

# Novolac Resin-Based Networks for Adsorptive Removal of Azo Dye (Orange-II)

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**Abstract:** Novolac resin-based networks 1 and 2 provide insight into the adsorptive removal of azo-dye Orange-II molecules from aqueous solution. The effects of pH and contact time were explored in this adsorption study. Favorable adsorption was observed at the pH values 2.30 and 7.20. Furthermore, the reusability of same network materials was demonstrated by the desorptive regeneration occurred at the very basic region.

**Keywords:** Novolac-Based Network Polymers, Adsorbents, Adsorption, Azo-Dye, Orange-II

## 1. Introduction

Azo-dye contamination of receiving water body presents a significant threat to human health and the environment. Some of the azo dyes and their degradation products may be toxic for living organisms [1-3]. Since Orange-II represents a popular model compound for many azo-dye colorants present in the effluent water of dyeing and textile industries, the search for facile treatment methods in eliminating Orange-II (sodium 4-[(2-hydroxy-1-naphthyl)azo]benzene sulfonate) has become a very important scientific goal [4-7]. Therefore, it is of great significance to remove these organic pollutants from contaminated water prior to their discharge. Many methods including coagulation and flocculation, oxidation or ozonation, membrane-filtration processes, ion exchange, chemical precipitation, and adsorption [8-13] have

been developed to remove these pollutants from wastewater or aqueous solutions. Adsorption-based process [14-19] has appeared a very effective method because of its low cost simplified design and operation. Polymeric sorbents [20-26] have received particular attention due to their wide variations in porosity and surface chemistry, ease of operation and recovery. Phenolic resins are of particular interest in the design of polymeric sorbent materials due to their versatile three dimensional structures, which can be modified to capture dye pollutants. In this context, there is a longstanding interest in the design of novolac type phenolic resin-based network polymers 1 and 2 (Figure 1) for the adsorptive removal of azo dye molecules [23, 24]. To continue interest in this research direction, this paper reports the adsorptive removal of azo dye Orange-II by these macromolecular network materials.

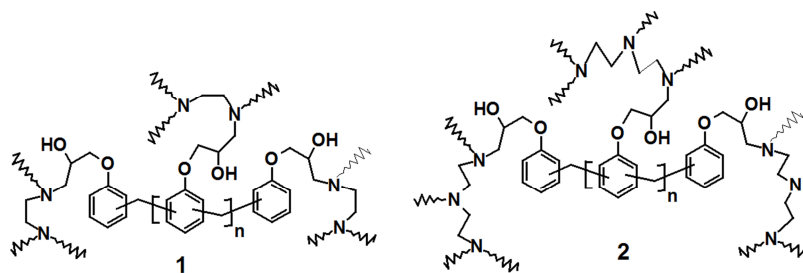


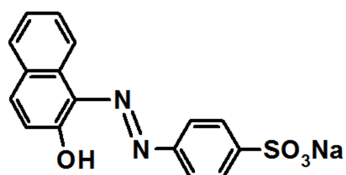
Figure 1. Novolac resin-based networks 1 and 2.

## 2. Experimental

The polymeric networks 1 and 2 as represented were produced using our published method [23, 24]. IR spectra were recorded on Perkin Elmer spectrophotometer using KBr discs. UV-vis spectra were recorded on Shimadzu UV-1800 spectrophotometer. Adsorption experiments were carried out by adding preweighed amount of sorbents to the solutions containing Orange-II at different pH values of 2.30, 7.20 and 10.96 and shaken. The pH was adjusted to a given value with dilute NaOH or HCl solutions. After different intervals, the solutions were separated from the adsorbents, and the residual concentration of Orange-II was determined by UV-vis spectrophotometer at  $\lambda_{\max}$  484 nm. The adsorbed amount (mg/g) at equilibrium was determined using the equation:  $q_e = [(C_0 - C_e)V]/W$ ; where  $C_0$  and  $C_e$  are the initial and equilibrium dye concentrations (mg/L) respectively.  $V$  is the volume of solution (L),  $W$  is the weight of the sample (g). Freundlich isotherm model was employed to assess the adsorption equilibrium. The logarithmic form of the Freundlich equation is represented by the following equation:  $\ln q_e = \ln K_f + 1/n \ln C_e$  where  $K_f$  and  $n$  are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.  $K_f$  and  $1/n$  were obtained from the linear plot of  $\ln q_e$  vs.  $\ln C_e$  (Appendix: Figures A1, A2).

## 3. Results and Discussion

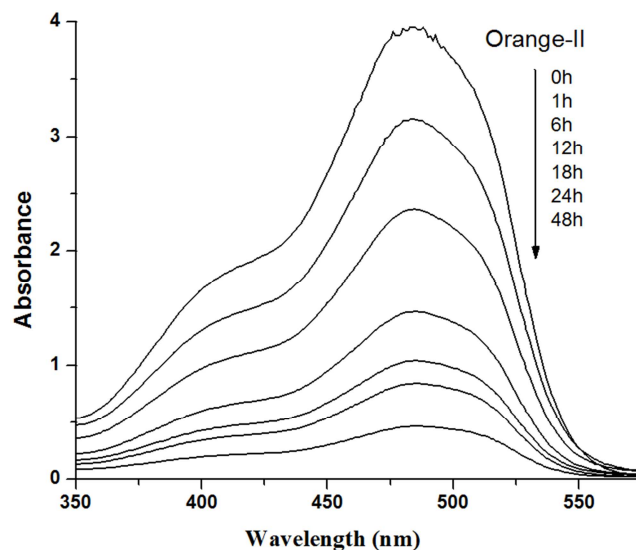
Molecular structure of Orange-II used in the evaluation of adsorption abilities of 1 and 2 is shown in Figure 2. The hydroxyl, azo and sulfonyl groups of Orange-II seems to promote adsorption onto polymer networks. Adsorption of Orange-II was examined as a function of contact time including solution pH (2.30, 7.20, 10.96) at 25°C.



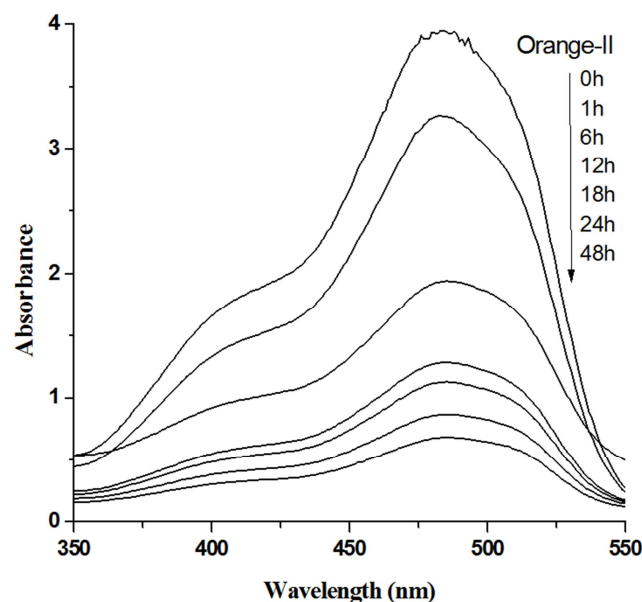
**Orange-II**

**Figure 2.** Molecular structure of Orange-II (sodium 4-[(2-hydroxy-1-naphthyl)azo]benzene sulfonate)

The pH of the medium is an important controlling parameter in the azo-dye adsorption process because it appears to manipulate the surface charge of adsorbents via protonation-deprotonation of functional groups. In addition the pH has marked influence on the degree of ionization of azo-dye adsorbates. Therefore, the pH effect on Orange-II adsorption was examined from acidic to basic regions. As seen in Figures 3 and 4, the adsorption of Orange-II onto 1 and 2 is accompanied by the gradual decrease in intensity of absorption centered at  $\lambda_{\max} = 484$  nm at different time intervals.



**Figure 3.** UV-vis spectral changes of the solutions of Orange-II ( $3.06 \times 10^{-4} M$ ) as a function of adsorption time for 1 (pH 7.20, time interval: 0, 1, 6, 12, 18, 24 and 48h, 25°C).



**Figure 4.** UV-vis spectral changes of the solutions of Orange-II ( $3.06 \times 10^{-4} M$ ) as a function of adsorption time for 2 (pH 7.20, time interval: 0, 1, 6, 12, 18, 24 and 48h, 25°C).

In the pH range from 2.30 to 7.20 (acidic to neutral condition) rapid adsorption of Orange-II was occurred and equilibrium could be achieved within 48 h (Figures 5 and 6). In contrast, when the pH value reached to 10.96, the dye removal performance of 1 and 2 declined. From Figure 3 it is also evident that the rapid adsorption is observed during the initial stage of contact probably due to the abundant porosity surface of the adsorbents. With progress of time, the dye adsorption began to decrease. This probably indicates slow diffusion of the dye molecules into the sorbents porous structure. The fast adsorption at the initial stage demonstrates the practical importance of reducing reactor volumes and times.

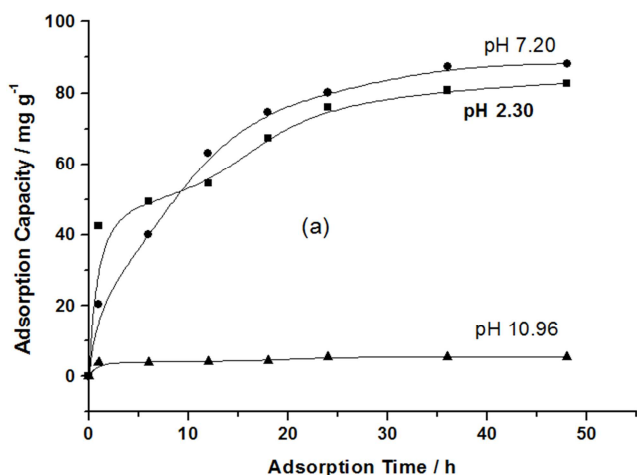


Figure 5. The effect of adsorption time on Orange-II adsorption capacity of 1.

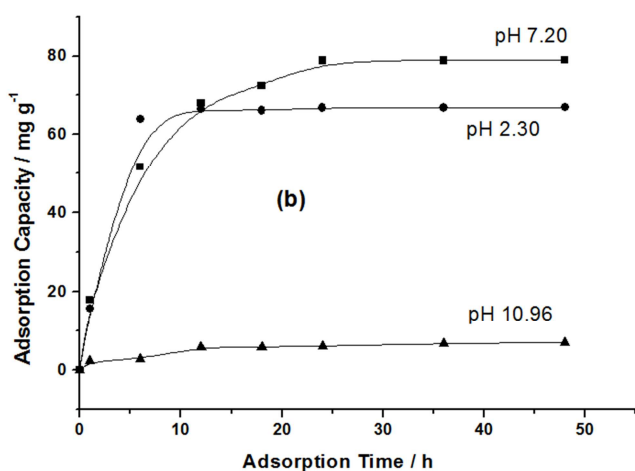


Figure 6. The effect of adsorption time on Orange-II adsorption capacity of 2.

The equilibrium adsorption isotherm data collected was fitted with Freundlich model [23, 24, 27]. The model parameters along with the correlation coefficients ( $R^2$ ) were presented in Table 1. The  $K_f$  values indicate the good adsorption capacity of 1 and 2. The values of  $n$  between 1 and 10 at  $\text{pH} = 2.30 - 7.20$  reveal a thermodynamically favorable adsorption. The values of  $R^2$  were between 0.88

and 0.9788, reflecting that the adsorption isothermal data were fair fitted by the Freundlich model [28]. Therefore,  $\text{pH}$  value of the solution provides an effective basis for the manipulation of Orange-II adsorption capacities of 1 and 2.

Table 1. Freundlich Constants of the Adsorption Isotherms for Orange-II onto 1 and 2 at different  $\text{pH}$  values.

Polymer network	pH	Freundlich Constants		
		$K_f$	$n$	$R^2$
1	2.30	3.212	1.096	0.8819
	7.20	63.596	6.997	0.9788
2	2.30	8.887	2.083	0.9123
	7.20	59.105	8.510	0.9483

To determine the involvement of interactions, FTIR spectral studies on both networks and dye-adsorbed networks have been carried out. The broad band located in the region  $3000 - 3500 \text{ cm}^{-1}$  assignable to O-H and N-H stretching frequencies was found to be better resolved in the dye-adsorbed networks. Furthermore, there were shifts to lower wavenumbers ( $\Delta\nu = 6-15 \text{ cm}^{-1}$ ) of asymmetric and symmetric stretching vibrations of  $\text{SO}_3^-$  group of Orange-II appearing at  $1173$  and  $1034 \text{ cm}^{-1}$  when adsorbed onto the networks. The shifting of these peaks to lower values underlines the involvement of  $\text{SO}_3^-$  groups in chemical interaction with polymer networks.

In accordance with previous reports [23, 24], the proposed  $\text{pH}$ -dependent adsorption mechanism is outlined in Figure 7. In this context, structure of Orange-II and network surface having a variety of interacting motifs (amino, hydroxy and ether functionalities) must be taken into account. In the acidic ( $\text{pH} = 2.30$ ) to nearly neutral region ( $\text{pH} = 7.20$ ) amino groups of sorbents are becoming protonated to the virtual appeal to the adsorption of Orange-II through the involvement of physical forces, such as strong electrostatic interaction as well as hydrogen bonding interactions involving sulphonate groups ( $-\text{SO}_3^-$ ) of adsorbate molecules ( $^+\text{N}-\text{H} \cdots \text{O}_3\text{S}-$  and  $-\text{O}-\text{H} \cdots ^-\text{O}_3\text{S}-$ ) (Figure 7). However, the adsorption capacity decreased in the basic region ( $\text{pH} = 10.96$ ), which was related to only weak hydrogen bonding forces. It is also believed that the hydroxyl ion ( $\text{OH}^-$ ) may compete with Orange-II dye anions for adsorption sites.

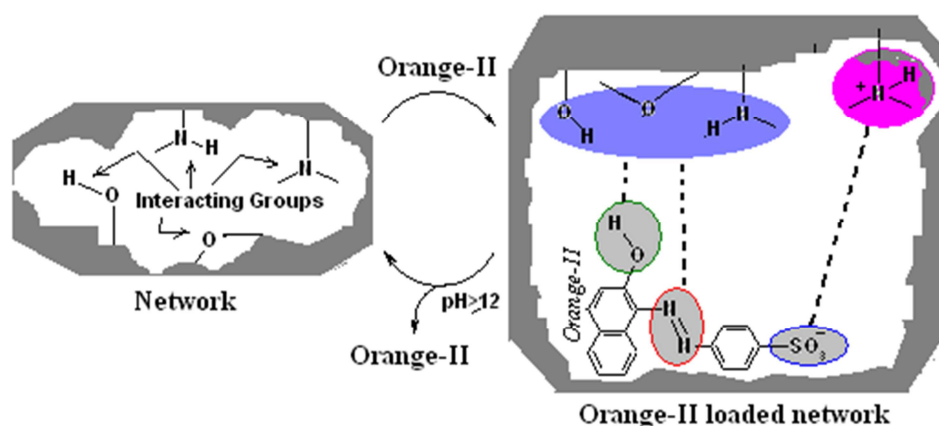


Figure 7. A proposed mechanism of adsorption: interactions occurring between network surface groups and anionic Orange-II molecule.

In order to explore the influence of salting-out agents on the removal ability, equilibrium adsorption study was also carried out in presence of sodium chloride (0.1 M). It was interesting to note that sodium chloride (0.1 M) has virtually no influence on the equilibrium adsorption. This suggests that the involved physical forces in the adsorption process are

essentially independent of salting-out effect. As shown in Figure 8, the yellow colored sorbents 1 and 2 turned into red, accompanied by the decolorization of Orange-II solution after the adsorption process. This accounted for a visual indication of Orange-II loaded sorbent surface.

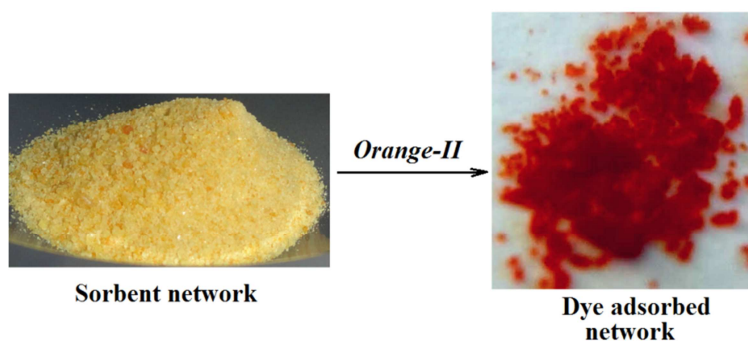


Figure 8. Photograph of Orange-II adsorbed sorbent network after 48h adsorption.

To further explore the reusability, desorption studies on Orange-II loaded sorbents were also conducted in the medium toward very basic region ( $\text{pH} \geq 12$ ). The results revealed about 90% desorption of Orange-II molecules adsorbed and hence designed sorbents are reusable. Moreover, the pH-induced adsorption-desorption cycle reflects the economic interest of the adsorption process.

#### 4. Conclusion

Novolac-based network polymers 1 and 2 were quite attractive and effective adsorbents for the removal of Orange-II azo dye from aqueous solutions. pH 2.30 and 7.20 under study enable more Orange-II dye to be adsorbed. Such influence might be caused by the optimization of surface charges of network structures for the adsorption of anionic Orange-II molecules. Equilibrium adsorption data were analysed using Freundlich isotherm. The result indicates that adsorption is a typical physical process ( $n > 1$ ). pH-driven adsorption-desorption cycle shows that networks are good reusable sorbents for Orange-II molecules. Thus, with a number of merits especially simple and inexpensive synthesis in terms of cost-effectiveness, efficient pH-driven adsorption-desorption cycle and regeneration, there is a scope of applying these sorbents in the decontamination of Orange-II dye-containing effluents. Further study is under progress in our laboratory.

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#### Appendix

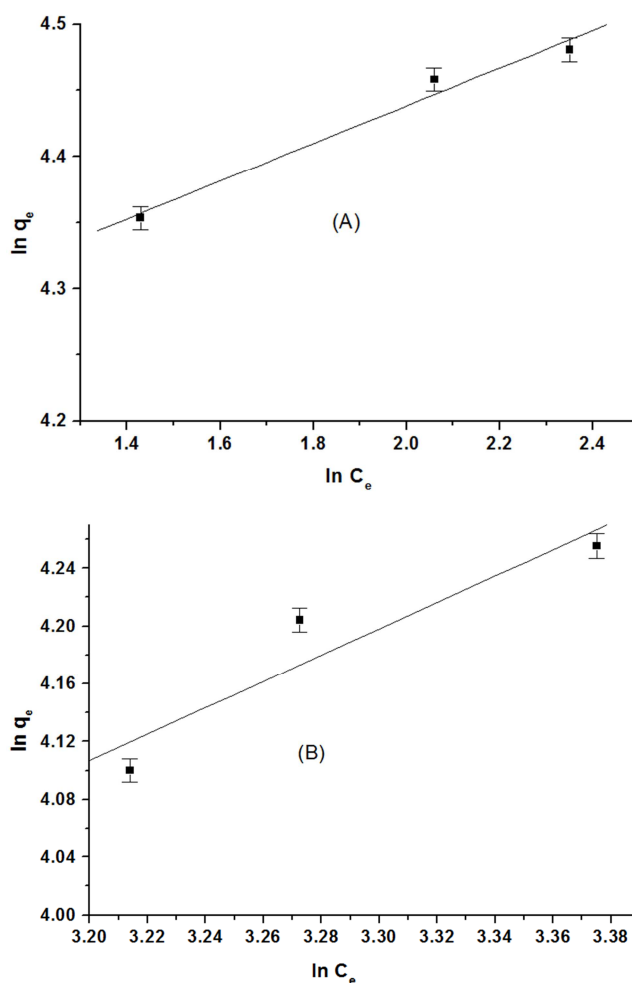


Figure A1. Freundlich isotherms for the adsorption of Orange-II onto 1 at pH 7.20 (A), pH 2.30 (B) at 25°C.

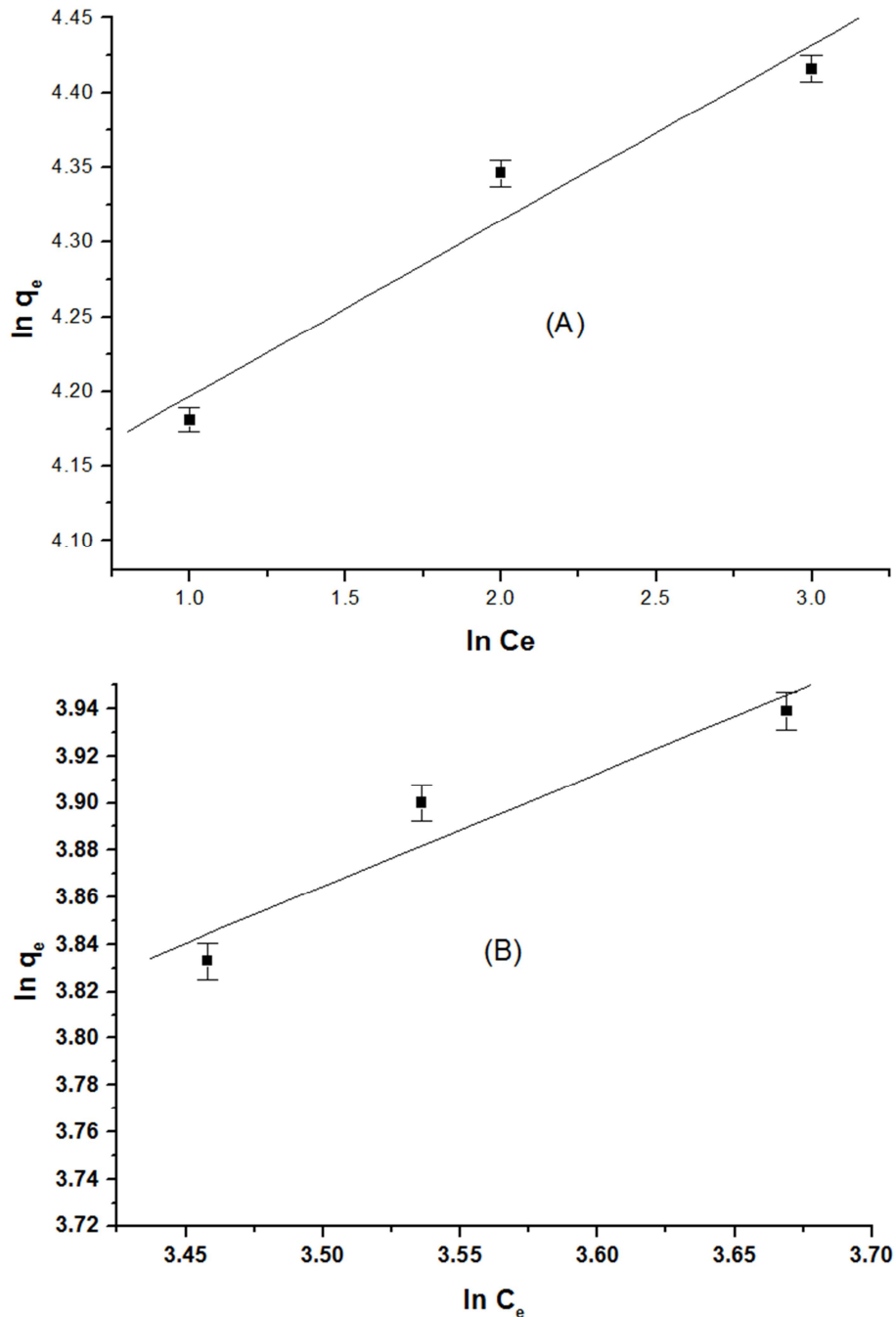


Figure A2. Freundlich isotherms for the adsorption of Orange-II onto 2 at pH 7.20 (A), pH 2.30 (B) at 25°C.

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