

Synthesis and Characterization of Natural Zeolite with Ordered Ion Imprinted Polymer Structures (IIP@AFINZ) for Selective Cr(VI) Adsorption from Aqueous Solution

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Abstract

In this paper, it is reported for first time about modification of activated natural zeolite from Flores Island Indonesia with ion imprinted polymer (IIP@AFINZ) for selective adsorption of Cr(VI) from aqueous solution. Here, the IIP@AFINZ was prepared by using template ion, complex agent, monomer, cross-linker such as: Cr(VI), 4-Vp, EGDMA, BPO respectively. Polymerization was leading in porogent ethanol : acetone. Several adsorption parameter such as pH effect, mass adsorbent, contact times, temperature and initial sample concentration toward adsorption process of Cr(VI) were also studied. The maximum adsorption capacity for IIP@AFINZ is 6.476 mg/L higher than on the NIP@AFINZ is 3.266 mg/L. The process of adsorption follows pseudo-second-order kinetic model and Langmuir isotherm model. The competitive adsorption studied showed a good performance of IIP@AFINZ to adsorption the Cr(VI) ion from water sample. Moreover, the reusability test for five times Cr(VI) adsorption using IIP@AFINZ showed there was no decrease of adsorption capacity was observed.

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Received 09 Jan 2019,

Revised 15 March 2019,

Accepted 17 March 2019

Keywords: natural zeolite; imprinted-polymer; selective Cr(VI) adsorption; IIP@AFINZ

1. Introduction

Hexavalent chromium (Cr(VI)) is one of carcinogenic and toxic pollutants group which is generated by leather tanning, metal finishing photography, electroplating, textile and dyes industries [1]. It has been known that Cr(VI) will cause the negative health for living organism. Thus, there were many research had been conducted to develop techniques eliminate Cr(VI) from water sample such as ion exchange [2], membrane separation [3] and adsorption [4].

Adsorption is the most frequently used methods to remove Cr(VI) from aquatic or aqueous solution because it offers the most efficient treatment and economical. Natural zeolite is one of the adsorbents that is used in adsorption of Cr(VI). However, as a conventional adsorbent naturally has low adsorption capacity for Cr(VI), especially for natural zeolites [5]. The previous research reported the attempts to modify natural zeolite for improving its Cr(VI) adsorption capacity [6,7,16,17,8–15]. Natural zeolites can be modified into zeolite ionic imprinted polymer to enhance its adsorption capacity and selectivity for Cr(VI). There are many research about ion imprinted polymer for adsorption of Cr(VI) that have been reported [18,19]. However, the reports about modification of natural zeolite into ionic imprinted polymer was used as an adsorbent material for Cr(VI) removal is still difficult to find out. Recently we publish one part of our research about modification of activated natural zeolite with poly(4-VP-co-MMA) for used in Cr(VI) adsorption [20]. Base on the results of our research before, in this paper, we report about another modification of natural zeolite from Ende-Flores Indonesia with poly(4-VP-co-EGDMA) to be used as a selective adsorbent for Cr(VI) from aqueous solution. The objectives of this work are to simplify the monomer used to synthesis the natural zeolite ion imprinted polymer. The material namely (IIP@AFINZ) was synthesized, characterized and was used for Cr(VI) selective adsorption from aqueous solution. Comparing with our previous work [20], here, the IIP@AFINZ was prepared from 4-vinylpyridine (4-VP) as a complex agent at once as functional monomer, Cr(VI) as a template ion, ethylene benzoyl peroxide (BPO) as initiator, glycol dimethyl acrylate (EGDMA) as a cross-linker agent and ethanol/acetone was using as a porogen. The optimization of adsorption parameters optimization, such as: adsorbent dosages, initial of pH, contact time and temperature were also studied. Kinetic, isotherm and thermodynamic adsorption and selectivity and reusability were also discussed.

1. Experimental

1.1. Reagents and materials

Sodium hydroxide, 1,5-diphenyl carbazide, potassium dichromate, sulphuric acid, hydrochloric acid, acetone, $\text{Pb}(\text{NO}_3)_2$, nitric acid, Ni_2SO_4 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, NH_4Cl , Mn_2SO_4 , 4-vinyl pyridine (4-VP), ethylene glycol dimethacrylate (EGDMA), benzoyl peroxide (BPO). The Acid activated of Indonesian (Ende-Flores) natural zeolite (AFINZ) which was used during the whole experiment. All reagents that is used in this research were purchased from Merck (Singapore) and Sigma Aldrich (Singapore).

2.2. Typical procedures for IIP@AFINZ and NIP@AFINZ synthesis

The IIP@AFINZ is synthesized by using the Cr(VI) as a template, EGDMA as a cross linker, 4-VP as complex, functional monomer, BPO as initiator and AFINZ as a host. It was synthesized directly through precipitation method in which 4-VP (12 mmol; 13 mL) and Cr(VI) (1 mmol; 0.3 g) and were sealed in a polymerization bottle (250 mL). This solution than was added to ethanol and acetone with proportion ethanol : acetone (2:1), and this solution was kept at room temperature for 30 minutes to form metal-complex 4-VP-Cr(VI). After this period, EGDMA (60 mmol; 11.3 mL), 1% BOP (0.1 g in 10 mL chloroform) and AFINZ (10 g) was slowly dropped into the polymerization bottle containing 4-VP-Cr(VI) complex. The mixture was purged with nitrogen gas for ten minutes, close a glass bottle and polymerization in water bath thermostatic at 65 °C for one hour then raised the temperature to 80 °C and kept constant

for five hours. After polymerization, the solid polymer was filtered and was stirred in ethanol : demineralization water (70 : 30) for 6 hours in order to remove the excess of the reagents. The imprint anion (Cr(VI)) was removed by stirring solid polymer in 4 M HNO₃ for 6 hours. The solid polymer was filtered through 0.45 µm filter paper and a fresh nitric acid solution was added, the process was continued until the optimized amount of removed Cr(VI) was achieved and determined by UV-Vis spectrophotometer. The solid polymer was then collected and was washed for several times with demineralization water until it reached neutral pH. The solid polymer was dried at 55 °C and it was being observed. For the comparison, NIP@AFINZ (non-ion imprinted polymer) was also prepared by using identical procedure without the addition of Cr(VI).

2.3. Optimization of adsorption parameters

Sorption of metal ions from aqueous solutions was studied using batch experiments. Several adsorption parameters where is studied such as adsorbent dosages, pH, contact time, and initial concentration. Effect of adsorbent dosages was carried out between concentration from 0.01 g to 0.2 g. Furthermore, pH effect was studied from pH 1 to pH 9. The pH of the Cr(VI) solution was adjusted by 0.1 M HCl or 0.1 M NaOH. Contact time effect was investigated from 0 minutes to 120 minutes. Adsorbent dosages effects, pH and contact time were investigated by using 50 mL of Cr(VI) solution 14 mg/L. Other hand, the initial concentration was performance from 6 mg/L to 20 mg/L by adding the suspension solution in close glass flask and stirrer at constant rpm at temperature 313 K. Cr(VI) in bulk sample was determined by filtered the solutions and were added with 2.0 mL diphenyl carbazide, mix and added again with H₂SO₄ to conditioning pH of 2 ± 0.5. After that, dilute to 100 mL with aqua demineralization and let stand 5 to 10 min for full-color development and measure it is with UV-Vis spectrophotometer at 540 nm. Some metal ions sorbed onto the unit mass of adsorbent was calculated from:

$$q_e = \frac{(C_o - C_e)V}{m} \left(\frac{\text{mg}}{\text{g}} \right) \quad (1)$$

Where, C_o is the initial concentration of Cr(VI) in solution (mg/L), C_e is the equilibrium concentration (mg/L), q_e is the equilibrium adsorption capacity (mg/g), m is the mass of adsorbent (g), and V is the volume of solution (L).

2.4. Analysis and characterization

The phases of IIP@AFINZ and NIP@AFINZ were characterized by X-ray diffraction by using Philips X'pert type. The morphological surface was examined by using SEM (JEOL, Tokyo, Japan). The surface area (SBET), total pore volume, and pore size distribution were determined by using Quantachrome Instruments NOVA 1200 (High-Speed Gas Sorption Analyzer Versions 10.0 – 10.03). pH was measured by using Pasco pH meter (spark PS-2008A) and the Cr(VI) ion before and after adsorption with IIP@AFINZ or NIP@AFINZ was analyzed spectrophotometrically (Shimadzu UV-1240) at 540 nm by using 1,5-diphenyl carbazide as the complexing agent. Other while total chromium, Ni(II), Mn(II), Pb(II) ion were analyzed by using AA500 atomic absorption spectrometer which is made in PG instruments.

3. Result and Discussion

3.1. Characterization of IIP-AFINZ and NIP-AFINZ

3.1.1. XRD characterization

XRD spectra (Fig.1) confirms that the crystal phase poly 4-VP has changed from amorphous phase to semi-crystalline phase after polymerization together with AFINZ. The other structure of AFINZ did not change after polymerization,

confirming the characteristic peak of mordenite and quartz such as: $2\theta = 9.70, 13.43, 19.60, 22.27, 25.63, 26.29$ and 27.71 for mordenite and $2\theta = 20.84, 26.62, 36.51$ for quartz (spectra was comparing with COD data number 96-900-3354 and 96-900-0766). To confirm that Cr(VI) was imprinted in a matrix of polymer, XRD spectra for unleached and leached IIP@AFINZ were identified by comparing with data chrom data standard (*2theta Peak height FWHM 96-901-2614*). It shows that the unleached IIP@AFINZ have three peaks at $2\theta = 39.45, 42.49, 44.45, 45.75$ and 48.43 and after leached those peaks were not shown again. This result indicated that IIP@AFINZ was successfully synthesized.

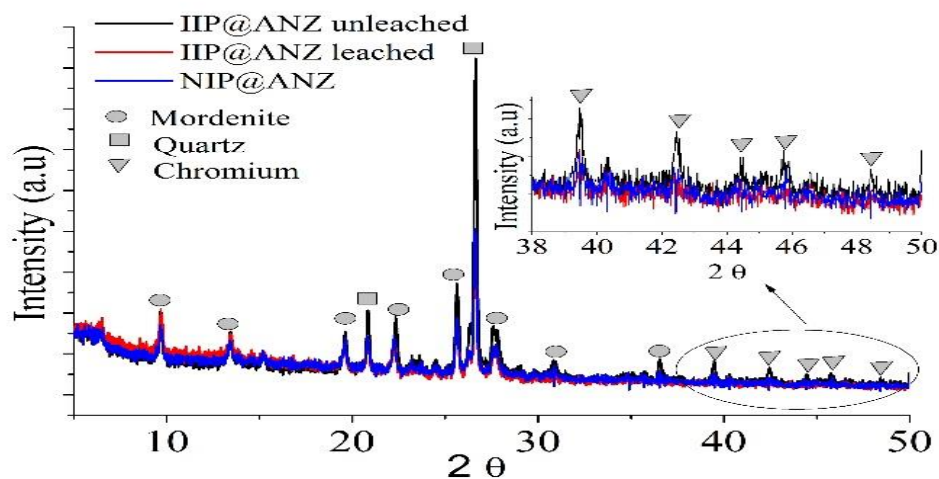


Figure 1. XRD patterns of IIP@AFINZ unleached, IIP@AFINZ leached and NIP@AFINZ

3.1.2. FTIR characterization

FTIR spectroscopy was performed to identify the complex formation between Cr(VI) and pyridine group of the polymer (Fig. 2). The broad band at 3371.01 cm^{-1} indicated --OH stretching vibration in the structure of the EGDMA and water. Two peaks at 2991.29 cm^{-1} and 1761.99 cm^{-1} belong to characteristic group frequencies for methylene vibration and ester configuration in EGDMA respectively. The peak at 1636.53 cm^{-1} is a new band was observed in IIP@AFINZ and this band was assigned the characteristic stretching vibration of pyridine groups absorption after complexation of Cr(VI) ion. The peaks at 1597.92 cm^{-1} belong to pyridine ring of both Cr(VI)-imprinted and non-imprinted polymers. This result confirms research findings of Bayramoglu & Arica, 2011; Yiğitoğlu & Arslan, 2009.

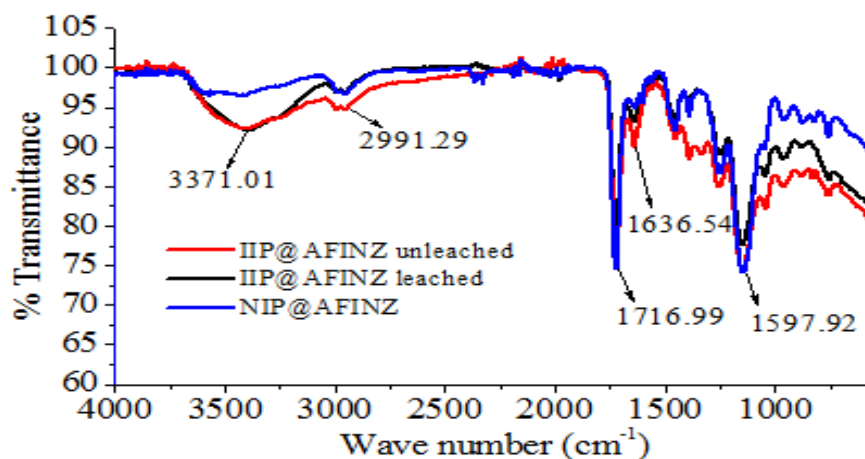


Figure 2. The FTIR Spectra of IIP@AFINZ unleached, IIP@AFINZ leached and NIP@AFINZ

3.1.3. SEM-EDX characterization

SEM-EDX characterization was performed to see the surface morphology and elemental composition qualitatively from unleached IIP@AFINZ, leached IIP@AFINZ and NIP@AFINZ. The result of the SEM-EDX analysis for IIP@AFINZ unleached, IIP@AFINZ leached and NIP@AFINZ are shown in Fig.3a – 3c. The surface of SEM images for IIP@AFINZ (Fig. 3a) more grainy comparing with IIP@AFINZ leached (Fig. 3b), and NIP@AFINZ (Fig. 3c) was seen at 5000x magnification.

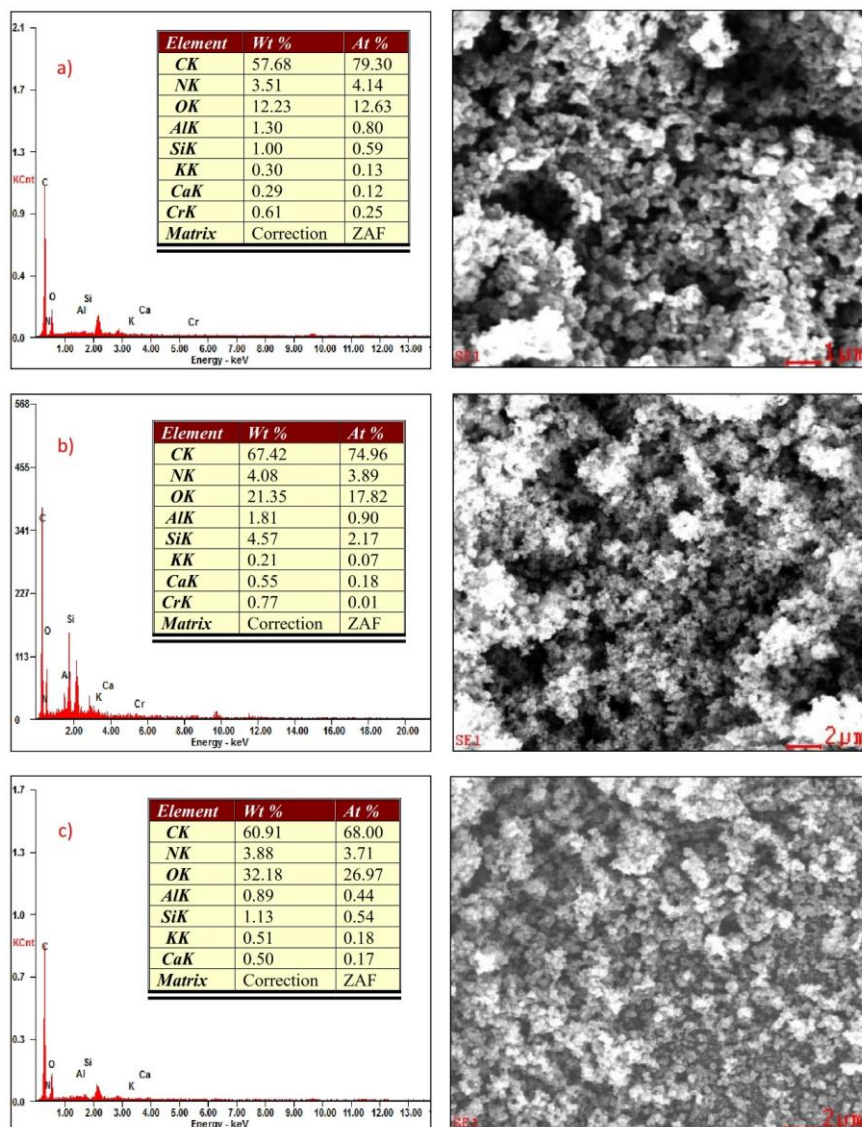


Figure 3. SEM-EDX analysis for: a) IIP@AFINZ unleached, b) IIP@AFINZ leached and c) NIP@AFINZ

Based on SEM image it is shown that surface morphology of unleached IIP@AFINZ (Fig. 3a) more a grainy with big pores comparing with IIP@AFINZ leached (Fig. 3b). This result indicated the surface morphological of IIP@AFINZ unleached more roughness may be influenced by the availability of chromium metal in a polymeric matrix. On the other hands, NIP@AFINZ has a rough surface with small pores. Base on EDX data it shows that content in unleached IIP@AFINZ such as: C (79.30 %), N (4.14 %), O (12.63 %), Al (0.80 %), Si (0.59 %), K (0.13 %), Ca (0.12 %), and Cr (0.25 %) while this compound was changed after leached process into C (75.96 %), N (3.89 %), O (17.82 %), Al (0.90 %), Si (2.17 %), K (0.07 %), Ca (0.18 %) and Cr (0.01 %). The elements contained in NIP-AFINZ are C (68.00 %), N (3.71 %), O (26.97 %), Al (0.44 %), Si (0.54 %), K (0.18 %) and Ca (0.17 %). EDX data obtained

is by the data characterization using XRD and FTIR done previously.

3.1.4. BET-BJH

The characterization of BET and BJH was conducted to determine the surface area, pore diameter, and volume of pore diameter of the synthesized imprinting polymer. N₂ adsorption isotherm and pore size distribution of IIP@AFINZ unleached, IIP@AFINZ leached and NIP@AFINZ was presented in Fig. 4.

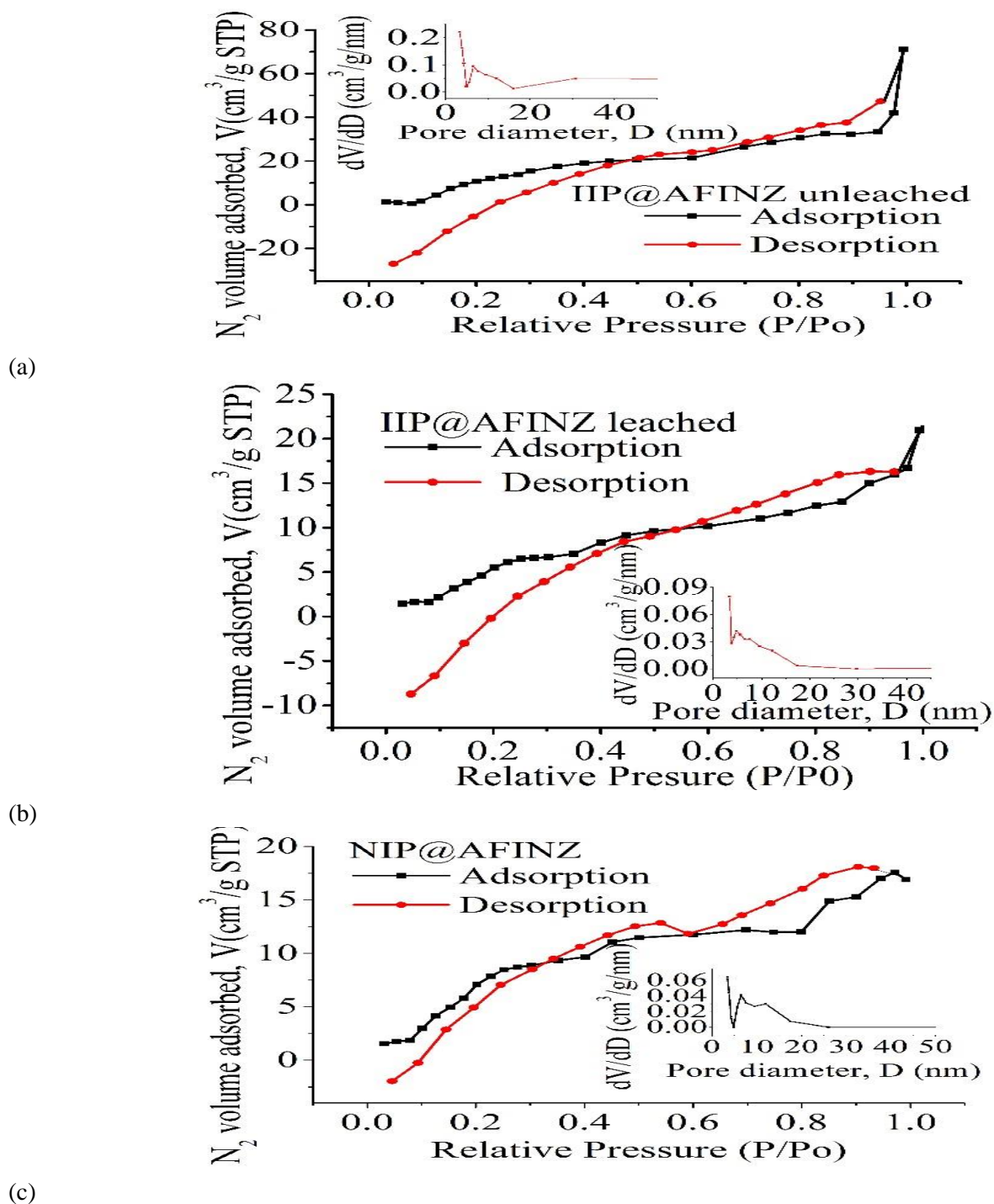


Figure 4. N₂ adsorption isotherm and pore size distribution of: (a) IIP@AFINZ unleached, (b) IIP@AFINZ leached and (c) NIP@AFINZ

As seen in Fig. 4 that the isotherm/desorption adsorption of nitrogen on IIP@AFINZ unleached, IIP@AFINZ leached and NIP@AFINZ follows the adsorption isotherm of type IV and it also called hysteresis loop. Isotherm of this kind is generally occurred in the adsorbent with a pore size in the form of mesopore. One way to determine whether a form of zeolite mesopore hysteresis loop by looking at P/P0 from 0.75 to 0.95. Based on the pore size distribution is seen that IIP@AFINZ unleached has a pore size distribution in the amount of 56.00 Å. The IIP@AFINZ leached has a pore size distribution of 39.12 Å, whereas for NIP@AFINZ has a pore size distribution of 65.21 Å. This result confirms that this material has a mesopore structure. Table 1 it shows that BET surface area and pore volume was increased after the leaching process was conducted to IIP@AFINZ. Total of pore volume, mesopore volume and the average pore size were decreased. Increasing on BET surface areas and volume micro indicating that Cr(VI) trapped in the mold of imprinted polymer was successfully extracted out from the micropores framework of IIP@AFINZ. This result also implies that IIP@AFINZ has most micropores channels.

Table 1. Physical parameters of IIP@AFINZ unleached, IIP@AFINZ leached and NIP@AFINZ measured by N₂ adsorption–desorption isotherms.

Samples	BET surface area ^a (m ² /g)	Total pore volume ^b (cm ³ /g)	Micropore volume ^c (cm ³ /g)	Mesopore volume (cm ³ /g)	Average pore diameter (Å)
IIP@AFINZ unleached	142.268	0.0721	0.0000	0.0721	56.00
IIP@AFINZ leached	146.697	0.2205	0.1612	0.0593	39.12
NIP@AFINZ	54.456	0.0261	0.003	0.0231	65.21

Exp.: a: Multi point BET, b: total pore volume at P/P0 = 0.99893 (IIP-AFINZ unleached), 0.99319 (IIP-AFINZ leached) and 0.99197 (NIP-AFINZ), c: Mesopore volume = Total pore volume – Micropore volume.

3.2. Adsorption of Cr(VI) onto IIP@AFINZ and NIP@AFINZ

3.2.1 Adsorbent dosages effect

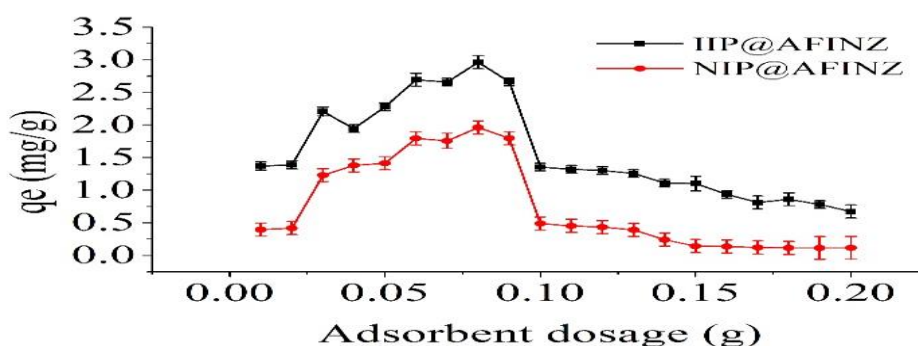


Figure 5. Effect of IIP@AFINZ and NIP@AFINZ dosages on the Cr(VI) anion adsorption (Experimental condition: T: 313 K; initial concentration: 14 mg/L)

The effect of adsorbent dosages of Cr(VI) anion adsorption onto surface of IIP@AFINZ and NIP@AFINZ was shown in Fig. 5. Fig. 5 shows that, the adsorption capacity of Cr(VI) anion was increased from 1.37 mg/g to 2.962 mg/g when the mass of IIP@AFINZ was applied from 0.01 g to 0.2 g respectively. The adsorption capacity then was drastically decreased and relatively constant as big as ± 1.033 mg/g although adsorbent dosage continued to increase

until 0.2 g usages respectively. Figure 5 shows that the best adsorption capacity of Cr (VI) anions on IIP@AFINZ surfaces occurs on the use of 0.08 g of IIP@AFINZ. Meanwhile for the use of NIP@AFINZ as an adsorbent, although the best adsorption capacity of Cr (VI) anion also took place on the use of NIP@AFINZ as much as 0.08 g however the adsorption capacities is lower than IIP@AFINZ it is about 1.962 mg/g. These results indicate that the adsorption capacity of Cr (VI) is influenced by the imprinting of Cr (VI) present in the IIP@AFINZ matrix. As shown in Fig. 5, the adsorption capacity of Cr(VI) anion was increased from 1.37 mg/g to 2.962 mg/g when the mass of IIP@AFINZ was applied from 0.01 g to 0.2 g respectively. The adsorption capacity then was drastically decreased and relatively constant as big as ± 1.033 mg/g although adsorbent dosage continued to increase until 0.2 g usages respectively. Figure 5 shows that the best adsorption capacity of Cr (VI) anions on IIP@AFINZ surfaces occurs on the use of 0.08 g of IIP@AFINZ. Meanwhile for the use of NIP-ZAA as an adsorbent, although the best adsorption capacity of Cr (VI) anion also took place on the use of NIP@AFINZ as much as 0.08 g however the adsorption capacities is lower than IIP@AFINZ it is about 1.962 mg/g. These results indicate that the adsorption capacity of Cr (VI) is influenced by the imprinting of Cr (VI) present in the IIP@AFINZ matrix.

3.2.2. Effect of pH

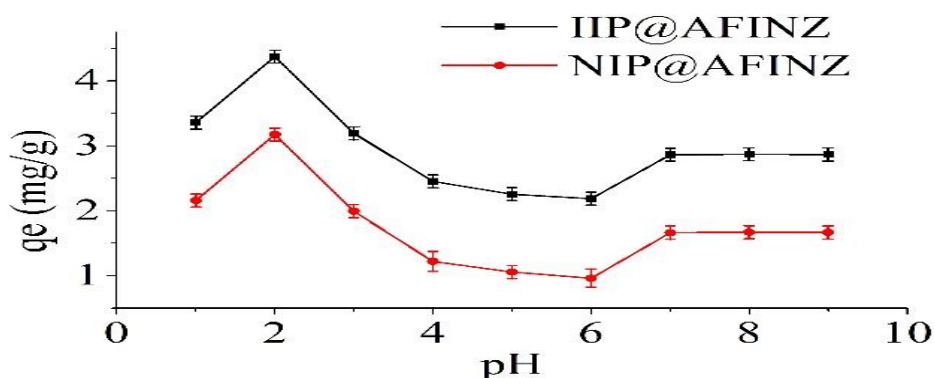


Figure 6. Effect of pH on Cr(VI) adsorption onto surface of IIP@AFINZ and NIP@AFINZ (Experimental condition: T: 313 K; initial concentration of Cr(VI) anion: 14 mg/L)

The determination of the pH is important in the process of adsorption of Cr(VI) because conditions of pH will significantly affect the solubility of metal ions in solution and affect the charge on the surface of the adsorbent during the adsorption process takes place. Fig. 6. shows that adsorption of Cr(VI) onto IIP@AFINZ was biggest at pH = 2 with adsorption capacities is 4.373 mg/g. Other hand the the good performance of adsorption of Cr(VI) onto NIP@AFINZ particle also occurred at pH 2 with adsorption capacities is 3.173. As see in Fig 6 that pH pH gives the effect to adsorption of Cr(VI) from water sample using IIP@AFINZ or NIP@AFINZ as sorbent. The condition of Cr(VI) in water depends on pH, for example at under pH 1 Cr(VI) is present as H_2CrO_4 , while at pH 1 to 6 Cr(VI) are present in several forms like $HCrO_4^-$, $HCr_2O_7^{2-}$ and CrO_4^{2-} . At pH 7 Cr(VI) is only present as CrO_4^{2-} [23]. At pH 5 to 8 with high of OH^- ion, Cr(VI) will react with OH^- to form $Cr(OH)_6$. Base on this research showed that optimum adsorption of Cr(VI) occurs at pH = 2 that there may be as $HCrO_4^-$. The result of this research is similar to the research which was conducted by Ma, Lu, Chen, Ma, & Wang (2014).

3.2.3. The effect of contact time

The amount of IIP@AFINZ and NIP@AFINZ was used to adsorption the Cr(VI) anion from water samples and the effect of time contact was studied using 14 mg/L of Cr(VI) sample at several different contact time from 15 minutes to

120 minutes respectively. Effect of adsorption time was found out between 15 to 120 minutes. From Fig. 7 of this research showed that the optimum sorption of Cr(VI) at 30 minutes with $q_e = 6.386$ mg/g. The base of Fig. 7 shows that after 30 minutes sorption of Cr(VI) was steady constant. This result showed that the equilibrium of adsorption Cr(VI) onto IIP@AFINZ was achieved at 30 minutes.

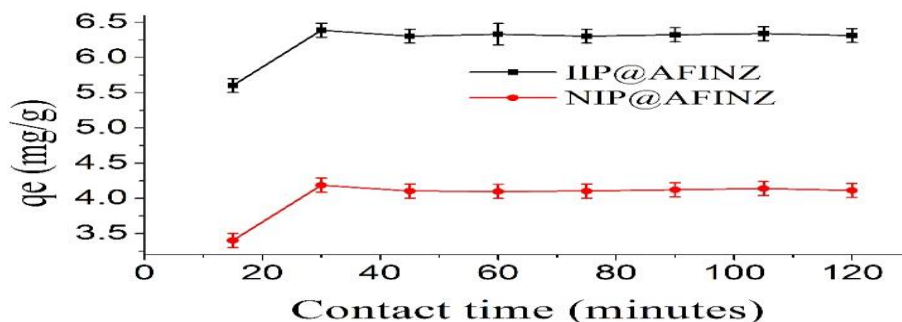


Figure 7. Effect of contact time for adsorption of Cr(VI) anion on IIP@AFINZ and NIP@AFINZ particles (Experimental condition: initial concentration of Cr(VI): 14 mg/L; pH = 2; T: 313K)

Base on Fig. 7, it shows that adsorption capacities of Cr(VI) anion onto IIP@AFINZ and NIP@AFINZ increased with increase in contact time from 15 minutes ($q_e = 5.602$ mg/g for IIP@AFINZ and $q_e = 3.402$ for NIP@AFINZ) then became slow up to 30 minutes ($q_e = 6.387$ mg/g for IIP@AFINZ and $q_e = 4.187$ for NIP@AFINZ) and saturation after 30 minutes event contact time was up to 120 minutes. Rate adsorption of Cr(VI) on IIP@AFINZ or NIP@AFINZ were efective at 30 minutes contact time condition.

3.2.4. Adsorption capacity and initial concentration

The adsorption capacities and initial concentration of Cr(VI) was performed by using the batch system. The result is given in Fig. 8.

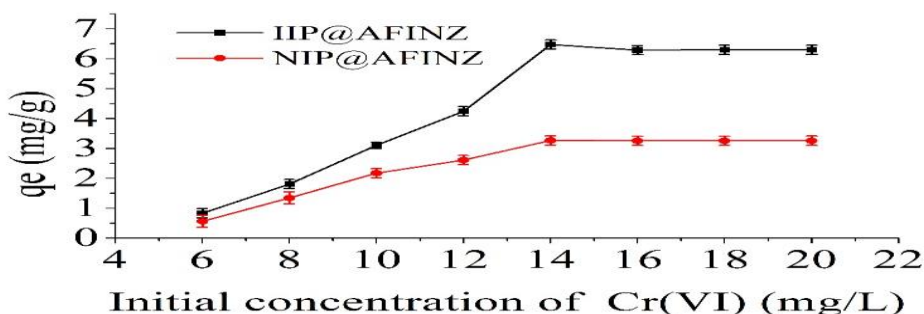


Figure 8. Effect of initial concentration of Cr(VI) on the IIP@AFINZ and NIP@AFINZ (Experimental condition: initial concentration 6 mg/L to 20 mg/L, T: 313 K, pH: 2, volume of sample: 50 mL)

It is proved from Fig. 8 that the capacities adsorption of Cr(VI) on IIP@AFINZ and NIP-AFINZ increased with increase in initial concentration from 6 mg/L to 12 mg/L, then became slow up to 14 mg/L and almost saturation from 14 mg/L to 20 mg/L of initial concentration of Cr(VI) anion. The adsorption of Cr(VI) on IIP@AFINZ and NIP@ANZ depends on the initial concentration [25]. In the case adsorption was higher in 14 mg/L as initial concentration and gradually constant after this point. Base on this result it can be assume that IIP@AFINZ can be used

effectively for adsorption and analysis Cr(VI) anion from water sample at low concentration. Base on the curve it shows that the adsorption capacity of Cr(VI) on IIP@AFINZ at 14 mg/L is 6.476 mg/L higher than on the NIP@AFINZ is 3.266 mg/L. There is a great influence of Cr(VI) imprinted in IIP@AFINZ matrix, which causes the Cr(VI) adsorption capacity to be large at low initials concentration. In addition, by this result also shows that Cr(VI) was adsorb on IIP@AFINZ via monolayer adsorption because the Cr(VI) equilibrium adsorption occurs at low concentrations.

3.3. Kinetics Adsorption Modelling

Kinetic adsorption modeling was performed to reveal whether the adsorption mechanism of Cr(VI) follows physical or chemical reaction. Two kinetic models were used to fit experimental data, such as: pseudo first-order and pseudo second-order models plot for adsorption of Cr(VI) onto IIP@AFINZ and NIP@AFINZ. The conformity between experimental data and model values was expressed by correlation coefficients (R^2 , values closer or equal to 1). Graphic of three kinetic modeling's was shown in Fig. 6. The equation of pseudo-first- order by Lagergren expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

Integrating at condition $t = 0 - t$ and $q_t = 0 - q_t$, expressed as:

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_1 t \quad (3)$$

And the linear form of the pseudo-first-order equation is expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

Where: q_e is the adsorption equilibrium capacity (mg/g), q_t is the amount of Cr(VI) adsorbed (mg/g) at time t , k_1 is the rate constant of pseudo-first-order (min^{-1}), The plot of $\ln(q_e - q_t)$ versus t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively [26–30]. Several cases of adsorption sometimes follow the pseudo-second-order model with expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

for $t = 0 - t$ and $q_t = 0 - q_t$, the linear expression of this equation written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (6)$$

Where: q_e (mg g^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) find out from plot t/q_t versus t , with $h = k_2 q_e^2$ ($\text{mg g}^{-1} \text{min}^{-1}$) is rate of initial sorption of Cr(VI) at $t \rightarrow 0$ [28,30–33].

Fig. 9 and Table 3 showed that sorption of Cr(VI) onto the surface of IIP@AFINZ and NIP@AFINZ follows the pseudo-second-order modeling with $R^2 > 0.95$. The data indicate that chemisorption processes controlled Cr(VI) adsorption, meaning that the rate of Cr(VI) sorption onto the surface of adsorbent is faster than the rate of their solubility in aqueous solution. The same result about this phenomena was reported by Debnath & Ghosh, (2008).

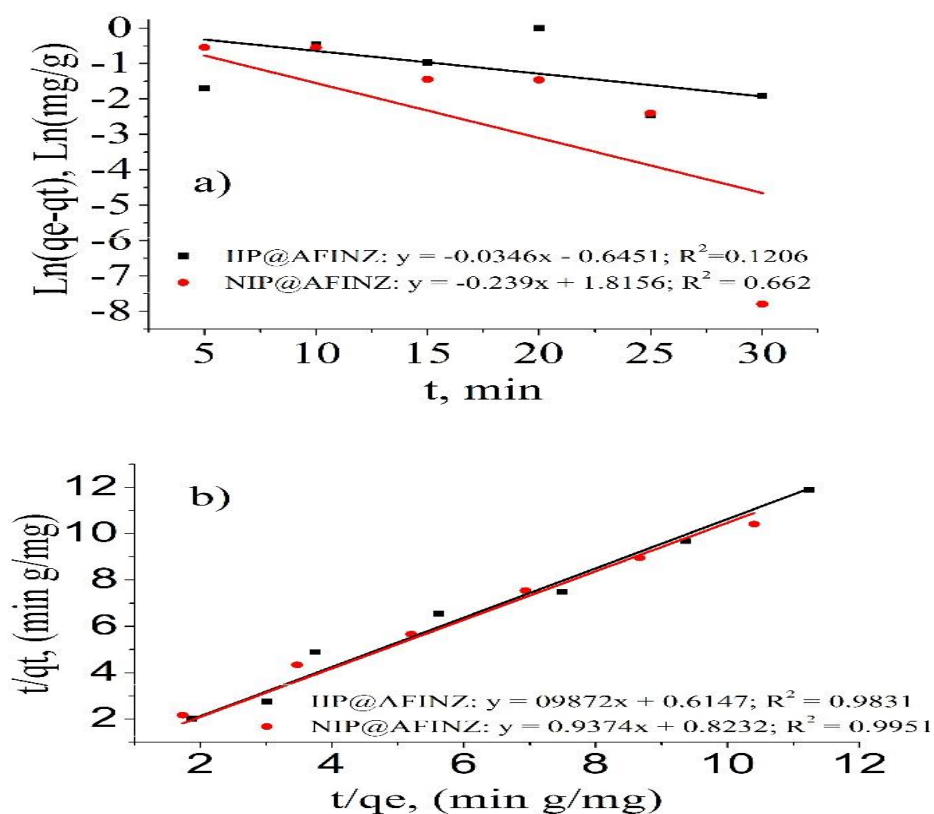


Figure 9. Kinetic models of IIP@AFINZ and NIP@AFINZ: a) Pseudo-first order, b) pseudo-second-order

3.4. Isotherm adsorption studies

The isotherm adsorption, investigation was only at optimum temperature condition. Two model isotherm adsorptions were used in this experimental, such as: Langmuir isotherm and Freundlich isotherm. The Langmuir isotherm is usually utilized for a monolayer adsorption at specific homogeneous active sites on IIP@AFINZ or NIP@AFINZ surface. Equation (8) is the Langmuir expression:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e \quad (7)$$

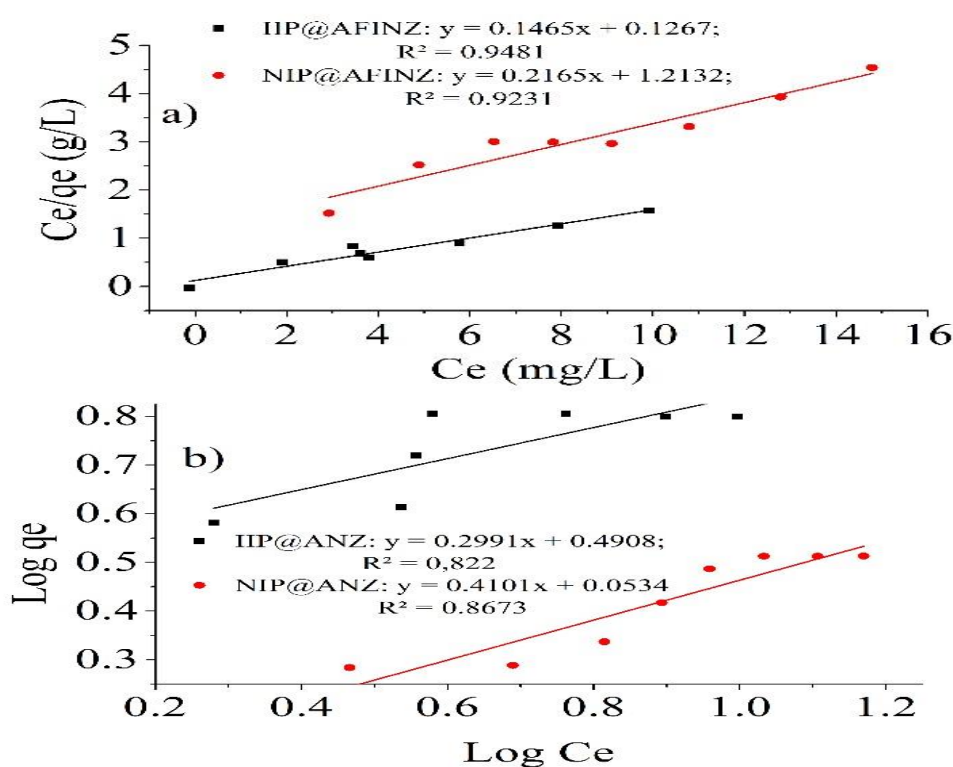
where: q_{\max} = monolayer sorption capacity (mg/g) and K_L = Langmuir equilibrium constant (L/g) [35]. A plot of C_e/q_e versus C_e yields a straight line, is shown in Fig. 7(a) and values were listed in Table 4. Freundlich isotherm [36] is the earliest known relationship describes the non-ideal and reversible adsorption, not restricted to the formation of a monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [36]. Equation (9) is the Freundlich expression [35]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

K_F and n are Freundlich constants, the K_F is adsorption capacity while n is sorption intensity; q_e = amount of Cr(VI) per unit mass of adsorbate (mg/g); C_e = equilibrium concentration (mg/L). The q_e versus C_e plot allows determining the Freundlich constants. The results of adsorption isotherm models are shown in Fig. 10. The adsorption constants and the correlation coefficients are also listed in Table 2. The fit of the data are found well with $R^2 = 0.948$ for IIP@AFINZ and $R^2 = 0.923$ for NIP@AFINZ (Table 4) with the Langmuir isotherm model.

Table 2. Isotherm parameters for the adsorption of Cr(VI) by IIP@AFINZ and NIP@AFINZ

Isotherm Adsorption models	Parameters	Adsorbents	
		IIP@AFINZ	NIP@AFINZ
Langmuir	Q_{\max} (mg/g)	7.892	0.824
	K_L (L/mg)	6.825	4,619
	R^2	0.948	0,923
Freundlich	n	3.343	2,438
	K_F (mg/kg)	3.096	1,131
	R^2	0.822	0,867

**Figure 10.** Isotherm adsorption models adsorption of Cr(VI) onto IIP@AFINZ and NIP@AFINZ: a) Langmuir, b) Freundlich

3.5. Thermodynamic study

The thermodynamic concept is needed to understand whether the Cr(VI) adsorption on adsorbent is spontaneously or not. Varying concentration of Cr(VI): 6, 8, 10, 12 and 14 mg/L at optimum condition of pH, adsorbent dosage, contact time and the temperature were used to find out the thermodynamics parameter of Cr(VI) adsorption on IIP@AFINZ or NIP@AFINZ. The concepts of thermodynamics were originally assumed that energy cannot be gained or lost in an isolated system and the entropy change is the driving force (Yuh-Shan, 2003). The heat of adsorption of the adsorbents, the free energy ΔG° (kJ/mol), ΔH° (kJ/mol) and entropy ΔS° (kJ/mol K) for the adsorption process can be calculated by fitting the Langmuir constant, K_L , to the Van Hoff equation using the following Eqs. (9)–(11) [37]. The b constant is simply recalculated as dimensionless by multiplying it by 55.5 (no. moles water):

$$\Delta G^\circ = -RT \ln(55.5)K_L \quad (9)$$

Where: R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature. The relationship between ΔG° , ΔH° and ΔS° is expressed by the following equation [38]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

The standard of enthalpy change (ΔH°) and the standard of entropy (ΔS°) for Cr(VI) sorption on NZ or ANZ were obtained using Van't Hoff equation.

$$\ln K_L = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (11)$$

Where K_L is the adsorption coefficient from the Langmuir adsorption isotherm, ΔH° is the standard enthalpy change (J/mol), ΔS° is the standard of entropy change (J/mol/K), R is the gas constant (8.314 J/mol/K) and T is the temperature in K. The values of $\ln K_L$ versus $1/T$ was plotted according to Eq. (10) and shown in Fig. 11.

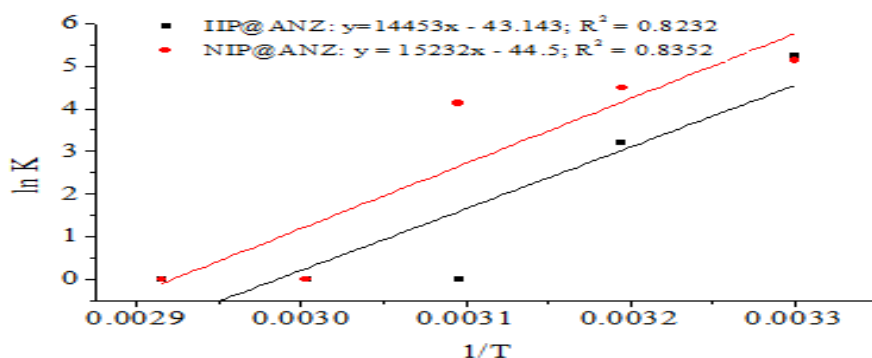


Figure 11. Plot to determine thermodynamic parameters of Cr(VI) adsorption on IIP@AFINZ and NIP@AFINZ

The linear regression on Fig. 8, the standard of enthalpy change adsorption, standard of entropy change, and standard of Gibbs free energy change were calculated and was reported in Table 3.

Table 3. The result of thermodynamic experiment for adsorption Cr(VI) onto IIP@AFINZ and NIP@AFINZ

T (K)	ΔG° (kJ/mol)		ΔH° (kJ/mol)	
	IIP@AFINZ	NIP@AFINZ	IIP@AFINZ	NIP@AFINZ
303	-228.846	-14.537	-120.162	-126.639
313	-232.432	-10.837	ΔS° (kJ/mol)	
323	-236.019	-7.138	IIP@AFINZ	NIP@AFINZ
333	-239.606	-3.438	0.359	-0.370
343	-243.193	0.262		

The negative value of ΔH° for those adsorbents indicates that the adsorption is exothermic. negative value of ΔH° suggests the decrease in sorbate concentration in solid solution interface, i.e., the increase in sorbate concentration onto the solid phase. This properties is the proper consequence of physical sorption [39]. The positive value of ΔS° for IIP@AFINZ, indicating an increase in the randomness at the solid/liquid interface. Besides, the values of ΔS increase with increasing temperature, suggests that the degree of randomness increase is getting larger [40]. The negative value of ΔS° for NIP@AFINZ obtained reflects the decreased randomness at the solid/solution interface during the

adsorption process [38]. Change in the standard free energy ΔG° has negative values for IIP@AFINZ and NIP@AFINZ, except for NIP@AFINZ at 243 K is positive. The negative values of Gibbs standard free energy change (ΔG°) indicate that this adsorption process is spontaneous; therefore, there is no energy input to the system that was required.

3.6. Selectivity studies

Adsorption capacities of IIP@AFINZ and NIP@AFINZ in the presence of competitive ions, such as: Cr(VI)/Pb(II), Cr(VI)/Mn(II), Cr(VI)/Ni(II) and Cr(VI)/Cr(III) was studied in a batch system and the result was presented in Table 4. Table 4 shows that the adsorption capacity of Cr(VI) on IIP@AFINZ is much higher than Pb(II), Mn(II), Ni(II) and Cr(III) when they exist in the same medium. It should be noted that the IIP@AFINZ particle showed excellent for the target ion (Cr(VI)) due to the presence of particular cavities on IIP@AFINZ particle.

Table 4. Competitive adsorption of Cr(VI)/Pb(II), Cr(VI)/Mn(II), Cr(VI)/Ni(II) and Cr(VI)/Cr(III) on the IIP@AFINZ and NIP@AFINZ

Ion		qe (mg/g)	
		IIP@AFINZ	NIP@AFINZ
Cr(VI)/Pb(II)	Cr(VI)	2.921	0.197
	Pb(II)	0.273	0.038
Cr(VI)/Mn(II)	Cr(VI)	4.678	2.441
	Mn(II)	0.504	1.127
Cr(VI)/Ni(II)	Cr(VI)	7.625	7.280
	Ni(II)	1.829	1.847
Cr(VI)/Cr(III)	Cr(VI)	3.741	2.978
	Cr(III)	1.035	1.291

To study the competitive adsorption between the target and competing ion should be used the distribution coefficient equation (Eq. 12) [41]:

$$K_d = \frac{C_i - C_f}{C_f} \left(\frac{V}{m} \right) \quad (12)$$

Where: K_d , C_i and C_f represent the distribution coefficient, initial concentration and final solution concentration (mg/L). V and m are the volumes of the solution (L) and mass of the IIP@AFINZ or NIP@AFINZ (g). Selectivity coefficient for binding of ion target in present of an ion competitor can use the Eq. 13:

$$k = \frac{K_d (\text{template metal})}{K_d (\text{interferent metal})} \quad (13)$$

Where: k is the selectivity coefficient of interfering metal (i.e., Pb(II) ions). A comparison of the k values of the imprinted polymer with those of metal ions allow an estimation of the effect of imprinting on selectivity. To evaluate an imprinting effect, a relative selectivity coefficient (k') was defined as follows Eq. 14 [41,42]:

$$k' = \frac{k (\text{imprinted})}{k (\text{non imprinted})} \quad (14)$$

Where k' is the indicator of the effect of imprinting on the selectivity of Cr(VI) adsorption on IIP@AFINZ. The calculated K_d , k and k' parameters are given in Table 5. As seen, The relative selectivity coefficient of IIP@AFINZ

for Cr(VI)/Pb(II), Cr(VI)/Mn(II), Cr(VI)/Ni(II) and Cr(VI)/Cr(III) were almost 2.73, 7,564, 1.476, 2.191 times greater than the NIP@AFINZ respectively. It is also known that k' must be greater than equal to 3, so it can be said that adsorbent material has excellent selectivity for adsorption of Cr(VI) from a water sample. The result shows that Cr(VI) anions could be selected adsorption by using IIP@AFINZ even in the presence of Pb(II) or Mn(II) ion but it is less selective if the presence of Ni(II) or Cr(III) ions.

Table 5. The distribution coefficient (Kd), selectivity coefficient (k) and relative selectivity coefficient (k') for IIP@AFINZ and NIP@AFINZ

Ions		IIP@AFINZ		NIP@AFINZ		k'
		Kd (L/gr)	K	Kd (L/gr)	k	
Cr(VI)/Pb(II)	Cr(VI)	0.313	-	0.197	-	-
	Pb(II)	0.022	14.199	0.038	5.184	2.73
Cr(VI)/Mn(II)	Cr(VI)	0.718	-	0.242	-	-
	Mn(II)	0.062	11.532	0.159	1.524	7.564
Cr(VI)/Ni(II)	Cr(VI)	4.239	-	3.094	-	-
	Ni(II)	4.127	1.027	4.447	0.696	1.476
Cr(VI)/Cr(III)	Cr(VI)	0.467	-	0.322	-	-
	Cr(III)	0.441	1.058	0.668	0.483	2.191

3.7. Reusability

Reusability of adsorbent is very important in industrial application [19]. The eluting solution was 0.1 M NaOH solution. IIP@AFINZ (0.2 g) with a saturation adsorption of Cr(VI) were eluted for several times in a bottle containing 20 mL of the elute solution with stirring. When the Cr(VI) could not be detected, the regeneration of IIP@AFINZ was complete. In offer to investigate the reusability of the IIP@AFINZ, the adsorption-desorption cycle was repeated five times, and the result is shown in Fig. 12. Based on Fig. 12, it is shows that the variation of the adsorption capacity of Cr (VI) using IIP@AFINZ was repeated five times, such as: 4.744; 3,269; 3.329; 3,443; 3.416 mg/g. The data shows that the adsorption capacity for IIP@AFINZ was decreased ± 1.104 mg/g after application for two until five times. This data means that it has a ± 1.104 mg/g of Cr(VI) ion that can not be leached out from IIP@AFINZ matrix so it will cause the decreased of Cr(VI) adsorption after once usage. It can be seen that variation of adsorption capacity is small for the adsorbent, so that it can be revealed that the adsorbent has a good regeneration ability to use as much as five times.

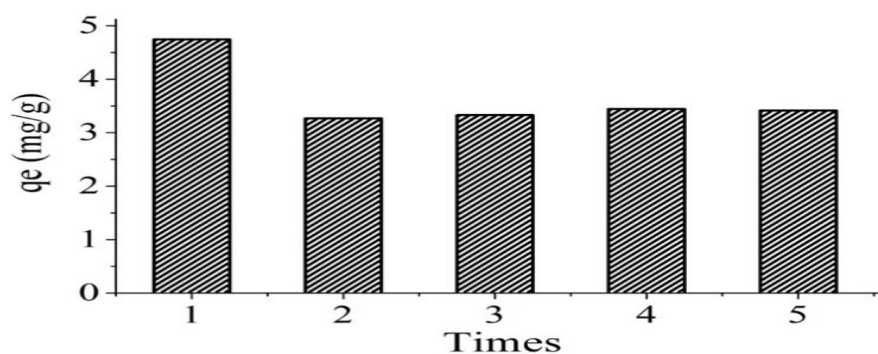


Figure 12. Reusability of IIP@AFINZ

4. Conclusion

A new adsorbent, Indonesian (Ende-Flores) natural zeolite with ion imprinting polymer (IIP@AFINZ) for Cr(VI) selective adsorption from aqueous solution has been synthesized, has been characterized and has been applied. In this study, the effect of adsorption condition is to maximize the adsorption capacity of Cr(VI) took place on initial Cr(VI) concentration of 14 mg/L in 50 mL of sample, adsorbent amount is 0.08 g, pH = 2, contact time is 30 minutes and temperature condition is 313 K. The temperature has adverse effect on adsorption capacity, whereas pH and contact time have positive implications for the response. Adsorption capacity was found around 6.476 mg/L for IIP@AFINZ higher than on the NIP@AFINZ is about 3.266 mg/L. The kinetic study verified that the adsorption of Cr(VI) by the prepared adsorbent obeyed the pseudo-second-order kinetic model. The Cr(VI) adsorption behavior on the IIP@AFINZ fits with the Langmuir isotherm model, indicating that homogenous adsorption occurred. This adsorbent can be used in the presence of competing ions such as Pb(II) and Mn(II) ions, but it becomes less selective if Ni(II) or Cr(III) ions present. The prepared IIP@AFINZ also has good reusability. In summary, the newly synthesized adsorbent has a good potential application in related of wastewater treatment or to use in solid phase extraction.

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