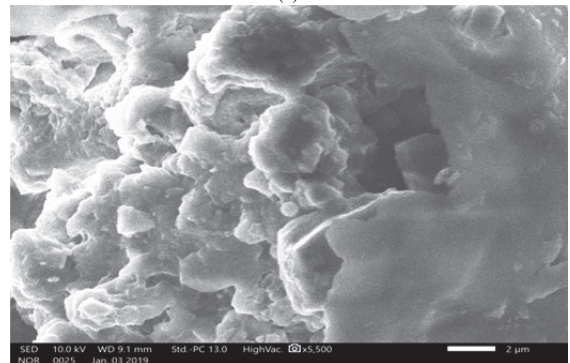
(a)



(b)



(c)

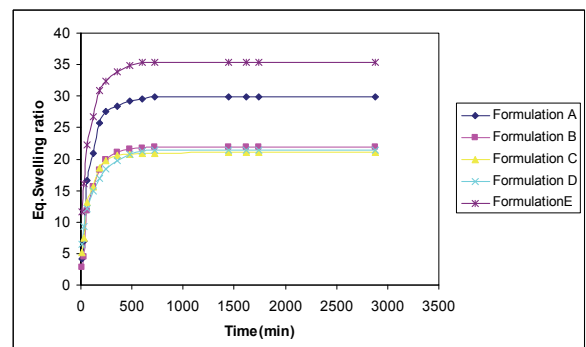


(d)

**Fig. 3 SEM images of (a) Pure PPAA hydrogels (b) EDX of PPAA hydrogels and (c) PPAA hydrogels loaded with Phenol (d) PPAA hydrogels loaded with Resorcinol**

### 3.3 Swelling Studies

The PPAA hydrogels swelling studied in water with time are shown in Fig. 4. The figure indicates that the hydrogels maximum swelling was obtained at 720 min. Swelling ratio of PPAA hydrogels in water was the minimum for formulation C and the maximum for formulation E. The maximum swelling ratio of different formulations of PPAA hydrogels, as shown in Table 1, were 30, 22, 20.8, 21.3, 35 in double-distilled water. Equilibrium swelling ratio of formulations A, B, C and D decreased. This is partly due to the presence of the low amount of AMPS monomer and partly due to the increase in the amount of cross linking agent MBA. Equilibrium swelling ratio of formulations E increases; this is due to increases the amount of AMPS monomer. The AMPS monomer concentration change from 0.5 to 1.0 gm the swelling ratio is increased. This is due to increase in the hydrophilic nature of PPAA hydrogels as increase in the hydroxyl, sulfonic acid groups of PPAA hydrogels.



**Fig. 4 Swelling kinetics of PPAA hydrogels (A-E)**

### 3.4 Effect of pH

The pH of solution has been identified as one of the most important factors influencing the active performance of PPAA hydrogels towards adsorption of phenolic compounds (phenol and resorcinol). This suggests that pH estimates not only the state of adsorbate but also the surface charge of the adsorbent in the test solutions (Murshed *et al.* 2019).

In order to optimize the pH for maximum adsorption efficiency, experiments were conducted. For the effect of pH on adsorption capacity, this was conducted by weighing about 100 mg of PPAA hydrogels after mixing in 100 mL of solution of phenol and resorcinol with different pH value ranging from 1.0 ~ 10.0. The effect of pH on phenol and resorcinol adsorption by PPAA hydrogels at different pH values were studied, and the results are shown in Fig. 5.

The maximum adsorption of phenol and resorcinol occurred at pH 3. Below this pH, the surface of the PPAA hydrogel was positively charged. In contrast, above this pH, the surface of the hydrogel was negatively charged. Actually at low pH, phenol and resorcinol were in the neutral form, but the oxygen atom of the phenol and resorcinol had partial negative charge, so the adsorption of phenol and resorcinol with PPAA hydrogels increased up to pH 3. This is due to the attraction forces between PPAA hydrogels with phenol and resorcinol. Above the pH 3, the adsorption capacity decreased. This is due to the repulsion forces occur between PPAA hydrogels with phenol and resorcinol because the phenolic compounds are converted into phenolate ions (Gaurav *et al.* 2017).

### 3.5 The effect of Contact time

The adsorption efficiency of PPAA hydrogels were analyzed based on contact time, weighing about 100 mg of PPAA adsorbents mixed in 100 mL of 100, 200 and 300 mg/L of concentrations of phenol and resorcinol solutions maintaining pH at 3. It was studied in the range of 30 ~ 300 min. Figures 6 and 7 show the effect of contact time on the adsorption of phenol and resorcinol by PPAA hydrogels. The equilibrium time for the maximum adsorption of phenol and resorcinol from aquatic solutions on PPAA hydrogels was 240 minutes.

### 3.6 The effect of Adsorbent dosage

The effect of adsorbent dosage, ranging from a small quantity of 0.05 ~ 0.6 g, was used, on the removal efficiency of phenol and resorcinol. The results are provided in Fig 8. It can be

observed that the removal efficiency increased with the increase in the adsorbent does like PPAA hydrogels up to 0.5 g where the maximum adsorption of the phenolic compounds was reached. It is mainly due to the increase of dosage of adsorbent in the phenolic solutions as well as the increases of availability of replaced sites. But, the adsorption capacity remained the same at PPAA hydrogels dosage up to 0.6 g, which shows saturation. Therefore, the adsorbent dosage was fixed as 0.5 g for further experiment, and the maximum percent removal efficiency was about 87.35% for phenol, 90.54% for resorcinol.

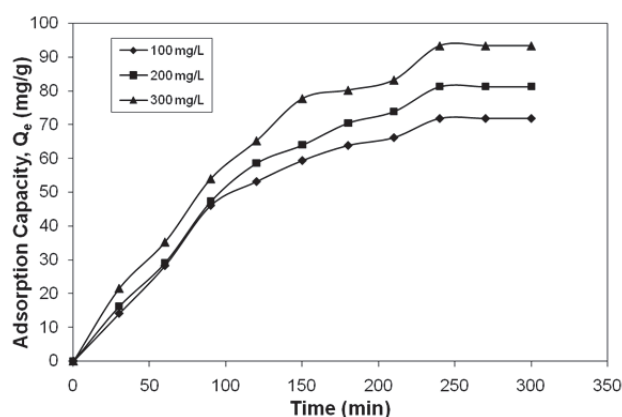


Fig. 6 The effect of contact time on adsorption of phenol on PPAA hydrogels

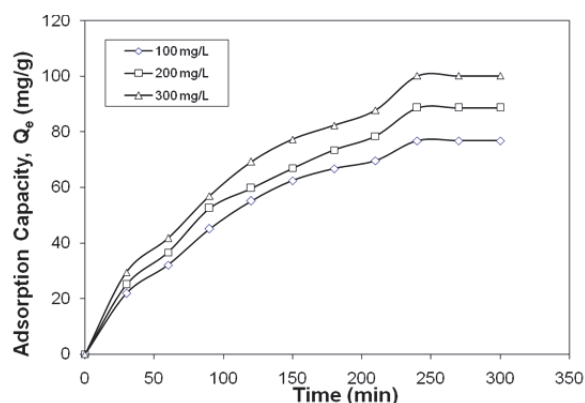


Fig. 7 The effect of contact time on adsorption of resorcinol on PPAA hydrogels

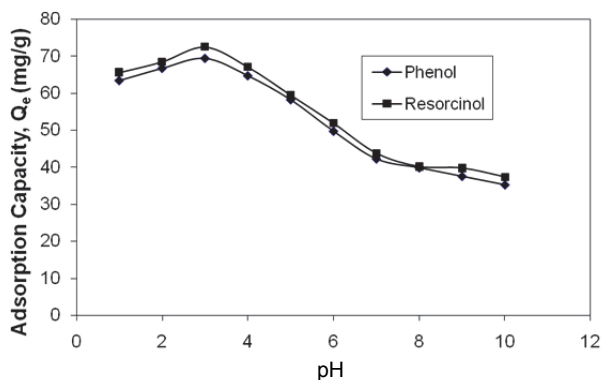


Fig. 5 The effect of pH on adsorption of phenol and resorcinol on PPAA hydrogels

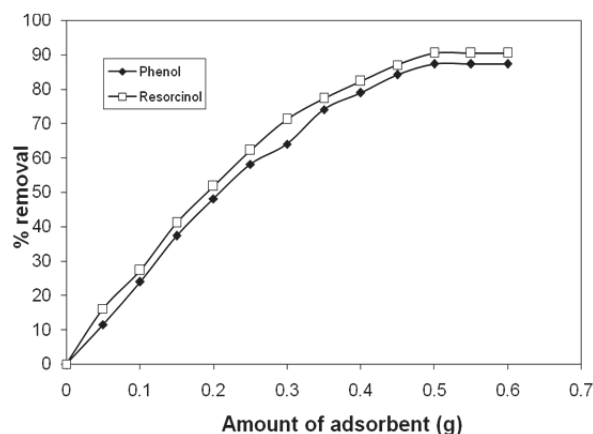


Fig. 8 Effect of adsorbent dose on adsorption of phenol and resorcinol on PPAA hydrogels

### 3.7 Adsorption Kinetics

The pseudo first order and second order kinetic model for both phenol and resorcinol by fitting the experimental data obtained from the adsorption experiments at three different initial concentrations 100, 200 and 300 mg/L, using PPAA hydrogels, are clarified below.

#### 3.7.1 Pseudo-first-order kinetics

The adsorption rate constant was determined by the Eq. (3) which represents the pseudo first order rate expression that was given by Lagergren.

The pseudo-first-order kinetic model is given by the following equation (3)

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303} t \quad (3)$$

where  $Q_e$  and  $Q_t$  are the amount of phenol and resorcinol adsorbed on the PPAA hydrogels at equilibrium and any time,  $t$  (min), respectively, and  $K_1$  is the rate constant of Pseudo-first order adsorption ( $\text{min}^{-1}$ ). From the plot of versus time ( $t$ ) with different initial concentration, gives a straight line which gives  $K_1$  is the rate constant of Pseudo-first order adsorption ( $\text{min}^{-1}$ ).

#### 3.7.2 Pseudo-second-order kinetics

The kinetic data of phenol and resorcinol adsorption was also analyzed through pseudo second order model. The linear form of the second order kinetic model is given by the following equation (4)

$$\frac{t}{Q_t} = \frac{1}{Q_e^2 K_2} + \frac{t}{Q_e} \quad (4)$$

where  $Q_e$  and  $K_2$  are the adsorption capacity of adsorbents at the equilibrium and pseudo second order constant ( $\text{g}/(\text{mg min})$ ). A plot of  $t/Q_t$  versus time ( $t$ ) gives a straight line, which gives  $K_2$ , the rate constant of Pseudo-second order adsorption ( $\text{g}/(\text{mg min})$ ).

A kinetic study of adsorption could offer information about the mechanism and effectiveness of the adsorption process. The experimental data obtained were analyzed by both pseudo first order and second order kinetic models. The kinetic parameter  $R^2$  values obtained for both the models are given in Tables 2 and 3. Besides, the kinetic plots are given in Figs. 9, 10, 11 and 12. Based on the data derived from the Correlation Coefficient ( $R^2$ ) acquired from Pseudo-first order and Pseudo-second order models, the best fit for the experimental kinetic data is Pseudo-second order model.

#### 3.7.3 Intraparticle diffusion

The adsorbate present in the solution in large quantities is transported to the surface of the adsorbent of PPAA hydrogels via intraparticle diffusion. Weber and Morris proposed an experimental model that is used for determination of the intraparticle diffusion mechanism.

The mathematical equation for Weber-Morris intraparticle diffusion model (Weber *et al.* 1963) can be expressed as follows:

$$Q_e = k_{id} t^{1/2} + C \quad (5)$$

where  $k_{id}$  is the intraparticle diffusion rate constant ( $\text{mg/g min}^{1/2}$ ) and  $C$  is the intercept. The value  $k_{id}$  and  $C$  can be calculated from the slope and intercept, respectively when a graph is plotted between  $Q_e$  and  $t^{1/2}$ . It can be observed that all the plots have an initial curved portion, followed by a linear portion and a plateau region. The initial curve of the plot is due to the diffusion of phenol and resorcinol through the solution to the external surface of PPAA hydrogels. The linear portion of curves refers to the gradual adsorption stage, where the intraparticle diffusion of phenol and resorcinol on PPAA takes place and the final plateau region indicates equilibrium uptake. The rate constants of Weber-Morris intraparticle diffusion model are shown in Table. 4, and the plots are given in Figs. 13 and 14.

**Table 2 Lagergren first-order rate constants for phenol and resorcinol adsorption on PPAA hydrogels**

Initial concentration (mg/L)	Phenol		Resorcinol	
	$K_1$	$R^2$	$K_1$	$R^2$
100	0.0131	0.9972	0.0117	0.9947
200	0.0124	0.9949	0.0101	0.9916
300	0.0117	0.9842	0.0099	0.9960

**Table 3 Pseudo second-order rate constants for phenol and resorcinol adsorption on PPAA hydrogels**

Initial concentration (mg/L)	Phenol		Resorcinol	
	$K_2$	$R^2$	$K_2$	$R^2$
100	$4.2 \times 10^{-5}$	0.9199	$6.2 \times 10^{-5}$	0.9856
200	$3.1 \times 10^{-5}$	0.9337	$5.0 \times 10^{-5}$	0.9849
300	$4.0 \times 10^{-5}$	0.9648	$4.6 \times 10^{-5}$	0.9831

**Table 4 Weber-Morris rate constants for phenol and resorcinol adsorption on PPAA hydrogels**

Initial Concentration (mg/L)	Phenol			Resorcinol		
	$K_{id}$	$C$	$R^2$	$K_{id}$	$C$	$R^2$
100	4.6963	2.7935	0.9611	4.8514	1.1982	0.9822
200	5.3297	4.7640	0.9684	5.5360	2.0441	0.9891
300	6.0380	4.1022	0.9726	6.2260	1.8681	0.9893

### 3.8 Adsorption Isotherms

#### 3.8.1 Langmuir isotherm

To study the equilibrium of phenol and resorcinol adsorption, the experiments were carried out with different initial concentrations of phenol and resorcinol, 50 ~ 100 mg/L, and the dosage of adsorbent was 0.1g/100 mL of PPAA hydrogels. Langmuir isotherm model assumes mono-layered interaction of adsorbent surface with the solute molecules. This isotherm is based on the hypothesis that the highest adsorption of solutes relates to a saturated mono layer of the solute molecules on the surface of adsorbent and that the energy of adsorption is constant.

It is applicable for mono layer and the linear form of the Langmuir isotherm (Langmuir *et al.* 1916) is

$$\frac{1}{Q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m} \quad (6)$$

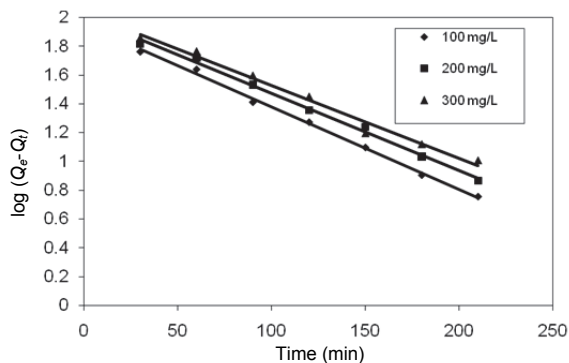


Fig. 9 Legergren first-order kinetic plots at different initial concentrations of phenol on PPAA hydrogels

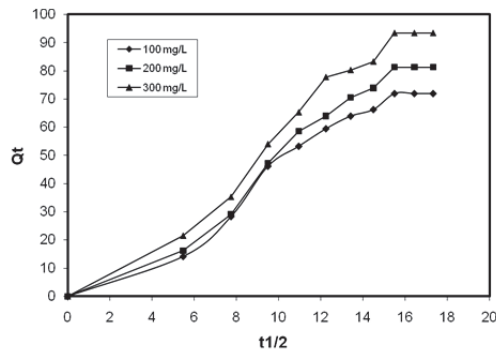


Fig. 13 Weber-Morris plots at different initial concentrations of phenol on PPAA hydrogels

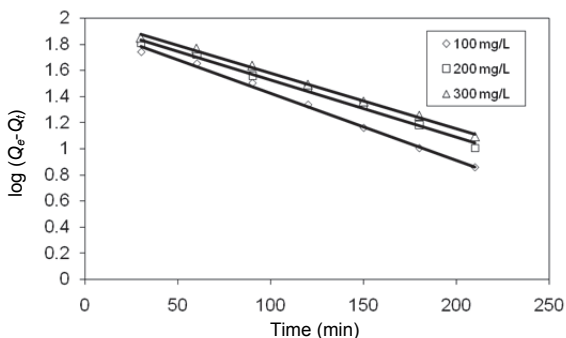


Fig. 10 Legergren first-order kinetic plots at different initial concentrations of resorcinol on PPAA hydrogels

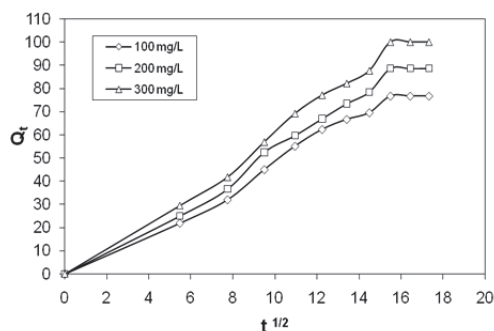


Fig. 14 Weber-Morris plots at different initial concentrations of resorcinol on PPAA hydrogels

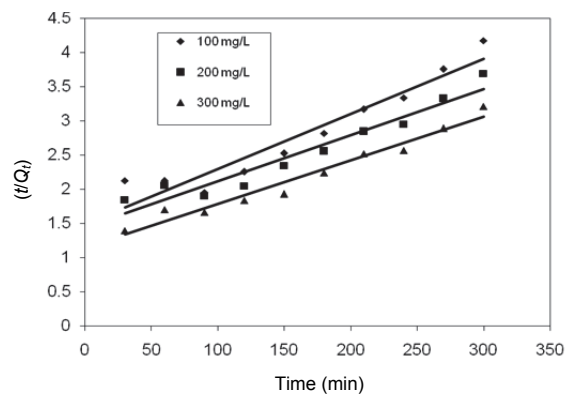


Fig.11 Psuedo-second order kinetic plots at different initial concentrations of phenol on PPAA hydrogels

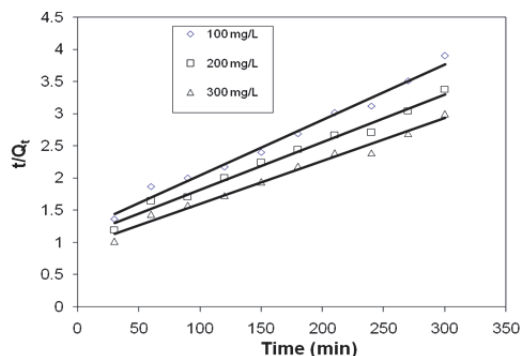


Fig. 12 Psuedo-second order kinetic plots at different initial concentrations of resorcinol on PPAA hydrogels

where is the  $C_e$  equilibrium concentration of the adsorbate (mg/L),  $Q_e$  is the amount of adsorption at equilibrium (mg/g),  $Q_m$  and  $b$  are Langmuir constants. The experimental data were plotted as  $1/C_e$  against  $1/Q_e$  in order to get the values of Langmuir constants  $Q_m$  and  $b$  and the plots are depicted in Figs.15 and 16 for adsorption of phenol and resorcinol on PPAA hydrogels.

### 3.8.2 Freundlich isotherm

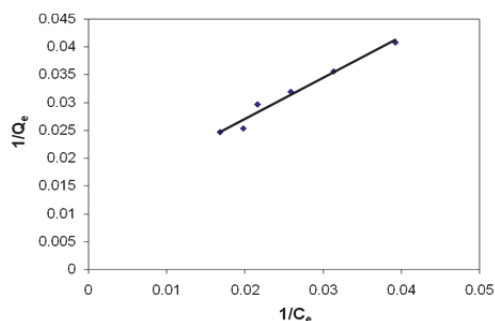
The Freundlich isotherm (Freundlich *et al.* 1906) is applicable for heterogeneous layer (or) multi layer, in the Eq.(7), a linear form of Freundlich isotherm (Freundlich,1906) is presented.

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

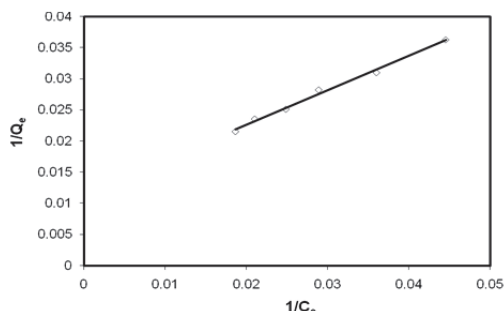
where,  $Q_e$  is the amount of phenol and resorcinol adsorbed at equilibrium (mg/g),  $C_e$  is the concentration of phenol and resorcinol (mg/L) at equilibrium.  $K_f$  and  $n$  are Freundlich constants. The value of  $1/n$  refers if the adsorption is irreversible ( $1/n = 1$ ), favorable ( $0 < 1/n < 1$ ) or unfavorable ( $1/n > 1$ ). The experimental data were plotted as  $\log Q_e$  against  $\log C_e$  in order to get the values of Freundlich constants  $K_f$  and  $n$  and the plots are given in Figs. 17 and 18, and the constants values like Langmuir and Freundlich isotherms are shown in Table. 5 for adsorption of phenol and resorcinol on PPAA hydrogels.

**Table 5 Langmuir and Freundlich isotherm constants for phenolic compounds sorption on PPAA hydrogels**

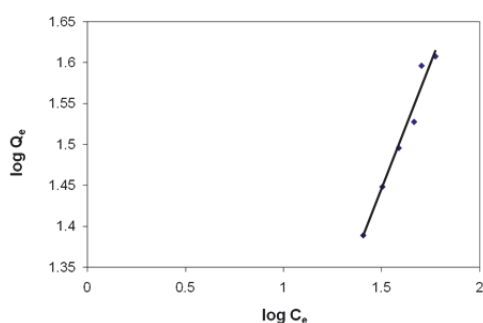
Phenolic compound	Langmuir			Freundlich			
	$Q_m$ (mg/g)	$b$ (L/mg)	$R^2$	$K_f$	$1/n$	$n$	$R^2$
Phenol	80.64	0.0168	0.974	3.326	0.615	1.624	0.969
Resorcinol	86.20	0.0210	0.993	4.596	0.579	1.724	0.992



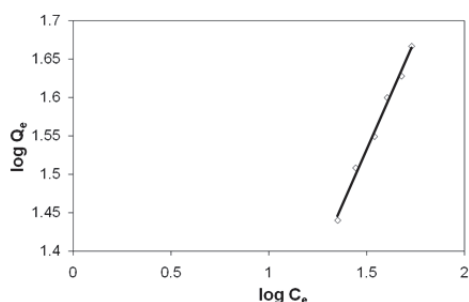
**Fig. 15 Langmuir isotherm plot for adsorption of phenol on PPAA hydrogels**



**Fig. 16 Langmuir isotherm plot for adsorption of resorcinol on PPAA hydrogels**



**Fig. 17 Freundlich isotherm plot for adsorption of phenol on PPAA hydrogels**



**Fig. 18 Freundlich isotherm plot for adsorption of resorcinol on PPAA hydrogels**

#### 4. CONCLUSION

In summary, an efficient technique has been developed for phenol and resorcinol removal by PPAA hydrogels. The PPAA hydrogels were characterized by FTIR, SEM and EDX. The adsorption studies suggested the use of PPAA hydrogels as novel adsorbents for the removal of phenolic pollutants like phenol and resorcinol from aqueous solutions. The maximum removal efficiency of phenol and resorcinol from aqueous solutions was obtained at pH 3. Therefore, we conclude that the suitable conditions for the adsorption of phenol and resorcinol from aqueous solutions include pH 3, adsorbent dosage (0.5 g/ L) and a contact time of 240 min. The kinetic study of the adsorption process followed the pseudo-first order, pseudo-second order and weber-Morris kinetic models. The equilibrium data were described by the Langmuir and Freundlich isotherm models, and from the Langmuir isotherm model, the maximal adsorption capacity was 80.64 for phenol and 86.20 mg/g for resorcinol, respectively. It is therefore clear that the PPAA hydrogels exhibit high efficiency for the adsorption of phenol and resorcinol from aqueous solutions.

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