

Synthesis of activated carbon-nanomagnetite-pyrazolone(1-phenyl-3-methyl-5-pyrazolone) composite as adsorbent for Cd^{2+}

D Pratiwi¹, D Saprudin¹ and E Rohaeti¹

¹ Department of Chemistry, Bogor Agricultural University, INDONESIA.

E-mail: dewi_pratiwi12@yahoo.co.id , dedensaprudin@yahoo.com , etirohaeti@ipb.ac.id

Abstract. Pyrazolone was impregnated onto activated carbon-nanomagnetite (AC-NM) composite and used as an adsorbent for cadmium (Cd(II)). AC-NM composite has been synthesized by hydrothermal method. The single phase of spinel magnetite and crystallinity of nanomagnetite (NM) and AC-NM composite were confirmed by X-ray diffraction (XRD). It has been found that the crystallinity of AC-NM composite was lower than NM. The synthesized activated carbon-nanomagnetite-pyrazolone (AC-NM-PZ) was characterized by Fourier Transform Infra-Red (FTIR). Moreover, the sorption capabilities for Cd(II) ions were evaluated by three adsorbent AC, AC-NM, and AC-NM-PZ. The pH range, adsorption time, and adsorbent dosage were optimized by Response Surface Method (RSM). Cd(II) ions sorption process was studied and evaluated by two adsorption isotherms and found to follow the Langmuir model. A value of 20.64 $\mu\text{mol/g}$ was identified as the maximum sorption capacity of AC. AC-NM composite was found to increase the sorption capacity to be 36.73 $\mu\text{mol/g}$. The sorption capacity for AC-NM-PZ composite was 27.67 $\mu\text{mol/g}$, it was lower than KA-NM but higher than AC.

1. Introduction

Cadmium (Cd) is known to be toxic and effect on human health in a certain number. The Environmental Protection Agency provides maximum limit Cd level in drinking water is 0.005 mg/L while the World Health Organization is 0.003 mg/L. Poisoning of Cd can cause hypertension, bone fragility, malfunction of kidney, and even lung cancer [1,2]. Cd metal may enter and accumulate in the human body through foods, beverage, respiration and skin. Therefore, it is important to reduce the concentration of Cd in environment, especially the aquatic environment. One of the most common method to reduce the concentration of heavy metal is adsorption, for example using activated carbon.

Activated carbon (AC) has commonly been used as adsorbent due to the advantages, such as high surface area, micro-pore structure, and the presence of functional groups on the surface of the adsorbent. AC pore structure can be modified through surface functionalization of AC that can easily adsorb heavy metal ions. Functionalization of AC surface has been done by oxidation using nitric acid [3] and ammonium peroxydisulfate solution [4] which could increase the adsorption capacity of AC. Chemical or biological modification on the surface of AC has also been recognized as an effective way to increase adsorption capacity of AC [5]. One of the chemical modification on AC surfaces was peroxide acid which could increase the adsorption capacity of Hg(II) [6]. Therefore, the increase of adsorption capacity of AC by modification is very interesting to be explore.



Nanomagnetite (NM) immobilized on AC can increase the surface area of AC and also cause increase the adsorption capacity. Zach-Maor et al obtained the adsorption capacity of AC was 68% while NM modified AC adsorption capacity of 91% for the adsorption of Cr(VI) while the adsorption capacity to Cu(II) increased from 32% to 85% by activated carbon and activated carbon immobilized NM, respectively [7]. However, NM can form aggregates of magnetic properties [8]. Formation of aggregates causing adsorption process becomes less efficient so we need NM surface modification.

NM surface modification using specific ligands can improve the efficiency of heavy metal adsorption. One ligands have been reported on the extraction of heavy metals is EDTA. EDTA immobilized NM successfully applied to the extraction of Cu, Cd, Co, and Pb metal ions [9]. However, it cannot adsorb one heavy metal ions specifically because the extraction percentage of those metals did not differ significantly. Adsorption capacity of EDTA-immobilized NM for Cd extraction was found 0.32 $\mu\text{mol/g}$ [9]. Thus its needed the development and selection of other ligands to determine the selectivity of the adsorbent.

Pyrazolone (PZ) compounds and its derivatives have been used for the extraction of lanthanide and transition metals such, La(III), Eu(III), Lu(III), Cu(II), Ni(II), Zn(II), Cd(II), Hg (II), Pb (II), Mo (VI) [10-13]. Keto group in pyrazolone compounds can form complexes with metal ions. Todorova et al modified silica gel and kieselguhr with pyrazolone compound (1-phenyl-3-methyl-5-pyrazolone) and the largest adsorption capacity was kieselguhr composite with pyrazolone was found 0.71, 0.26, 0.58, and 0.83 mmol/g for Cu(II), Mn(II), Cd(II) and Pb(II), respectively [14]. Heavy metal adsorption using AC from apricot modified with pyrazolone also studied by Lakov et al which resulted with adsorption capacity of Cd was 0.54 mmol/g [15].

The activated carbon-nanomagnetite-pyrazolone (AC-NM-PZ) has been synthesized successfully and determined the adsorption capacity for Cd(II). In addition to the adsorption capacity, the synthesis process was observed by XRD's diffractograms and FTIR's spectras.

2. Materials and Methods

2.1. Materials and Instrumentation

2.1.1. Materials. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), urea, activated carbon, pyrazolone, ethanol, and standard solution of cadmium (Cd), copper (Cu), lead (Pb) from Merck, New Jersey, USA.

2.1.2. Instrumentation. The evaluation of metal ions content was performed using FAAS AA-6800 (Shimadzu, Kyoto, Japan) and the wavelength used for monitoring Cd, Pb and Cu was 228.8; 283.3; and 213.4 nm, respectively. Adjustment of pH was carried out using pH meter HM-20S (TOA, Tokyo, Japan). Unitronic OR P shaker water batch (J. P. Selecta, Barcelona, Spain) was used for batch adsorption. Infrared spectrums were recorded on a FTIR Bruker (Tensor, Billerica, USA). XRD patterns were obtained on XRD 7000 diffractometer (Shimadzu, Kyoto, Japan).

2.2. Method

2.2.1. Synthesis and Characterization of NM, AC-NM, and the AC-NM-PZ. The NM and AC-NM were synthesized using hydrothermal method. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 0.2 M was added by 0.4 M sodium citrate and 0.6 M urea dissolved in 100 ml of distilled water. The mixture was added five grams of AC for AC-NM. The solution was stirred using a magnetic stirrer for 30 minutes and then put in teflon hydrothermal and heated in oven at 200 °C for 12 hours. Black solids that formed were washed with distilled water and ethanol. The sample was dried at 60 °C for 12 hours and then synthesized and characterized with FTIR and XRD.

Five grams of AC-NM was added 10 grams of PZ and then dissolved in 250 ml NaHCO_3 10%. The solution was stirred using a stirrer for 20 hours. The sample was then separated from the solution with centrifugation at 3000 rpm and washed with distilled water; acetone plus distilled water in the ratio

1:1; and distilled water to pH neutral. The resulting AC-NM-PZ was dried at 60°C for 12 h and then characterized with FTIR.

2.2.2. Determination of Optimum Condition Adsorption of Cd (II) with RSM. Optimization was conducted at pH (4-8), adsorbent dosage (0.1-0.5 g) and adsorption time (5-25 min). RSM was employed to investigate the optimum condition for Cd(II) adsorption. The method was performed by inputting the combination of variables in statistics software, Minitab.v.16 English.

2.2.3. Determination of Adsorption isotherms. The adsorbent (0.5 g) was contacted with 50 ml of Cd(II) metal ion solution in various concentration (10, 20, 30, 40, and 50 mg/L) in a shaker batch under optimum condition. Unadsorbed Cd(II) ions in the solution was determined with FAAS. Adsorption isotherm of adsorbent was analyzed by using Langmuir and Freundlich isotherm models.

2.2.4. Effect of Other Coexisting Metal Ions. To investigate the selectivity of AC, AC-NM, and the AC-NM-PZ adsorbent in this study, 0.5 g of adsorbent was shaken with a mixture of metal ions (Cd, Pb, and Cu) under optimum condition using a shaker batch. Unadsorbed Cd, Pb, and Cu metal ions in the solution were evaluated by FAAS.

3. Result and Discussion

3.1. Characterization

3.1.1. Characterization of AC and AC-NM by XRD. XRD characterization is aimed to determine NM formed on the sample, the degree of crystallinity, crystal size and synthesized crystalline form. The XRD results is shown in Figure 1. Diffractograms obtained were compared with JCPDS 19-0629 2002 PCPDFWIN program version 2.3 of the International Centre for Diffraction Data. Figure 1 shows that the peaks are produced in accordance the standards of magnetite in JCPDS 19-0629 with the highest intensity at 2θ ° 35.422, 35.353 °, and 35.445° respectively for the standard magnetite, NM synthesized, and composites AC-NM. The XRD pattern showed no XRD pattern for γ -Fe₂O₃ is at the height of 210 and 211 [16, 17]. So that the synthesized powders and composites are magnetite with AC also did not change the crystal structure of magnetite. The difference is in the background of AC-NM, it was greater than the NM because AC amorphous. The XRD pattern of AC amorphous appears at 2θ values of 20-30 [18]. Amorphous nature of the air conditioner can also reduce the degree of crystallinity of samples that has been synthesized from 64.07% to 38.42%. Synthesized NM and AC-NM crystal size by Scherrer equation was obtained 39.6 nm and 30.3 nm, respectively. While the crystal form follows the pattern face centered cubic crystalline form.

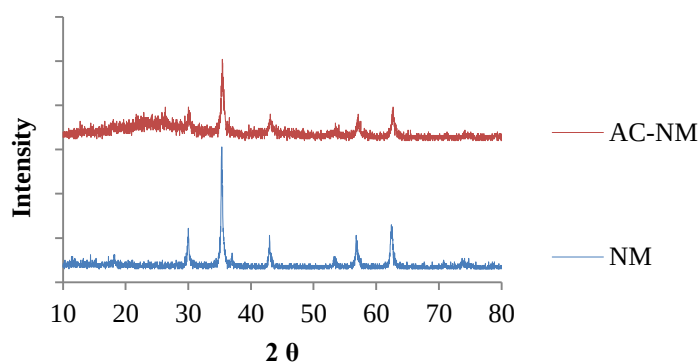


Figure 1. XRD diffractograms of NM and AC-NM.

3.1.2. Characterization of AC, NM, PZ, AC-NM, and AC-NM-PZ by FTIR. To confirm the presence of specific functional groups and additional functional groups in the materials of this study, FTIR were performed to AC, NM, PZ, AC-NM, AC-NM-PZ as shown in figure 2. AC did not indicate specific functional group absorption. It is caused AC did not functionalized well, indicated by no functional group present. The FTIR spectrum for synthesized NM indicated by a sharp peak at wave numbers 565 cm^{-1} . It is a sharp peak absorption area bond Fe-O which lies in the area absorption wave numbers $<570\text{ cm}^{-1}$ [18, 19]. The FTIR spectrum for AC-NM composite showed no significant difference with the results of the analysis of functional groups AC. It concluded that the composite does not indicate the formation of a new bond is formed. But there is a change in the regional OH absorption wave numbers $3650\text{--}3200\text{ cm}^{-1}$ [16] and Fe-O with a weak peak, which indicates NM.

Pyrazolone (PZ) has several particular peaks such as carbonyl and phenyl group. The band at 1805 cm^{-1} indicates C=O (carbonyl) group of pyrazolone ring. C=C group of phenyl is shown by an absorption at 1601 cm^{-1} . Absorption at 1151 cm^{-1} shows the vibration of the C-N. Vibration at 1027 cm^{-1} shows the C-H of ethyl group (CH_2). The band at 3056 and 3029 cm^{-1} shows the vibration of C-H group (methyl). Absorption at 3128 cm^{-1} shows the vibration of C-H aromatic groups. While vibration O-H is seen at 3422 cm^{-1} . Pavia stated that the vibration of carbonyl group located at $1820\text{--}1660\text{ cm}^{-1}$, C=C aromatic vibration at $1600\text{--}1475\text{ cm}^{-1}$ and CN at $1350\text{--}1000\text{ cm}^{-1}$, CH vibration of the aromatic hydrocarbon group at about 3000 cm^{-1} , CH vibration of the methyl group located at $3100\text{--}2500\text{ cm}^{-1}$ and OH vibration is located at $3600\text{--}3200\text{ cm}^{-1}$ [20].

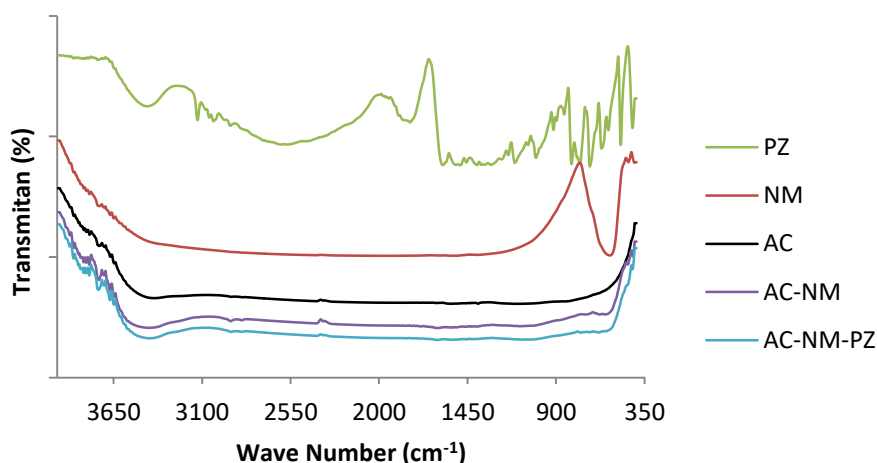


Figure 2. FTIR spectra AC, NM, PZ, AC and AC-NM-NM-PZ.

3.2. Optimum conditions Adsorption of Cd (II)

RSM was applied to develop an appropriate regression model to find out the optimal values of pH, adsorbent dosage, and adsorption time in order to enhance the adsorption efficiency. Central Composite Design (CCD) with 20 runs consisted of 8 runs for full factorial, 6 star points, 6 replicates at the centre point were successfully employed for batch experimental design. The adsorption efficiency of AC, AC-NM, and AC-NM-PZ in optimum condition is shown as the darkest green colour of contour plot shown in Figure 3(a), 3(b), 3(c) for AC, AC-NM, and AC-NM-PZ, respectively. The results are suitable with the data analysis using CCD where the optimum condition obtained were pH 6, adsorbent dosage 0.5 g, and adsorption time 25 minutes. Weights and pH optimum was accordance that conducted by Narin et al using the conventional method on Cd(II) adsorption with AC [17]. While AC-NM was obtained at pH 4, adsorbent dosage 0.5 g, adsorption time 5 minutes and AC-NM-PZ at pH 8, adsorbent dosage 0.5 g, adsorption time 25 minutes. The optimum condition was then used to determine the adsorption capacity and isotherm adsorption of the third adsorbent to Cd(II) metal ions.

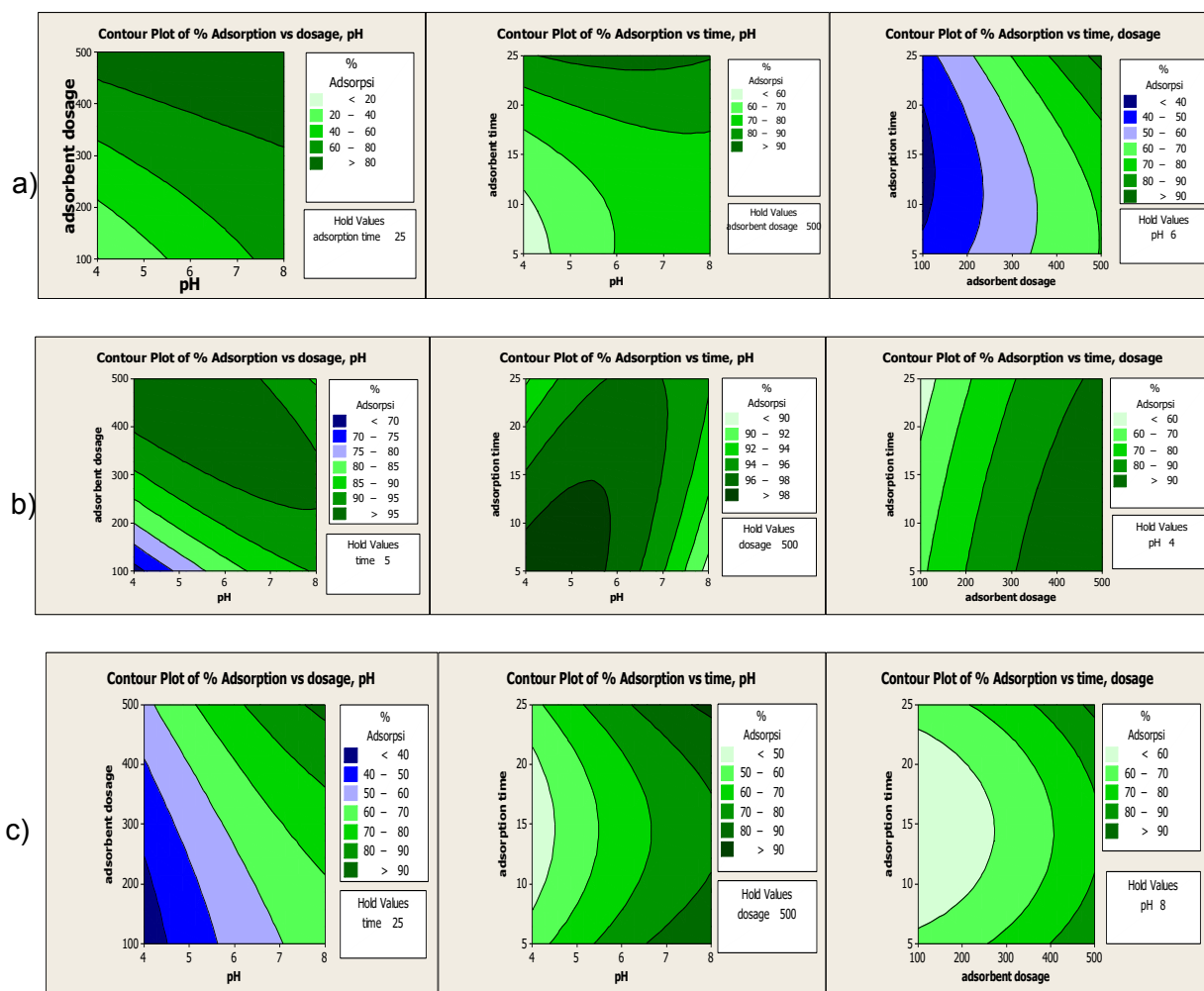


Figure 3. Contour plot of adsorption efficiency of Cd (II) by AC (a), AC-NM (b), and AC-NM-PZ (c) with various of pH, adsorption time, and amount of adsorbent.

3.3. Adsorption Isotherm

Determination of adsorption capacity and isotherm adsorption of AC, AC-NM, and AC-NM-PZ were investigated at the optimum condition with different initial concentrations of Cd(II) solutions (10-50 mg/L). Thermodynamic factors were not inserted as parameters and the determination was conducted only at room temperature. Table 1 shows the adsorption capacity and adsorption efficiency of AC, AC-NM, and AC-NM-PZ for each Cd(II) initial concentration. The efficiency adsorption of Cd (II) adsorbed by the third adsorbent decreases with the increase in the initial concentration of Cd(II) as can be seen in Table 1. While the adsorption capacity was increase.

Table 1. Adsorption efficiency and adsorption capacity of AC, AC-NM, and AC-NM-PZ.

[Cd(II)] (mg/L)	% Adsorption			Adsorption Capacity ($\mu\text{mol/g}$)		
	AC	AC-NM	AC-NM-PZ	AC	AC-NM	AC-NM-PZ
10	70.75	88.82	88.50	7.83	11.48	12.28
20	65.04	86.95	67.86	14.68	23.66	20.28
30	49.61	72.28	50.65	16.28	28.82	22.42
40	48.02	60.43	49.37	18.41	28.56	22.42
50	35.85	51.92	41.92	17.79	34.61	26.60

Isotherm adsorption of the third adsorbent was analyzed by using two isothermal equation models, Langmuir and Freundlich, showed in Fig.4a and 4b. Based on the results, the isotherm adsorption of the third adsorbent follows the Langmuir model since the R^2 value is higher than that of the Freundlich equation. This demonstrates that the third adsorbent has a homogeneous surface that based on adsorption occurs only in a single layer (monolayer) on the active side of the adsorbent.

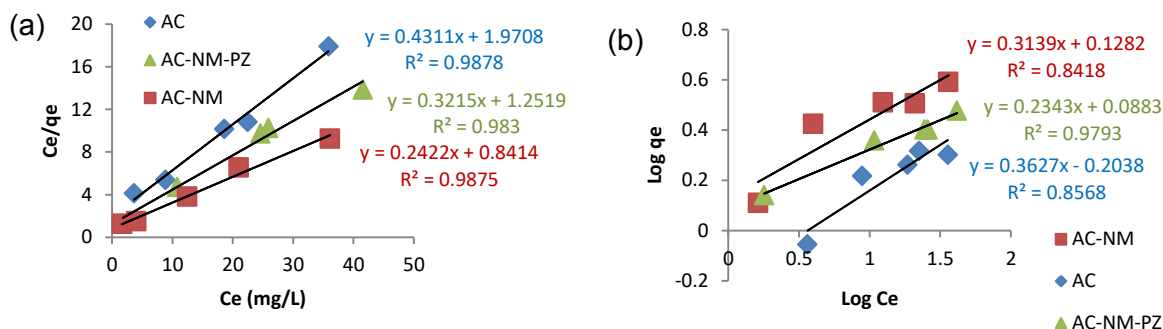


Figure 4. Isotherm adsorption Model for Cd (II) adsorption by AC, AC-NM, and AC-NM-PZ (a) Langmuir (b) Freundlich.

Cu and Pb metal ions were often in polluted waters except Cd. Therefore, Cu and Pb were used in this research to determine the selectivity of AC, AC-NM, and AC-NM-PZ in adsorbing Cd (II) in the mixture. Figure 5 shows that the three adsorbents (at optimum condition) were not selectively adsorb Cd (II) metal ion in spite of the existence of other metal ions in the mixture. The adsorption capacity for Cu (II) was higher than for the other two metal ions (Cd and Pb) by the three adsorbents. The high adsorption capacity of Cu (II) can be explained due to Cu (II) is more electronegative than other two metal ions (Cd and Pb). Therefore, Cu (II) more easily attracts the lone pair of adsorbent. Electronegativity value of Cu (II) > Pb (II) > Cd (II) according to Pauling scale estimates with electronegativity values 2.00, 1.87, and 1.69, respectively [21]. Allen and Brown states that the more electronegative metal ions, the metal ions are increasingly attracted to the adsorbent surface [22].

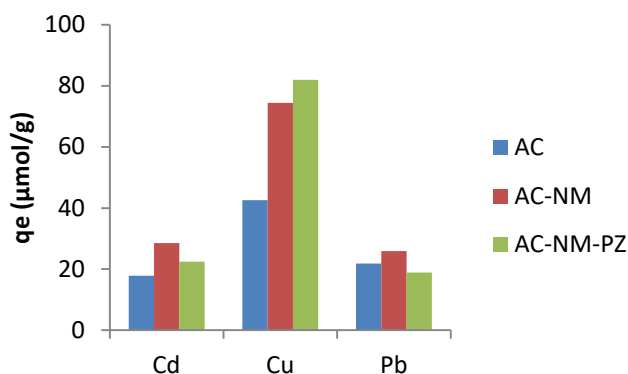


Figure 5. Effect of metal ions Cu (II) and Pb (II) on the adsorption capacity of Cd (II).

The existence of Cu (II) and Pb (II) was affects the efficiency and adsorption capacity of the third adsorbent adsorption at Cd (II) adsorption. The presence of Cu (II) and Pb (II) was reduces the adsorption capacity of the third adsorbent to Cd (II). The value adsorption capacity of Cd (II) at 50 mg/L was 17.79, 34.61, and 26.60 $\mu\text{mol/g}$ for AC, AC-NM, and the AC-NM-PZ, respectively (Table 1). While the value adsorption capacity of Cd (II) in a mixture was 5.50, 9.92, and 8.58 $\mu\text{mol/g}$ for AC, AC-NM, and the AC-NM-PZ, respectively. Adsorption capacity of AC decreased was $\pm 69\%$ for Cd (II). While AC-NM and AC-NM-PZ decreased to $\pm 71\%$ and $\pm 68\%$, respectively.

4. Conclusion

Adsorption capacity of Cd(II) on activated carbon-nanomagnetite-pyrazolone composite was lower than activated carbon-nanomagnetite composite but higher than activated carbon. The maximum adsorption capacity of activated carbon, activated carbon composite-nanomagnetite, and activated carbon composite-nanomagnetite-pyrazolone were 20.64, 36.73, and 27.67 $\mu\text{mol/g}$, respectively. Isotherm model of three adsorbents followed Langmuir isotherm models. Activated carbon, activated carbon-nanomagnetite, and activated carbon-nanomagnetite-pyrazolone did not show selectivity in adsorption cadmium ions when mixed with Cu (II) and Pb (II). The results of XRD analysis showed the magnetite phase on activated carbon-nanomagnetite composite. The FTIR spectrum did not indicate any new absorption.

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