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## Nitrite Adsorption from Aqueous Solutions Using Amberlite IRA-67

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### ABSTRACT

Adsorption of nitrite ions in aqueous solution onto anion exchange resin Amberlite IRA-67 has been studied. The influence of different operating parameters was evaluated in batch experiment including resin dosage, contact time and initial concentration. Adsorption followed pseudo second order kinetics model with maximum nitrite removal capacity of 16.23 mg/g. Experimental data could be well fitted using Langmuir isotherm with correlation coefficients above 0.99. Scanning Electron Microscopy (SEM) and Fourier-transform Infrared Spectra (FT-IR) were employed to characterize the resin.

**Keywords:** Nitrite, Adsorption, Resin, Amberlite

### INTRODUCTION

Nitrogen pollution in hydrosphere is one of the causes of eutrophication problem. Nitrite contamination of surface or ground waters results mainly from agricultural application of fertilizers as well as from many industrial processes [1]. Nitrite has been used as a food additive for decades to preserve meat, poultry, and fish [2]. A high concentration of nitrite in water may cause methemoglobinemia in infants and it is toxic to aquatic life [3]. The allowed concentration of nitrite in drinking water according to the world health organization is 0.2 mg/l [4]. Chemical and biological processes can further reduce nitrite to various compounds or oxidize it to nitrate [5]. The use of traditional treatment techniques are very expensive, continuous use of chemicals may cause further environmental damages [6]. The adsorption process is in general low-cost, simply designed, as it is identified as an easy applicable technique [7]. In the present study, the adsorption behavior of a weak basic resin Amberlite IRA-67 has been tested for the removal of nitrite from synthetic solutions.

### MATERIALS AND METHODS

All the chemicals used in the study were of analytical grade. A weak base anion exchanger resin Amberlite IRA-67 acquired from BDH chemicals containing only tertiary amine functional groups was used for nitrite removal from aqueous solution without further treatment. A stock solution of nitrite was prepared by dissolving a known quantity of Sodium Nitrite ( $\text{NaNO}_2$ ) supplied from Sigma-Aldrich with 99.99% purity in distilled water and diluted to the required concentration. The concentrations of nitrite in the solutions before and after equilibrium were determined based on the reaction with Zambelli reagent [8]; using a double beam UV-VIS spectrophotometer (OPTIZEN 2120 UV) and employing 1 cm quartz cuvettes at a wavelength of 435 nm. Aliquots for analysis were filtered through Whatman filter paper No 40. The adsorbed amount of nitrite ions at the equilibrium in (mg/g) was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e) * V}{m} \quad (1)$$

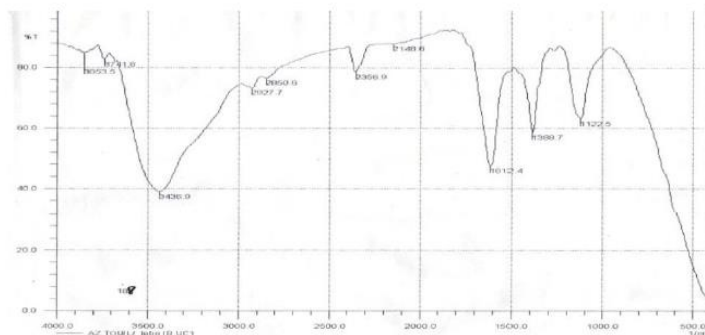
Where  $C_0$  is the initial concentration,  $C_e$  is the equilibrium concentration,  $V$  is the solution volume (L) and  $m$  is the mass of adsorbent (g).

### Adsorption experiments

Batch experiments were carried out to investigate the effect of adsorbent dosage, contact time, and the effect initial concentration. All experiments were performed at room temperature (25°C). The effect of the adsorbent dose was studied by varying the sorbent amounts from 1 to 10 g/l with 10 ml of nitrite solution (100 mg/l). The effect of contact time was tested by stirring at 0.250 g of IRA-67 resin and 50 ml of nitrite solution (100 mg/l) at different time intervals. Effect of initial concentration was carried in a series of glass vials containing 0.05 g of Amberlite IRA-67 resin and 10 ml of nitrite synthetic solution with different initial concentration ranging from 1 to 1000 mg/l, the vials then were shaken at 120 rpm for 24 h.

**RESULT AND DISCUSSION****Fourier transform infrared spectroscopy and IR spectroscopy**

IR spectra of Amberlite IRA-67 resin was recorded by a FTIR SCHIMADZU 8201-PC in the spectral range  $4000\text{ cm}^{-1}$ - $400\text{ cm}^{-1}$ . A mass of 1 mg of preground resin was mixed with 300 mg of dried KBr. Figure 1 shows FTIR spectroscopy of Amberlite IRA-67 resin. The broad and strong band at  $3436\text{ cm}^{-1}$  was owing to the overlapping of  $-\text{OH}$  and  $-\text{NH}_2$  stretching vibration. The peaks at  $1612\text{ cm}^{-1}$  were attributed to the stretching vibration of carboxyl group  $\text{C}=\text{O}$  [9].

**Figure 1: FTIR spectra of Amberlite IRA-67****Scanning Electron Microscopy (SEM)**

The surface morphology of Amberlite IRA-67 beads was observed using a scanning electron microscope (JEOL JSM-6360LV model) for determining the particle shape, and surface morphology of the resin. The sample was sputter-coated with gold before the observation [10]. SEM images of Amberlite IRA-67 particles showed a rough and porous surface (Figure 2).

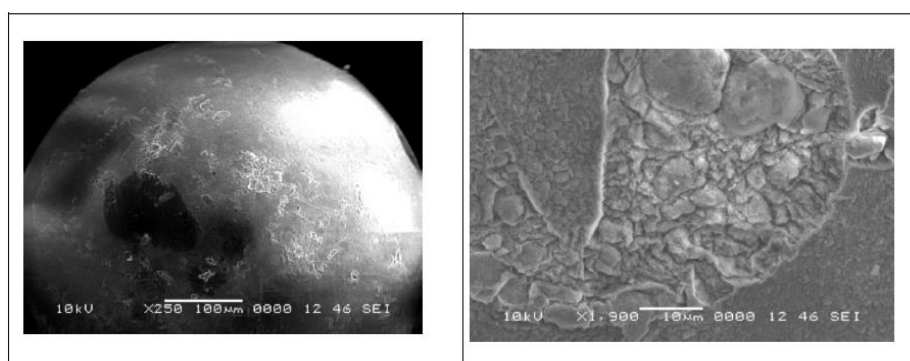
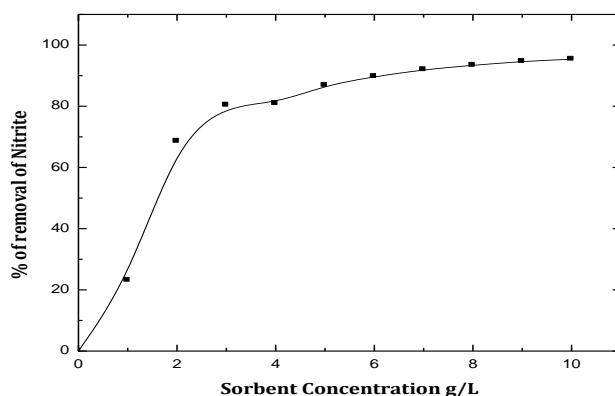
**Figure 2: SEM images of Amberlite IRA-67****Adsorbent dose effect**

Figure 3 shows the effect of adsorbent dosage on nitrite removal by Amberlite IRA-67. According to the results, it is revealed that the removal percentage of nitrite increases when the adsorbent dosage increases. The percentage of the adsorption amount values was increased from 23.13% to 86.83% with the increasing of adsorbent dosages from 1 to 5 g/L, due to the availability of adsorption sites and the increase of surface area. Any further addition of the adsorbent amount beyond did not cause any significant change. All experiments were performed with the optimum dosage of 5 g/L for the removal of nitrite by Amberlite IRA-67 resin.

**Figure 3: Adsorbent dose effect**

**Contact time effect**

**Kinetic models**

The kinetic experimental data of nitrite adsorption onto Amberlite IRA-67 resin are simulated by the pseudo-first order and pseudo second-order rate equation. The pseudo-first order kinetics is expressed by the equation (2) [11]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (2)$$

Where,  $q_e$  and  $q_t$  are the amount of the adsorbed nitrite (mg/g) at equilibrium and at time  $t$ , respectively while  $K_1$  is the rate constant ( $\text{min}^{-1}$ ).  $K_1$  can be determined from the slope of linear plot  $\ln(q_e - q_t)$  versus  $t$ .

The pseudo-second order kinetics is expressed by equation (3) [12]:

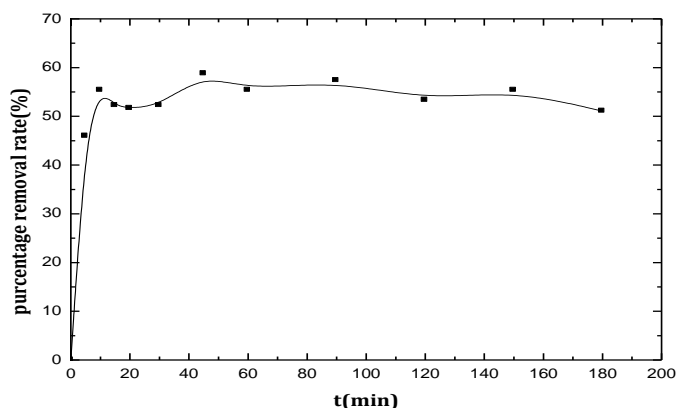
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (3)$$

Where,  $q_e$  and  $q_t$  are the amount of the adsorbed nitrite (mg/g) at equilibrium and at time  $t$  respectively, while  $k_2$  is the rate constant ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ).  $q_e$  and  $K_1$  can be determined from the plot of  $\frac{t}{q_t}$  versus  $t$ .

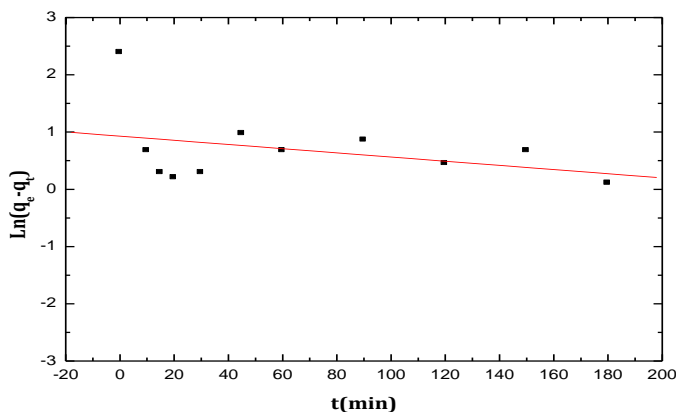
The kinetics parameters and  $R^2$  for nitrite adsorption are given in Table 1. The kinetic data can be well described by the pseudo-second order rate equation with a regression coefficient of 0.994 compared with pseudo-first order kinetic (Figures 4-6; Table 1), thus supporting the basic assumption in the model that chemisorption plays a major role in this sorption system [13].

**Table 1: Kinetic parameters for sorption of nitrite by Amberlite IRA-67**

Pseudo-First Order		Pseudo-Second Order	
$k_1 (\text{min}^{-1})$	$R^2$	$k_2 (\text{g. mg}^{-1}.\text{min}^{-1})$	$R^2$
0.00365	0.12649	0.0605	0.99437



**Figure 4: Removal of nitrite as a function of equilibrium time**



**Figure 5: Pseudo-first order kinetics of nitrite adsorption**

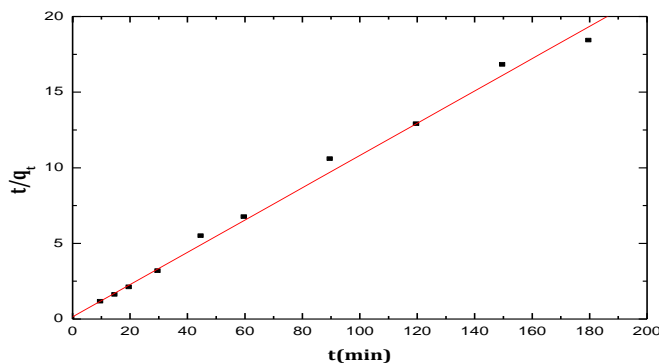


Figure 6: Pseudo-second order kinetics of nitrite adsorption

**Initial concentration effect**

**Isotherm models**

Langmuir and Freundlich isotherms models were used in this study to describe the sorption experimental data. Langmuir isotherm is represented by the following equation [14]:

$$q_e = \frac{q_{max} k_L C_e}{1 + k_L C_e} \tag{4}$$

The linear form of this model is as the follow equation (5):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} k_L} + \frac{C_e}{q_{max}} \tag{5}$$

$C_e$  is the equilibrium concentration in mg/l,  $q_e$  is the adsorbed amount at equilibrium per unit of adsorbent in mg/g,  $q_{max}$  is the maximum adsorption capacity in mg/g, and  $K_L$  is the Langmuir constant.

Freundlich isotherm is represented by equation (6) [15]:

$$q_e = K_F C_e^n \tag{6}$$

The linear form of this model is as the follow equation. (7):

$$Lnq_e = LnK_F + nLnC_e \tag{7}$$

As the results show in Figure 7, with the increasing of nitrite initial concentration the adsorbed amount is increased then becomes constant. The constants of Langmuir and Freundlich isotherm models are shown in Table 2. Based on the linear regression coefficients  $R^2$ , the absorption equilibrium data fits the Langmuir isotherm model with a maximum capacity of 16.23 mg/g (Figure 9). Langmuir model considers only superficial monolayer adsorption, considering a homogenous surface containing a limited number of ion exchange centers represented by the functional groups, but it covers a wide range of concentrations [16].

Table 2: Isotherm parameters for nitrite sorption using Amberlite IRA-67

Freundlich isotherm			Langmuir isotherm		
$K_F$ (mg/g)	n	$R^2$	$q_{max}$ (mg/g)	$K_L$ (L/mg)	$R^2$
1.1646	0.50501	0,95398	16,23	0,05628	0,99305

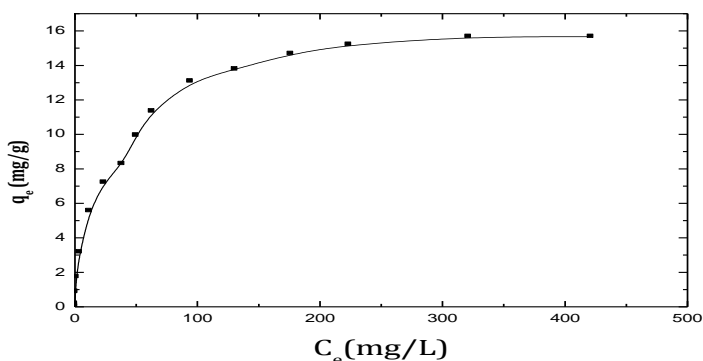


Figure 7: Initial concentration effect on of nitrite removal

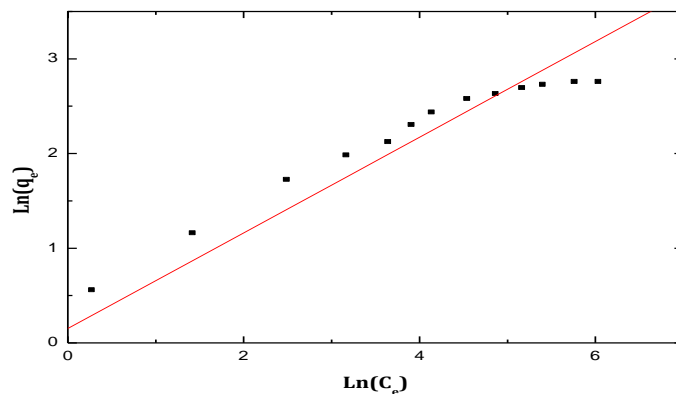


Figure 8: Freundlich isotherm model

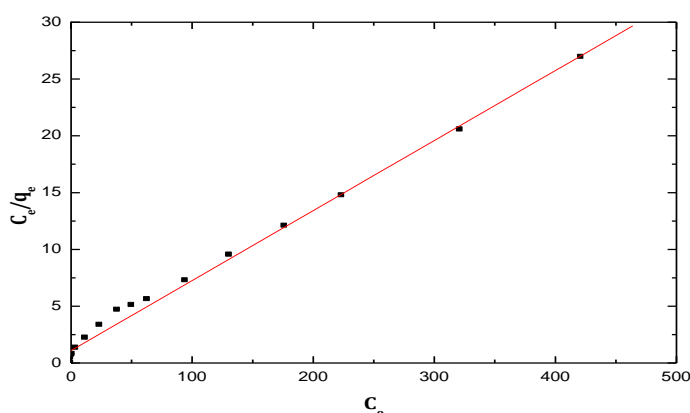


Figure 9: Langmuir isotherm model

## CONCLUSION

The surface roughness texture and functional groups of Amberlite IRA-67 resin were successfully characterized using FTIR spectroscopy and SEM. The adsorbed amount of nitrite increases with the increase in resin dosage and initial concentrations. Equilibrium data fitted well to the Langmuir models which indicated to monolayer adsorption nature of nitrite ions by Amberlite IRA-67 resin with a maximum adsorption capacity of 16,23 mg/g. The adsorption process kinetic was well described by the pseudo-second order model. The results of this research show that the Amberlite IRA-67 resin can be used for the removal of nitrite from aqueous solution.

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