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Acid and base modified Pectin from Orange Peel as an Effective Bio-adsorbent for Pb(II) and Cr(VI) from Textile Industry Wastewater

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Abstract

Modifying the methoxyl group on pectin from Siam orange peel (Citrus nobilis) has been done. Pectin was obtained from the peel of Siam orange by extraction method. The modified pectin obtained were analyzed using the FT-IR (Fourier Transform-Infra Red Spectroscopy) method, the XRD (X-Ray Diffractometry), and surface appearance images using SEM (Scanning Electron Microscopy). Pb(II) and Cr(VI) metals which can be adsorbed by the adsorbent then analyzed by UV-Visible Spectrophotometer. The results of the FT-IR analysis was found that the modification of the methoxyl group was successful. XRD analysis showed that the modified pectin adsorbent produced amorphous properties. The maximum pH for Pb(II) adsorption was obtained, namely pH = 6 and the maximum pH for Cr(VI) adsorption was pH =7. The best adsorption time variation for Pb(II) was 240 min and for Cr(VI) was 500 min. The best adsorbent for adsorption of Pb(II) was base-modified pectin adsorbent, while the best adsorbent for adsorption of Cr(VI) was base-modified pectin adsorbent. It could be proven that base-modified pectin was able to adsorb Pb(II) and acid-modified pectin was able to absorb Cr(VI) better (Pb(II) 80% adsorption percentage and 90% Cr(VI) adsorption percentage) than previous studies, namely pectin without modification (adsorption percentage obtained 60-70%).

Keywords: Pectin, Orange peel, bio-adsorbent, Pb(II), Cr(VI)

INTRODUCTION

One of the industrial activities that is currently still growing is the textile industry (Rashid, Shafiq, Akhter, Iqbal, & Hussain, 2021). The textile industry is one of the ten leading industrial product commodities in Indonesia (Jumina, Sarjono, Siswanta, Santosa, & Ohto, 2011). Banyuwangi is one of the regencies that continues to develop its batik production creations. The batik industry in Banyuwangi continues to increase along with the development of tourism in Banyuwangi. One of the developing batik industries is Batik Virdes, which is located in Tampo Village, Cluring District, Banyuwangi Regency. The batik industry is the oldest batik industry and has entered the international market (https://www.banyuwangikab.go.id). Based on these conditions, the Virdes Batik industry produces batik production creations on a large scale every day and the waste it produces is abundant. The dye waste from the Batik Industry contains a source of heavy metals (Qomariyah, Susanto, Apritanti, Retno, & Putri, 2022). Heavy metals are metals that are harmful to the environment and human health (Lakherwal, 2020; Rana, Prihanti, & Kalimantan, 2021). One of the dangerous heavy metals is Lead (Pb) and Chromium (Cr) which are toxic (Nuryono et al., 2019; Qomariyah & Hidayah, 2021).

Coloring in the batik-making process derived from synthetic dyes contains chemical compounds, especially heavy metals that can cause a decrease in the quality of the environment (Shi et al., 2009). Environmental pollution resulting from the production of batik must be controlled from an early age so as not to cause serious problems in the future (Papandreou, Stournaras, Panias, & Paspaliaris, 2011). Heavy metals that enter the body if the amount is excessive will cause toxic effects (Abdelkreem, 2013). The entry of Pb into the body through drinks, food, or air which can cause nerve disorders (Al-Jariri & Khalili, 2010).

Besides being famous as a rice barn in East Java, Banyuwangi is currently also a center for citrus garden production in East Java, especially the Siamese orange (*Citrus nobilis*). As of May 2013, the citrus harvested area in Banyuwangi covers 3.695 hectares with citrus production reaching 65.145 tons and the average citrus productivity in Banyuwangi is 172.93 quintals per hectare. The achievement of citrus productivity in Banyuwangi is quite promising for citrus farmers (https://www.banyuwangikab.go.id). Orange fruit is one of the fruits that can be consumed directly or can be processed into food products. From the results of this processing, orange peel waste will be produced which is thrown away (Fatimah, Isnaeni, & Tahir, 2018). Part of the orange peel waste contains a useful compound, namely pectin (Allen & Koumanova, 2005). From the results of research Kristiandi and Sitompul (2020), the pectin content in orange peel ranges from 35-40%. Pectin is a polymer compound of D-galacturonic acid found in plant cell walls connected by 1,4 glycosidic bonds and there are many active groups, so pectin can be used as a bioadsorbent (Bonnin, Garnier, & Ralet, 2014; Egbosiuba et al., 2020; Subroto et al., 2020).

In general, pectin of siam orange peel waste (*Citrus nobilis*) has a high methoxyl content and is not good when used to absorb metals (Pandharipande & Makode, 2020). This is because a gel will form at a low pH and a large ammount of dissolved solids will be formed (Maleki, Hayati, Najafi, Gharibi, & Joo, 2016). Therefore, it is important to modify the methoxyl functional group in pectin compounds from orange peel waste (Alqorni, Mahmudy, & Widodo, 2021; Manjuladevi, Anitha, & Manonmani, 2018).

In this study, modification of the methoxyl functional group on pectin from Siamese orange peel waste (Citrus nobilis) was carried out with various treatments, in order to obtain a more effective adsorbent for Pb(II) and Cr(VI) metals. Analysis of Pb(II) and Cr(VI) levels was carried out using a UV-Visible Spectrophotometer.

METHODOLOGY

Materials and Instrumentals

The equipment used were FT-IR (Fourier Transform Infra-Red Spectroscopy) Shimadzu IRPrestige21, XRD (X-Ray Diffractometry) Rigaku Miniflex, SEM (Scanning Electron Microscopy) Hitachi-10, Genesys 10S UV-Visible Spectrophotometer, mortar and pestle, oven (IKA Oven 125 Basic) and glassware. The materials used are orange peel waste from Sambirejo Village, Bangorejo District, Banyuwangi Regency, textile industry wastewater (Batik Virdes) in Tampo Village, Cluring District, Banyuwangi Regency, $PbNO_3$ solution (Merck), CrO_3 solution (Pudak Scientific), 95% ethanol, 5 M NaOH solution (Merck), 2 M HCl solution (Merck), distilled water, universal pH paper, and filter paper.

Methods

Extraction of pectin from orange peel waste

A total of 150 grams of orange peel waste that has been powdered was added with 980 mL of distilled water. The mixture was stirred until it forms a runny slurry. Added 30 drops of 1% HCl solution to reach pH = 1.5. The sour slurry was heated on a hotplate for 4 hours at 90°C, then filtered and cooled at room temperature. Add 100 mL of 95% ethanol which was acidified by adding 1 mL of concentrated HCl. The mixture was allowed to stand for 1 h to form a gel. The gel-like precipitate formed was then washed with 95% ethanol, acidified with 1 mL concentrated HCl and cooled for 17 hours at room temperature. The precipitate formed was dried at 40 °C for 8 hours. The obtained pectin was pulverized, sieved, and the concentration was calculated. These procedures based on previous study (Rivera-Utrilla, Bautista-Toledo, Ferro-García, & Moreno-Castilla, 2003).

Modification of the methoxyl group

To modify the methoxyl group in the resulting pectin (SBP), various pectin treatments were carried out as shown in Table 1.

Table 1. Variation of pectin treatment

Variation	Procedure
SPA	A total of 20 g of pectin was soaked in 2 M HCl for 12 h
SPB	A total of 20 g of pectin was soaked in 2 M NaOH for 12 h
SAP	A total of 20 g of pectin was smothered

Note: SBP, SPA, SPB, and SAP were washed with distilled water until neutral and then heated in an oven to 105°C.

Adsorbent Characterization

Characterization of adsorbent using FTIR, XRD and SEM was carried out at LPPT UGM.

Maximum wavelength determination

Each solution of Pb(II) and Cr(VI) with a concentration of 2 ppm as much as 10 mL was added with 1 mL of 60 ppm dithizone and allowed to stand for 10 min based on previous study (Ambaye, Vaccari, van Hullebusch, Amrane, & Rtimi, 2021). The absorbance was made to vary from 400–700 nm. The highest absorbance was selected to determine the maximum wavelength.

pH Variation

Each solution of Pb(II) and Cr(VI) 2 ppm as much as 10 mL was made with varying pH, namely pH = 2, 3, 4, 5, 6, 7, 8, 9. Added 1 mL of 60 ppm dithizone and absorbance measured by UV Vis spectrophotometer. Determined the highest absorbance to determine the maximum of pH (Qomariyah, Nuryono, & Kunarti, 2021).

Standard curve determination

Each standard solution of Pb(II) and Cr(VI) was prepared with concentrations of 1, 2, 3, 4, and 5 ppm. A total of 10 mL of each solution made the pH up to 6. Added 1 mL of 60 ppm dithizone and allowed to stand for 10 min. The absorbance was measured using a UV-Vis spectrophotometer with a wavelength of 405 nm for Pb(II) and 401 nm for Cr(VI). Next, a standard curve was made so that the equation for the curve y = ax + b was obtained.

Adsorbent Variation

As much as 0.5 g of SBP, SPA, SPB, and SAP were added 10 mL of 10 ppm $PbNO_3$ each. Adsorption was carried out for 3 h. The resulting filtrate was added with 1 mL of 60 ppm dithizone, allowed to stand for 10 min, and the absorbance was measured with a UV-Vis Spectrophotometer at a wavelength of 405 nm. The same was done for the adsorption of Cr(VI) using CrO_3 solution, UV Vis analysis at a wavelength of 401 nm.

Variation of adsorption time

As much as 0.5 g of SPB was added 10 mL of 10 ppm $PbNO_3$ solution. Adsorption was carried out with time variations of 30, 60, 120, 240, 360, 480, 600, and 720 min. The filtrate was separated by filtration, added 1 mL of dithizone and allowed to stand for 10 min. The absorbance of the filtrate was measured using a UV-Vis Spectrophotometer with a maximum wavelength of 405 nm. The same thing was done for the adsorption of Cr(VI) using SPA adsorbent with CrO_3 solution. The maximum wavelength used was 401 nm.

Adsorption of Pb(II) and Cr(VI) from industrial wastewater samples

The batik industry wastewater samples were taken at 3 locations 100 m apart, with the time of collection in the morning, afternoon, and evening. The samples obtained were diluted and analyzed for levels of Pb(II) and Cr(VI) using a UV-Vis Spectrophotometer according to the operating conditions in Table 2.

Table 2. Operating conditions of Pb(II) and Cr(VI) adsorption

Operating condition	Determination of Pb(II) levels	Determination of Cr(VI) levels
Maximum wavelength	405 nm	401 nm
Maximum pH	6	7
The best adsorbent	SPB	SPA
The best time adsorption	240 min	300 min

RESULTS AND DISCUSSION

Adsorbent Synthesis

Extraction of pectin from orange peel waste obtained a brownish color as shown in Figure 1. The yield of pectin is 64%. The resulting pectin (SBP) then modified its methoxyl group by adding acid (SPA), adding base (SPB) and ashing (SAP). The results of this adsorbent variation were further analyzed using FT-IR to determine the functional group, XRD to determine the sample's crystallinity, and SEM to determine the surface image of the sample.

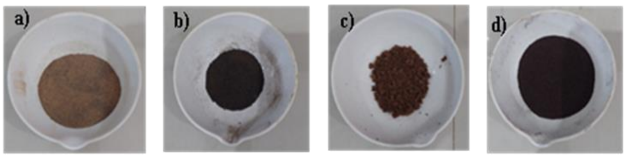


Figure 1. Variation of adsorbent: a) SBP, b) SPA, c) SPB, and d) SAP

Adsorbent Characterization

The functional groups present in various treatments of orange peel waste have been identified using an FT-IR Spectrophotometer. Figure 2 shows the different infrared absorption between pectin and modified pectin compounds. In unmodified pectin (SBP) there is a methoxyl group $-OCH_3$ in the 1700 cm^{-1} region. This shows the success of pectin synthesis and is in accordance with previous research. The wide absorption in the area of 3500 cm^{-1} on base-modified pectin (SPB) indicates the success of modifying the $-OCH_3$ group of pectin into -OH base. In acid-modified pectin (SPA) and ashed pectin (SAP) the methoxyl group changed to carboxyl, but the intensity decreased.

Based on the XRD test results (Figure 3), the modified pectin (SPA, SPB, SAP) or not (SBP), has amorphous properties. This is indicated by the sloping peak in the range of 2θ=22° which is characteristic of amorphous pectin.

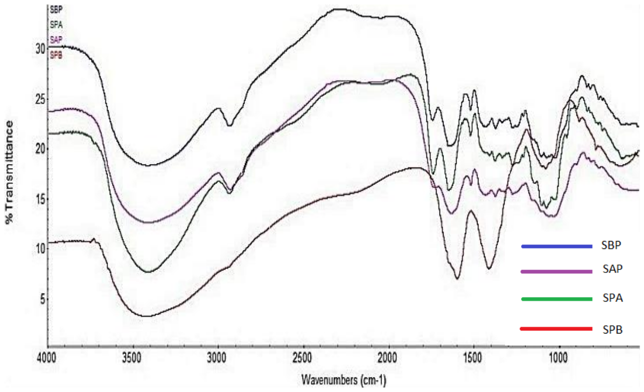


Figure 2. IR spectra of various adsorbents

This is consistent with previous research that pectin derived from orange peel has an amorphous structure (Gomes, Fontes, da Silva, de S. Mendonça, & Netto, 2001; Thavamani & Rajkumar, 2013). Orange peel which has an amorphous structure allows to absorb Pb(II) and Cr(VI) ions better. In Figure 3, the diffractogram for pectin with alkaline treatment (SPB) and acid treatment (SPA) forms an area of 2θ = 22° which is more sloping than the SPB and SPA diffractograms. This shows that the SPB and SPA adsorbents increase their amorphous properties, making it easier to adsorb.

Pb(II) and Cr(VI) ions. This result was also proven when the adsorption test of Pb(II) and Cr(VI) was carried out using a UV-Visible Spectrophotometer.

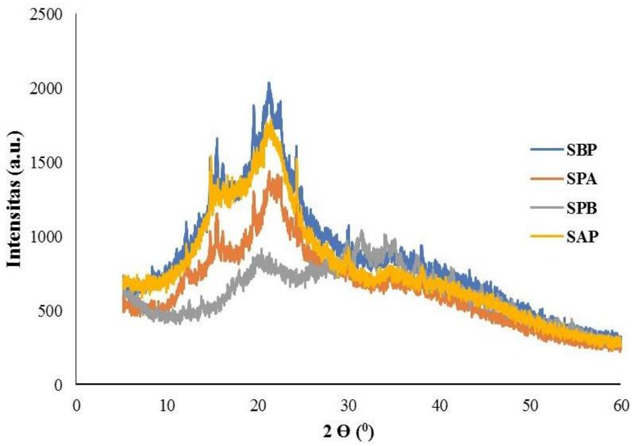


Figure 3. Diffractogram of various adsorbents

Based on the XRD test results (Figure 3), the modified pectin (SPA, SPB, SAP) or not (SBP), has amorphous properties. This is indicated by the sloping peak in the range of 2θ = 22° which is characteristic of amorphous pectin. This is consistent with previous research (Nguyen et al., 2015; Pandharipande & Makode, 2020) that pectin derived from orange peel has an amorphous structure. Orange peel which has an amorphous structure allows it to absorb Pb(II) and Cr(VI) ions better. In Figure 3, the diffractogram for pectin with alkaline treatment (SPB) and acid treatment (SPA) forms an area of 2θ = 22° which is more sloping than the SPB and SPA diffractograms. This shows that the SPB and SPA adsorbents increase their amorphous properties, making it easier to adsorb Pb(II) and Cr(VI) ions. This result was also proven when the adsorption test of Pb(II) and Cr(VI) was carried out using a UV-Visible Spectrophotometer.

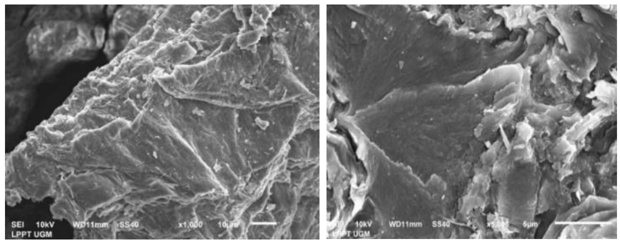


Figure 4. SEM image of pectin from orange peel

The surface structure characteristics of orange peel waste pectin are shown by SEM results in Figure 4 with a magnification of 1000 times and 5000 times using an energy of 10 kV. From Figure 4 it is clear that the surface of the sample is uneven and consists of clusters, which indicates that there are quite diverse grain sizes with uneven distribution on the surface. The separation between the clumps is also quite clearly visible, namely in the form of micro-cracking between the clusters. The presence of micro-cracking or these cracks makes the surface structure of pectin not smooth, making its adsorption ability increase because heavy metal ions Pb(II) and Cr(VI) are more easily trapped into the adsorbent.

Adsorption Process

The maximum wavelength is the wavelength at the highest absorbance obtained from the results of the analysis using UV-Vis spectrophotometer (Garg, 2004). The wavelength used for measurement is selected in the range of 400-700 nm and then reduced again to 401-410 nm. Before calculating the sample content on a UV-Vis spectrophotometer, the maximum wavelength was determined in order to provide maximum sensitivity for samples containing Pb(II) and Cr(VI) metals. The maximum wavelength obtained for Pb(II) is 405 nm and for Cr(VI) is 401 nm. At this wavelength, it is expected to provide maximum sensitivity of samples containing Pb(II) and Cr(VI).

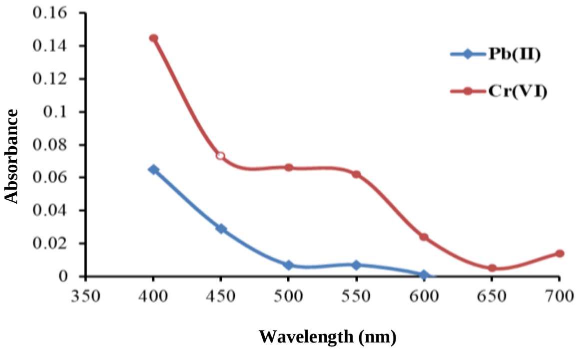


Figure 5. Determination of the maximum wavelength

In determining the optimum pH with the aim of knowing at what pH the Pb(II) and Cr(VI) complexes are maximally formed and are in a stable state. In Figure 6, different color changes can be seen at different pH. This shows the difference in the stability of the Pb(II)-Ditizone complexes. Determination of metals with one of the analytical optimum parameters that is carried out is pH determination which states that the pH condition of a solution can affect the stability of the complex formed and the concentration of analyte deposited on the working electrode as well as the resulting peak current. The optimum peak current occurred at pH 6 with an absorbance value of 0.172 for heavy metal Pb(II) and pH 7 with an absorbance value of 0.219 for heavy metal Cr(VI).

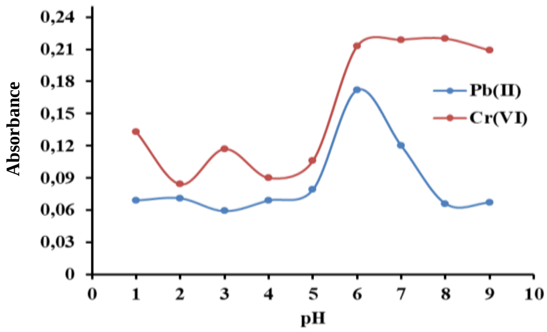


Figure 6. Adsorption of Pb(II) and Cr(VI) at various pH

Based on Figure 7, it can be seen that the best adsorbent for Pb(II) adsorption is SPB with a concentration of 8.561. From our research, there are 3 types of best adsorbent as bio-adsorbent for Cr(VI), namely SBP with a concentration of 9.731 ; SPA with 9.377 levels; and SAP with a grade of 9.421. However, according to the HSAB (Hard Soft Acid Base) concept, Cr(VI) metal which is a hard metal, will interact more optimally with acidic adsorbents (Lakherwal, 2020; Susanti et.al., 2022). Thus, the SPA adsorbent was chosen as the best adsorbent. The interaction of adsorbents SPB and SPA with Pb(II) and Cr(VI) is depicted in Figure 8.

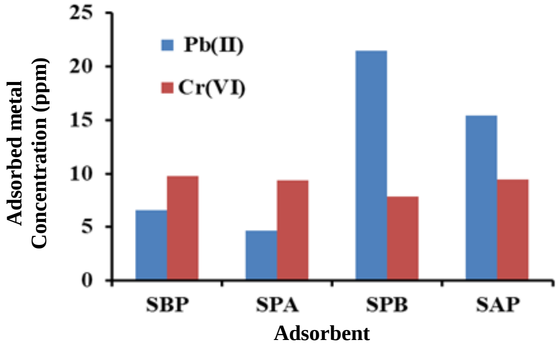
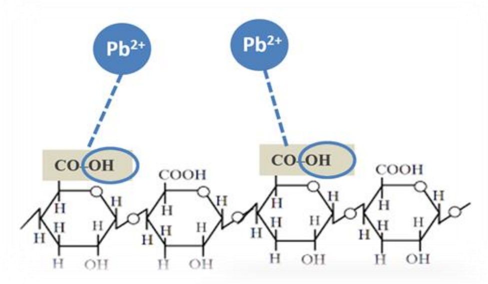
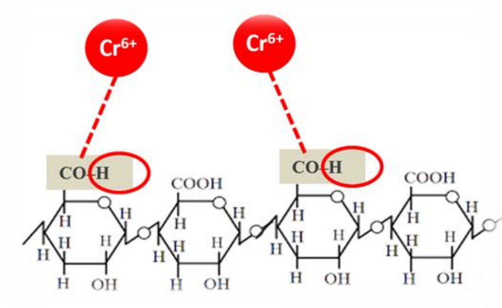


Figure 7. Variation of adsorbent for Pb(II) and Cr(VI) adsorption



(a)



(b)

Figure 8. Predicted interaction of Pb(II) (a) and Cr(VI) (b) with SPB and SPA adsorbents

In Figure 9, it can be seen that the contact time of 240 min showed the maximum absorption of Pb(II) ion concentration, and the contact time of 300 min showed the maximum absorption of Cr(VI) ion concentration. The contact time of 240 min is the effective time for SPB to adsorb Pb(II) ions and the contact time of 500 min is the effective time for SPA to adsorb Cr(VI) ions.

The levels of Pb(II) and Cr(VI) were obtained from samples of river water near the textile industrial area as shown in Table 3. Pb(II) metal was found to be the most adsorbed by SPB adsorbents, namely in samples obtained from location 1 with afternoon collection time during the day (80%). The metal

Cr(VI) was mostly adsorbed by the SPA adsorbent, namely the samples obtained from location 1 with the time taken during the day (90%).

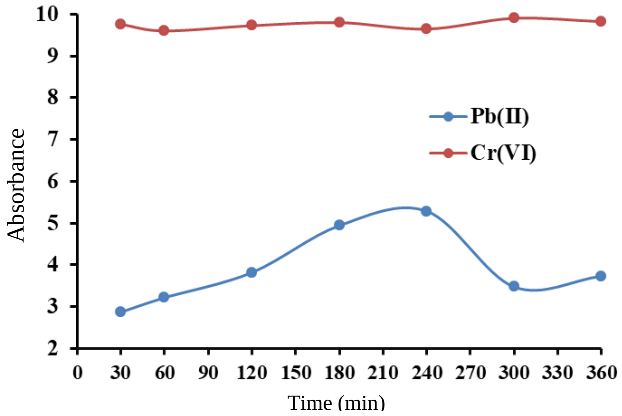


Figure 9. Variation of Pb(II) and Cr(VI) adsorption time

Table 3. Pb(II) and Cr(VI) levels from textile industry wastewater samples

Location	Time taken	Metal content in sample (ppm)		Adsorbed metal content (ppm)		Percentage Adsorbed (%)	
		Pb (II)	Cr (VI)	Pb(II)	Cr (VI)	Pb(II)	Cr(VI)
1	Morning	0.978	0.087	0.440	0.069	45	79
	Noon	0.459	0.052	0.276	0.042	60	90
	Afternoon	0.236	0.149	0.146	0.118	80	79
2	Morning	0.417	0.231	0.258	0.141	57	61
	Noon	1.724	1.493	0.620	0.657	36	44
	Afternoon	1.426	0.375	0.613	0.199	43	53
3	Morning	2.299	0.242	0.689	0.148	30	61
	Noon	1.157	0.083	0.405	0.064	35	77
	Afternoon	1.295	0.163	0.583	0.111	45	68

These results prove that modified pectin is able to adsorb Pb(II) and Cr(VI) better than previous studies (Dakiky, Khamis, Manassra, & Mer'eb, 2002), namely pectin without modification (adsorption percentage obtained is 60-70%).

CONCLUSIONS

The results of the study were obtained that the methoxyl pectin group from orange peel waste was successfully modified with acid, base, or ashing. The maximum pH for Pb(II) adsorption was pH=6 and the maximum pH for Cr(VI) adsorption is pH=7. The best adsorption time variation for Pb(II) was 240 min and for Cr(VI) is 500 min. The best adsorbent for adsorption of Pb(II) was base-modified pectin adsorbent, while the best adsorbent for adsorption of Cr(VI) is alkaline-modified pectin adsorbent. Therefore, it can be proven that base-modified pectin was able to adsorb Pb(II) and acid-modified pectin is able to absorb Cr(VI) better (Pb(II) 80% adsorption percentage and 90% Cr(VI) adsorption percentage) compared to previous studies, namely pectin without modification (adsorption percentage obtained 60-70%).

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