

Preparation of Amberlite IRN 77 Ion Exchange Resin Loaded with Magnetite Nanoparticles for Cr(III) Removal from Aqueous Solution

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ABSTRACT

A hybrid adsorbent named magnetite nanoparticles coated resin (IRN77-Fe₃O₄) has been developed for chromium removal by an oxidative hydrolysis of iron(II) sulphate hydrate in alkaline media with addition of Amberlite IRN 77 cation exchange resin. The characterization of the modified resin was performed using Field Emission Scanning Electron Microscopy (FESEM), Fourier-transform infrared spectroscopy (FTIR), and Energy-dispersive X-ray (EDX) spectroscopy. Batch adsorption experiments under various conditions, such as time, temperature, pH and amount of adsorbent were carried out to evaluate the adsorption characteristics of magnetite-loaded resin in the removal of Cr(III) from aqueous solutions. The adsorption of Cr(III) on modified resin was found to obey the Langmuir adsorption isotherm with maximum adsorption capacity of 32.72 mg/g, which much higher than unmodified resin (23.87 mg/g) under the same optimum conditions. Therefore, it was proven that modification of ion exchange resin with magnetite nanoparticles significantly improves the adsorption performance for Cr(III) removal.

Keywords: Ion exchange resin, magnetite, chromium, adsorption, oxidative hydrolysis

1.0 INTRODUCTION

Heavy metal contamination has become a widespread environmental and health problem. A considerable amount of heavy metals is often detected in industrial wastewaters can cause serious health problems and affect the environment if not treated well. Chromium is considered as one of the hazardous heavy metals. These trace metals can exist in various oxidation states ranging from -2 to +6, however, the trivalent and hexavalent chromium are the most common form found in the environment and industrial settings.

Human activities such as wood preservation, leather tanning, and metals finishing can increase the implications of chromium pollution towards the ecosystem [1]. The toxicological effects of chromium are dependent on the chemical forms of the element. Hexaaquachromium-(III), Cr(H₂O)₆³⁺ is the main species of Cr(III) that usually existed in water. The ecotoxicity of hexavalent chromium becomes the main concern due to hazardous to human health and other living organisms. Long-term exposure of Cr(VI) can cause adverse effects on the human respiratory system, increase the risk of cancer and

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allergic dermatitis for a sensitive person [2]. Due to the hazardous biological toxicity of Cr(VI), the United States of Environmental Protection Agency regulates maximum contamination level (MCL) for chromium in drinking water is 100 µg/L [3]. However, even though the inorganic Cr(III) was proven nontoxic and noncarcinogenic to humans and animals, Cr(III) can be oxidized to Cr(VI) in the high-temperature condition [4].

Various methods and technologies have been studied for chromium removal from an aqueous solution such as reduction, precipitation, ion exchange, adsorption and membrane [5-8]. In spite of that, some of these methods suffer some of the drawbacks such as high cost, low selectivity in various conditions, and generation large scale of sludge [9]. Ion exchange is the common method used for chromium removal in the industrial scale. Due to high exchange sites and porous structure on the surface of resin, the synthetic resin was known to have high selectivity towards certain contaminants, faster kinetics, ease of reusability, and can be modified by chemical treatment to increase the adsorption capacity [10].

The application of magnetic nanoparticles for heavy metal removal was gained a significant attention among scientific communities due to high surface area of adsorption, highly active sites and magnetic properties, which given some advantage of the high efficiency of removal of certain contaminants such as Cr(VI), Pb(II) and Cd(II) [11-13]. However, the application of this type of adsorbent in large scale requires an additional separation step to separate the nanoparticles from the solution [14]. In order to overcome this problem, it is essential to develop a hybrid material that will improve the adsorption

capacity and selectivity of heavy metal removal from aqueous solution. A previous study has shown that dispersing or loading of the magnetite nanoparticle can improve the performance of the ion exchanger for uranium recovery [15]. Similar research also reported that the gel-type C-100 cation exchange resin dispersed with the nano-scale zero valent iron had maximum adsorption capacity of 14.5 mg/g and improved the selectivity of Lead (Pb^{2+}) removal from wastewater containing other competing cation [9]. Nevertheless, there are no study was made for the Cr(III) removal by using modified cation exchange resin decorated with magnetite nano particles.

In the present study, the objective of this research was to develop the surface modified cation exchange resin with magnetite nanoparticles (IRN77- Fe_3O_4) and identify the maximum adsorption capacity of the adsorbent. The prepared adsorbent (IRN77- Fe_3O_4) was also characterized by field emission scanning electron microscope (FESEM), Fourier transforms infrared spectroscopy (FTIR) techniques and energy dispersive X-ray spectroscopy (EDX). In addition, the adsorption equilibrium and maximum adsorption capacity of Cr(III) was also investigated and compared with unmodified resin (IRN77).

2.0 METHODS

2.1 Materials

The Amberlite IRN 77 cation exchange resin (Rohm and Haas, France, SA) was used in this study. This nuclear grade cation exchange resin is generally used for the removal of radionuclides from the water and wastewater. Analytical reagent grade of iron (II) sulfate heptahydrate ($FeSO_4 \cdot 4H_2O$), sodium nitrate

(NaNO₃), sodium hydroxide (NaOH) and hydrochloric acid (HCl), obtained from Aldrich Chemical Company, USA, were used for modification of ion exchange resin with magnetite nanoparticles. 1000 ppm stock solution of Cr(III) was purchased from Sigma-Aldrich, USA for the adsorption study.

2.2 Modification of Amberlite IRN 77 with Fe₃O₄

The adsorbent was prepared by oxidative hydrolysis of iron sulphate in alkaline media as the method reported in the literature with some modification [16]. Magnetite loaded cation exchange resin was synthesized as follows: 15 grams of Amberlite IRN 77 were washed with 1 litre of water to remove impurities then dried for 2 - 4 hours at 90°C. FeSO₄·4H₂O (0.06 mol) and NaNO₃ (0.1 mol) were dissolved into 100 mL of ultra-pure water under nitrogen condition. 15 g of Amberlite IRN 77 was added to the solution and stirred for 15 minutes and heated up to 80°C. Then, 100 mL of 2.5M of NaOH was slowly added to the solution and continuously stirred for 2 hours. The adsorbent was separated from the solution and washed with ultra-pure water and 1 M of HCl to remove any metals unloaded Fe₃O₄ during synthesis. Then, the hybrid material was once again washed with ultra-pure water and dried in an oven for 24 hours at 80 °C.

2.3 Characterization of Adsorbents

Various methods have been employed to determine the physicochemical properties of modified and unmodified resins. The Field emission scanning electron microscope (FESEM) with the magnification of 10,000x and energy dispersive X-ray spectroscopy (EDX) was carried out using Carl Zeiss Ultra 55 model. Magnetite, IRN 77 and IRN77-Fe₃O₄ were analyzed with

Fourier transform infrared spectroscopy (FTIR) (Cary 620 spectrometer, Agilent Technologies, USA) at the wavelength range of 400 - 4000 cm⁻¹.

2.4 Batch Adsorption

Batch experiments were performed to evaluate the Cr(III) removal performance of IRN 77 and IRN77-Fe₃O₄. The 1000 ppm of Cr(III) stock solution was diluted with ultra-pure water at the desired concentration without adjusting the pH. Various amount of adsorbent was added to 100 mL of metal solution (100 mg/L) in order to determine the optimum dosage of the adsorbent. The final concentration of samples was analysed after 4 hours using atomic adsorption spectroscopy (AAS). The amount of Cr(III) adsorbed at equilibrium (q_e) was calculated by the following equation:

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

where C_0 and C_e are the initial and equilibrium Cr(III) concentration(mg/L), respectively, V is the volume of Cr(III) solution (L) and W is the amount of adsorbent (g)

The effect of contact time was performed by mixing 0.3 g of adsorbent with 500 mL of 100 mg/L Cr(III) solution at the rate of 250 rpm. 1 mL of samples was taken at every 10 minutes interval until 5 hours. Furthermore, for the effect of pH, 0.1 M of HCl and 0.1 M of NaOH were prepared for pH adjustment of 100 mg/L of Cr(III) solution. Each solution was added with 0.3 g of adsorbent and stirred at the rate of 250 rpm for a predetermined period.

2.5 Adsorption Capacity

Adsorption capacity study was performed with different initial

concentration metal solutions while maintaining a constant dosage of adsorbent at a constant condition. The experiments were conducted with the addition of 0.3 g of adsorbent in the

metal solution with an initial concentration of Cr(III) ranging from 50 - 200 mg/L and pH of 3.5. The mixture was stirred at 25 °C at 250 rpm.

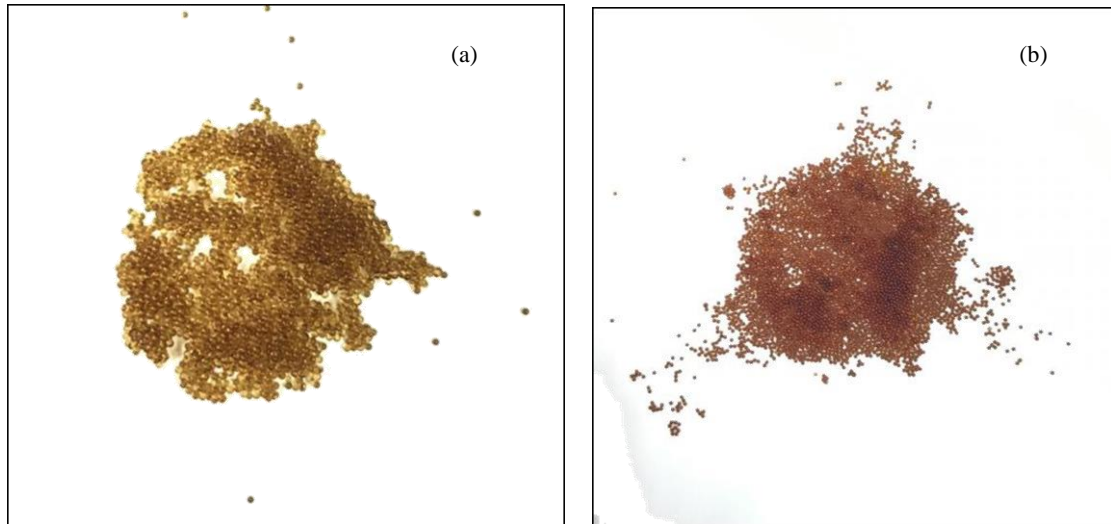


Figure 1 Photographs of (a)Amberlite IRN 77 (b)IRN77-Fe₃O₄

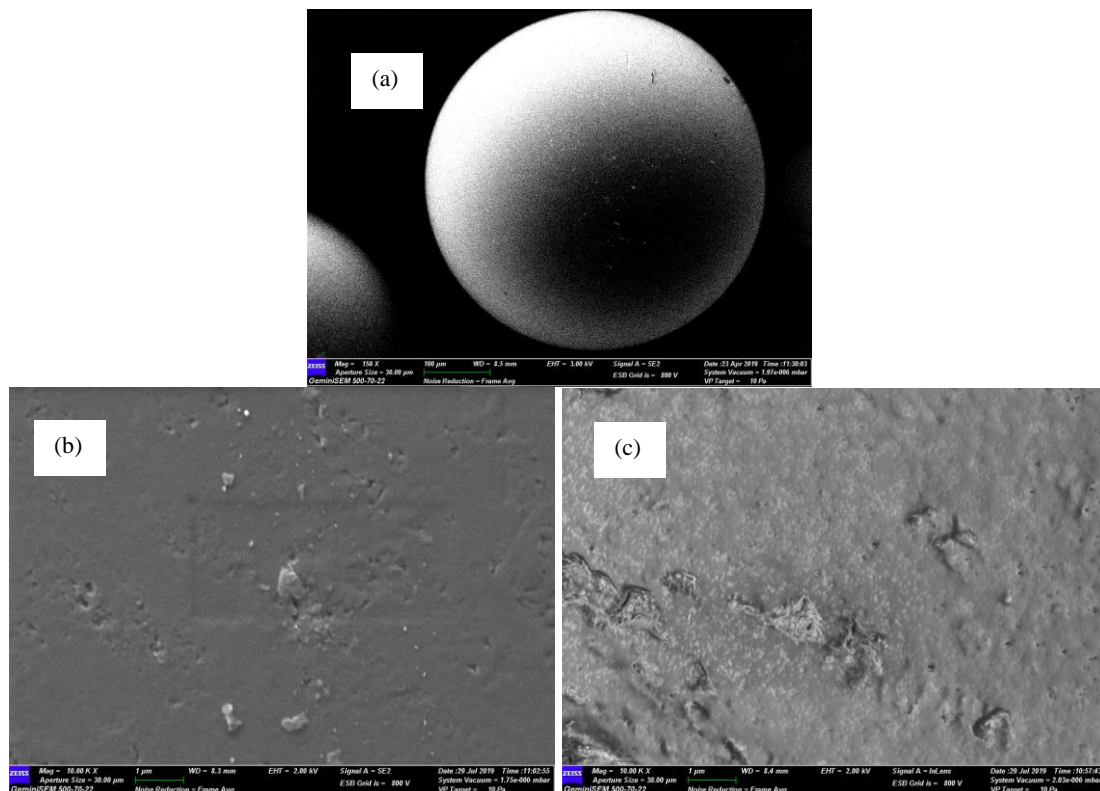


Figure 2 FESEM images of (a) IRN77- Fe₃O₄ (b) surface of Amberlite IRN 77 (c) surface of IRN77-Fe₃O₄

3.0 RESULTS AND DISCUSSION

3.1 Characteristics of Adsorbent

Photographs of both IRN77 and IRN77-Fe₃O₄ are shown in Figure 1(a) and 1(b), respectively. The color of the spherical adsorbents turned from light yellow to dark-red after deposition of the magnetite nanoparticles onto the surface of resin. The changes of the color occurred due to the formation of iron bond with the resin polymer. Similar result also was observed by

Sadeek *et al.* as they modified Amberlite IRA 402 with magnetite nanoparticles [15]. As in Figure 2(a), there was no changes in the structural shape of the resin after the modification. The FESEM images shown that the surface of the Amberlite IRN 77 cation resin (Figure 2b) was uniform and smooth, while the surface of IRN77-Fe₃O₄ (Figure 2c) was rough due to the deposition of magnetite nanoparticles onto the surface of the resin.

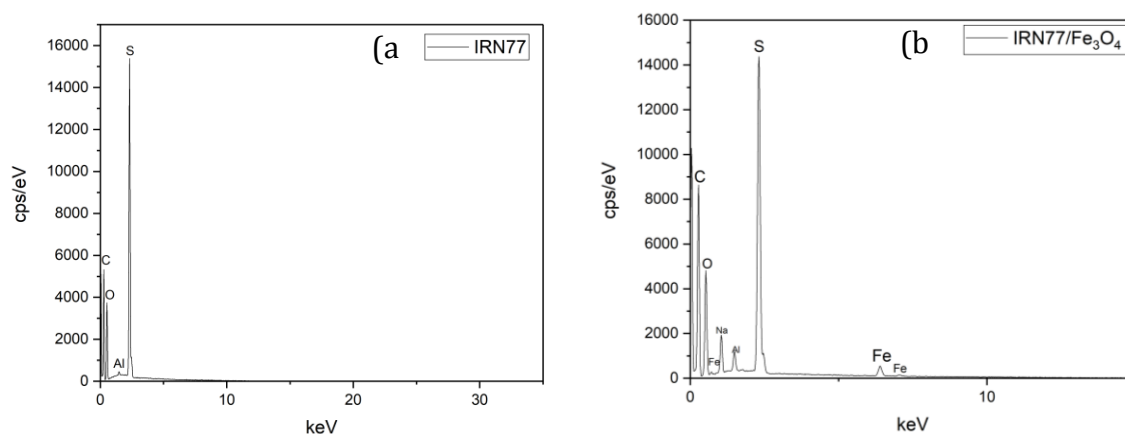


Figure 3 EDX analysis of (a)Amberlite IRN 77 (b)IRN77-Fe₃O₄

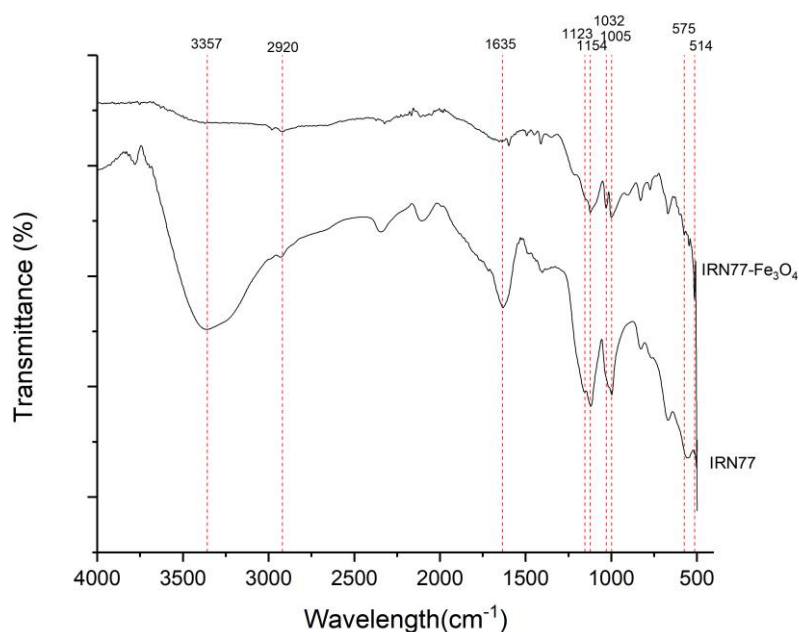


Figure 4 FTIR analysis of Amberlite IRN 77 and IRN77-Fe₃O₄

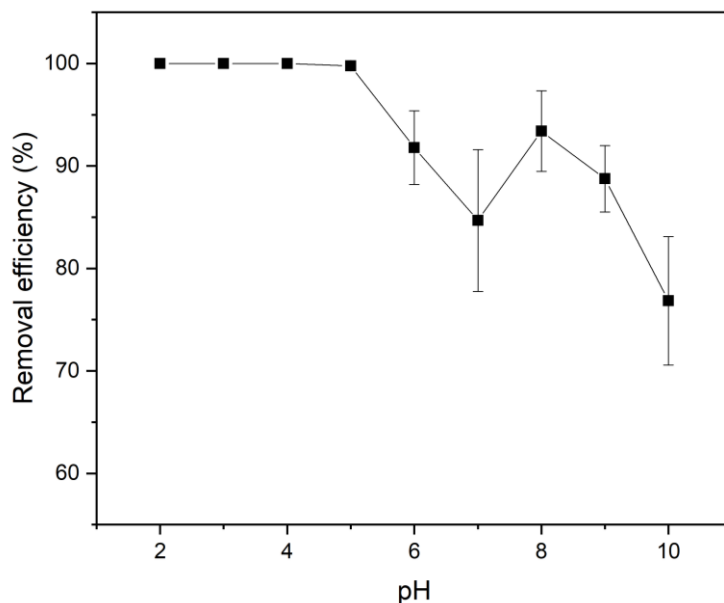


Figure 5 Effect of pH on the adsorption of Cr(III) using IRN77-Fe₃O₄

Figure 3(a) and Figure 3(b) show the EDX analysis of cation resin and IRN77-Fe₃O₄, respectively. The main composition of both adsorbents consists of carbon and sulphur, which is the main composition of the polymeric matrix and functional group of the cation resin. Meanwhile, about 1.1% of the iron element was detected in the elemental compositions of the IRN77-Fe₃O₄. Therefore, it is concluded that the magnetite nanoparticle was successfully loaded onto cation resin.

A broad peak at 3357 cm⁻¹ can be assigned to the O-H stretching vibration of the hydroxyl group on the FTIR spectrum of Amberlite IRN77 as illustrated in Figure 4 [17].

However, the O-H peak was diminished on the IRN77-Fe₃O₄ spectrum due to the drying of the adsorbent after modification. Meanwhile, a significant peak at 1481 cm⁻¹ indicates the C-H bending of the sulfonic acid functional group of cation resin [18]. Two additional peaks at 514 and 575 cm⁻¹ were attributed to Fe-O stretching vibration, which indicated

the presence of loaded ferric oxide onto anion resin [15].

3.2 Adsorption of Cr(III)

3.2.1 Effect of pH on Cr(III) Removal

Chromium (III) solution at various pH was used to determine the optimum pH of the adsorption for both resins. 0.3 g of adsorbent was added into the unbuffered 100 mg/l of Cr(III) solutions with initial pH varies from 2 – 10. The efficiency of Cr(III) was calculated by measuring unadsorbed chromium from the solution. As shown in Figure 5, the optimum initial pH for Cr(III) removal ranging from 2-5 and the adsorption capacity of the IRN77-Fe₃O₄ reduced as the pH increases. From the experimental condition, the removal efficiency of Cr(III) using modified resin was highly dependent on pH.

3.2.2 Effect of Adsorbent Dose

The effect of adsorbent dosage on the dependence of metal sorption was studied by varying the adsorbent mass at pH 3.5 in a fixed concentration of the metal ion. In Figure 6, the adsorption percentage increases as the adsorbent mass increases. The adsorbent sites increase with increasing the adsorption mass and reached 100% removal at 0.3 g for both IRN77 and IRN77-Fe₃O₄.

3.2.3 Effect of Contact Time

The performance of modified resin in terms of reaction time much higher than unmodified resin. Although both resins require the same period to achieve equilibrium, the IRN77-Fe₃O₄ adsorbed more Cr(III) ion at higher rate than unmodified (Figure 7). From the results, 0.3 g of IRN77-Fe₃O₄ needed for 100 mL of 100 mg/L Cr(III) adsorption at pH 3.5 and require at least 2 hours for adsorption equilibrium to be achieved.

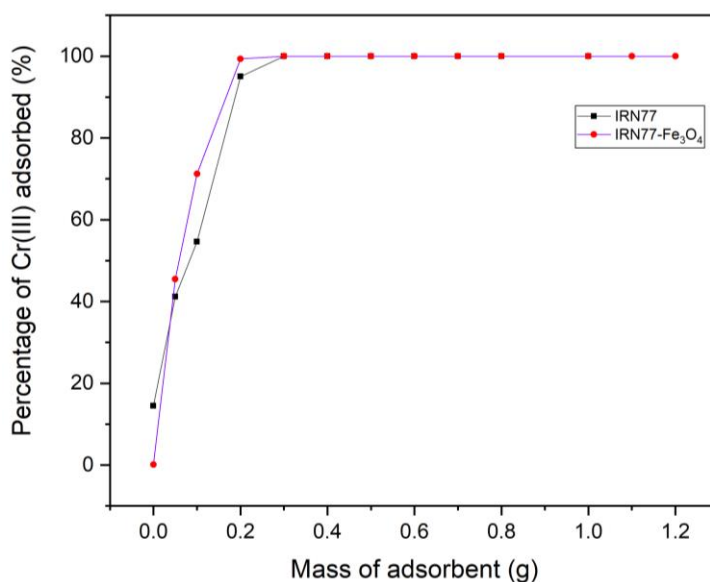


Figure 6 Effect of adsorbent mass on the adsorption of Cr(III) using Amberlite IRN

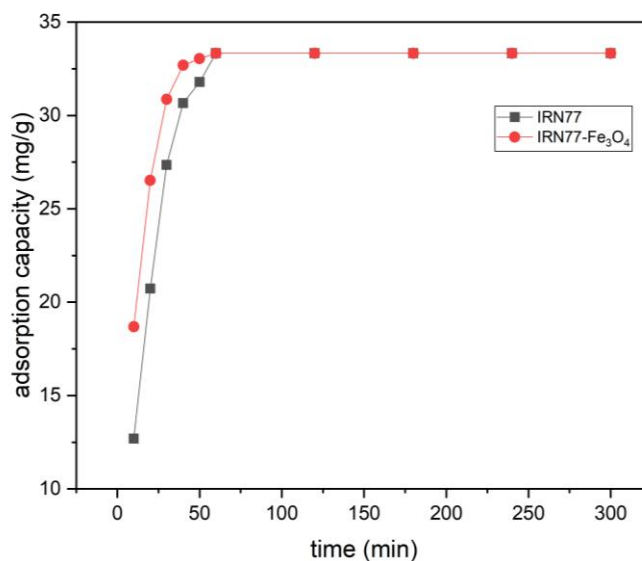


Figure 7 Effect of contact time on the adsorption of Cr(III) using Amberlite IRN 77 and IRN77-Fe₃O₄ (initial concentration of Cr(III) = 100 mg/L; resin dosage 0.3

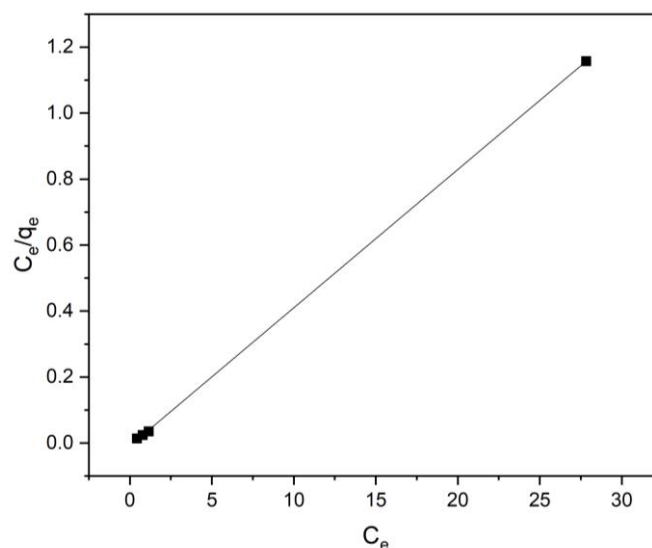


Figure 8 Langmuir linear adsorption plot of Cr(III) onto IRN77-Fe₃O₄

3.3 Adsorption Isotherm

The adsorption isotherm experiment was performed to identify the adsorption capacity of both modified and unmodified resin. Langmuir adsorption isotherm model was fit quite well ($R > 0.99$) with the experimental data for both resins. Maximum adsorption capacity calculated using the following linear equation:

$$\frac{q_e}{C_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \quad (2)$$

where, q_e is the amount of Cr(III) adsorbed at equilibrium (mg/g), C_e is the equilibrium Cr(III) concentration (mg/L), q_m and b are Langmuir constants which represent the maximum adsorption capacity (mg/g) and the energy of adsorption, respectively. These parameters are determined from the slope and intercept of the linear plot of C_e/q_e and C_e as illustrated at Figure 8. The maximum adsorption capacity of IRN77-Fe₃O₄ was 32.72 mg/g, which

is higher compared to IRN77 at 23.87 mg/g. The comparison of adsorption capacity of different Fe₃O₄ hybrid adsorbents for Cr(III) removal in the literature is provided in Table 1. In spite of the fact that some adsorbents from other researches had relatively higher maximum adsorption capacity compared to this study, the IRN77-Fe₃O₄ had a simpler procedure to synthesized, easier to separate from solution by filtration and stable during adsorption.

Table 1 Comparison of adsorption capacity of Cr(III) removal using Fe₃O₄ hybrid materials

Adsorbents	q_m (mg/g)	References
Fe ₃ O ₄ @aluminon	400	[19]
Magnetic iron oxide coated Amberlite XAD-7HP	6	[20]
PNIPAM-silica-PVP-MNPs	1666.67	[21]
IRN77-Fe ₃ O ₄	23.87	This study

3.4 Possibilities of Regeneration of the IRN77-Fe₃O₄

Some studies suggested that the Amberlite IRN 77 and magnetite nanoparticles can be desorbed by dispersing in diluted HCl [14], [22]. It is possible for the regeneration of IRN77-Fe₃O₄ by rinsing in the diluted acid and performing the adsorption. However, the removal efficiency might be reduced after a few cycles of regeneration procedure.

4.0 CONCLUSION

In this study, IRN77-Fe₃O₄ was successfully prepared by the loading of iron oxide onto cation resin through the oxidative hydrolysis method using FeSO₄ as the precursor. The presence of magnetite loaded on cation resin was confirmed by FTIR and EDX analysis. The optimal conditions for adsorption were obtained with the 0.3 g of IRN77-Fe₃O₄ needed to adsorb 100 mg/L of Cr(III) at a pH of 3.5 for 2 hours. Under the optimal conditions, the IRN77-Fe₃O₄ exhibits a remarkably increased adsorption capacity as compared to the case of Amberlite IRN 77 resin. The equilibrium adsorption data for both IRN77-Fe₃O₄ and cation resin fitted well to the Langmuir isotherm model. Based on the results, it can be suggested that IRN77-Fe₃O₄ would serve as a potential adsorbent for the removal of chromium from aqueous solution.

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