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Research Article

Orange Peel Wastes As Low-Cost Adsorbent For Removal Of Nickel And Chromium In Aqueous Solution

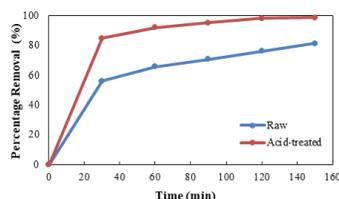N.F.M. Salleh[1,*], M. Syamsurizal[1], N.A. Ghafar[1], N. M. Shukri[1] and M. Hapani[1]

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ABSTRACT

Agricultural-by products such as orange peel (OP) was found to be abundant in quantity and had great components to adsorb the heavy metals. In this study, orange peel was used as adsorbent in adsorption process of heavy metal. The main aim of this study was carried out to examine the ability of adsorbents orange peel to remove nickel, Ni(II) and chromium, Cr(VI) ions from aqueous solution. From literature review, orange peel was proven can adsorb considerable quantities of Ni(II) and Cr(VI) ions in aqueous solution. The adsorption of Ni(II) and Cr(VI) ions were conducted in batch experiment to investigate the different parameters which are the effect of contact time, pH, adsorbent dosage and initial Ni(II) and Cr(VI) concentration. the optimum conditions for Cr(VI) were achieved when using 1.5 g of acid-treated orange peel at pH 3 in 20 mg/L of initial Cr(VI) concentration which successfully removed 47.45% of Cr(VI) from aqueous solution within 90 min of contact time. The optimum conditions for Ni(II) were achieved when using 1.0 g acid-treated orange peels at pH 7, with 40 mg/L of initial Ni(II) concentration which removed 83.85% Ni (II) from aqueous solution within 90 min of adsorption time. Statistical analysis showed that that there was a significant mean different between percent removal of heavy metal adsorb by raw and acid-treated corncobs. However, there is no significant relationship between dosage and percent removal of Cr(VI) from aqueous solution. Therefore, raw and acid-treated orange peel certainly can remove Ni(II) and Cr(VI) ions from aqueous solution.

Keywords: Orange peel, Adsorption, Nickel, Chromium, Biosorbent

1. INTRODUCTION

Water covers about 71% of the Earth's surface and is vital for all known forms of life. However, only 2.5% of the Earth's water is fresh water [1]. Due to industrialization and urbanization, wastewater were produced and transferred to the water bodies, resulting to the water pollution. This growing problem regarding the water has significant negative influence on economic development, human livelihoods, and environmental quality throughout the world [1].

Nowadays, water pollution that mostly came from the relesed of wastewater containing heavy metal pollutants. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Certain metals such as chromium (Cr) and nickel (Ni) have been linked with the chances of cancers development and bioaccumulation in the kidneys and liver of vertebrates and invertebrates [2]. As for the summary, heavy metal will give adverse effect to human health if we were exposed to it.

The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment. In recent years, various methods for heavy metal removal from wastewater have been extensively studied such as chemical precipitation, membrane filtration, adsorption and ion exchange. Adsorption is by far the most effective and widely used technique for the removal of toxic heavy metals from wastewater [3].

Adsorption knowm to be one of the alternative method to remove these heavy metals. Adsorption using biosorbents materials becoming the preferable way due to consume less cost, less time, less space, easy to conduct and also an environment friendly method for metal removal. A lot of biomass can be chosen as biosorbent such as waste material from food processing, agriculture and fruits such as using oranges' peel.

The great performance of orange peels as the adsorbent was drawn by its main components which consist of cellulose, pectin, hemicelluloses and lignin which contain functional groups as possible binding sites for metals. Therefore, the main objective of this study was to investigate the ability of adsorption efficiency of orange peel fruit to adsorb Cr(VI) and Ni(II) in aqueous solution.

2. EXPERIMENTS

2.1 Materials

In this study, the adsorbent (oranges) was obtained from the Supermarket at Kelantan. The orange peel was stored in airtight container to maintain the quality. Chemical used in this study were 37% hydrochloric acid (HCl), 99% sodium hydroxide (NaOH) pellet, nickel sulphate ($NiSO_4$) salt, chromium oxide (CrO_2) salt, distilled water and deionize water that were purchased from Merck, Germany. All reagents were prepared using deionized water.

2.2 Preparation of orange peel

In this study, orange peel were obtained from the Supermarket in Kelantan, used as the material of adsorbent. The orange peel were studied under two conditions of raw orange peels and acid-treated orange peels. Initially, the raw orange peels were cut off into smaller pieces. Then, the small pieces of orange peels were washed using distilled water. Next, the orange peels were filtered and then dried using oven at 70°C for 4.5 h. After that, the dried orange peels were grinded and stored in airtight container for further use.

In the preparation of acid-treated orange peels, the grinded orange peels were mixed with 150 mL of concentrated HCl. Then, it was stirred for 4 h using magnetic stirrer. The resulting sample was filtered and washed using distilled water and dried at 70°C for 1 h. After that, the sample was grinded and stored in airtight container for further use.

2.3 Characterization of orange peel

Element analysis for carbon, hydrogen, nitrogen, oxygen, and sulfur and functional groups present in the orange peels were identified using Fourier-transform infrared spectroscopy (FT-IR) Bruker Tensor 27. It is equipped with a room temperature DTGS detector, mid-IR sources, and diamond pellet. FT-IR absorbance data were collected in range of wavenumber 500-4000 cm^{-1}.

2.4 Preparation of wastewater solution

Stock solution of 1000 mg/L containing metal ions Ni and Cr were prepared by dissolving appropriate $NiSO_4$ and CrO_2 salts in deionized water. The aqueous solution was prepared from 10 mg/L to 50 mg/L from serial dilution of the stock solution. The concentration of Ni and Cr in aqueous solution was determined by PerkinElmer Analyst 800 Flame Atomic Absorption Spectrophotometer (FAAS). The container of aqueous solution must be keep tightly closed and wrapped in aluminum foil to prevent changing of concentration due to other material addition or reduction.

2.5 Batch adsorption study

The effect of various parameters, such as pH, contact time, adsorbent dosage, and initial concentration of heavy metals were investigated using a batch adsorption study. The 1.0 g of sample was added to beaker containing 100 mL of 10 mg/L of Ni and Cr solution that were diluted from 1000 mg/L stock solution. Then, sample was stirred using magnetic stirrer until reach equilibrium time.

After 30 minutes, 10 mL samples were taken, filtered and centrifuged. The adsorption process was repeated at different time at 60, 90, 120, and 150 minutes. Triplicated runs for each contact time gave sample, n=15 for each type of sample. Then, the samples were analyzed by FAAS. The experiment was continued for different parameter such as pH (3,5,7,9,11), adsorbent dosage (1.0, 1.5, 2.0, 2.5, 3.0 g) and initial concentration of heavy metal (10, 20, 30, 40 ,50 mg/L). This entire process was repeated three times to give sample size n=15 for each parameter. The removal percentage (%) was calculated by using the following equation:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where C_0 and C_e are the concentration of initial and after adsorption respectively.

2.6 Data analysis

The data were analyze using Statistical Package of Social Science (SPSS) software. Descriptive statistic and inferential statistic were applied to obtain the frequency and percentage. Independent t-test were used to test r hypothesis 1, while hypothesis 2 were tested using correlation test.

3. RESULTS AND DISCUSSION

3.1 Characterization of orange peel

3.1.1 Raw and acid-treated orange peel

FTIR spectra were obtained to recognize the functional groups present on the adsorbent surface. Figure 1 presents the FTIR peak values and the corresponding functional groups. The functional groups of orange peel had peaks around 3325 cm^{-1} assigned to O–H stretching due to inter- and intramolecular hydrogen bonding of polymeric compounds and carboxylic acids showing the presence of "free" hydroxyl groups on the adsorbent surface. The band

at 1782 cm^{-1} arise due to C=O steaching hemicelluloses and the band around 1434 cm^{-1} assigned to symmetrical COO^{-} streaching motion and band to the bending vibration of aliphatic group. The peak at 1739 cm^{-1} is due to the stretching vibration of the bond due to non-ionic carboxyl groups and corresponded to carboxylic acids or their esters. The strong band at 1013 and 1033 cm^{-1} were allocated to the C-O of alcohols and carboxylic acids.

The peaks between 1014-750 cm^{-1} were due to the vibration of C–O–C, C–O–P and O–H of polysaccharides [4]. The pattern of FTIR spectra and presence of functional group were similar between raw and acid-treated OP with different intensity. It can be observed that, the intensity of peak of acid-treated OP was higher compared to raw OP that indicated for the high availability of each functional group in acid-treated OP.
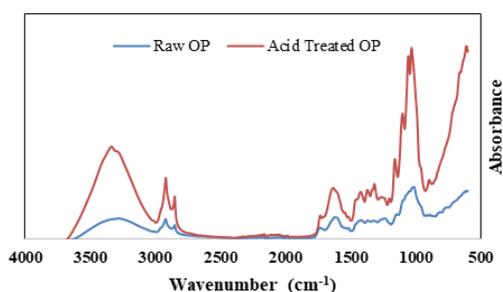

Figure 1 FTIR spectra of raw orange peel and acid-treated orange peel with HCL.

3.1.1 Orange peel before and after batch adsorption process

Figure 2 and 3 show the FTIR analysis for acid-treated orange peel after Ni(II) adsorption and acid-treated of orange peel after Cr(VI). The FTIR spectra of these peels indicated that these adsorbents contained carboxyl and hydroxyl groups which can react with heavy metal ions in aqueous solutions [3].
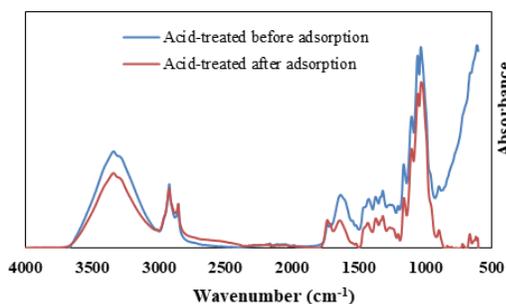

Figure 2 FTIR spectra of acid-treated before and after Cr(VI) adsorption.
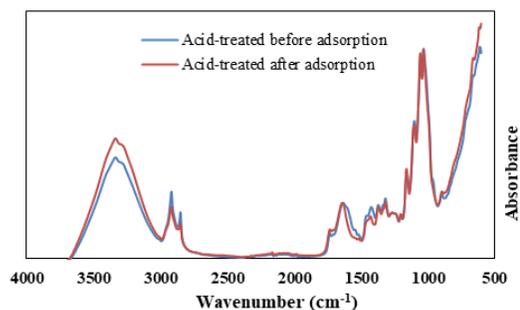

Figure 3 FTIR spectra of acid-treated before and after Ni(II) adsorption.

The FTIR spectra of the orange peel shows the characteristic of sorption band at 2922 cm^{-1} stands for the streaching vibration for C-H from –CH$_2$ group. The spectral analysis of orange peel before and after Cr(VI) binding indicated that the -COOH group was involved in Cr(VI) adsorption.

3.2 Determination of optimum condition for adsorption of Ni and Cr

In order to determine the optimum condition of adsorption of the Ni(II) and Cr(VI), the experiment was conducted under 4 types of parameter, which were the contact time, pH of the solutions, adsorbent dosage, and initial concentration of Ni(II) and Cr(VI).

3.2.1 Effect of contact time

The effect of contact time on removal of Cr(VI) and Ni(II) from aqueous solution were observed at 30, 60, 90, 120, and 150 minutes of contact time. Based on Figure 4 and 5, the removal of Cr(VI) and Ni(II) with application of acid-treated OP were higher than the raw OP. The adsorption percentage of Cr(VI) and Ni(II) using raw and acid-treated orange peel increase with the increase contact time until equilibrium was reached. Moreover, the optimum time to remove the Cr(VI) and Ni(II) was 90 minutes with percentage removal of 53.5% and 95.1%, respectively.
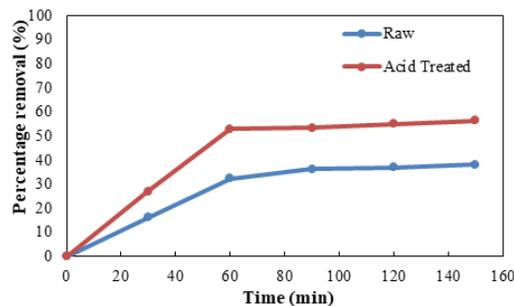

Figure 4 Effect of contact time on percent removal of Cr(VI). (1.0 g of adsorbent dosage, 10 mg/L of initial concentration).
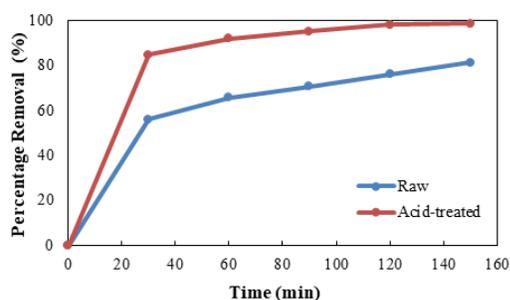
Figure 5 Effect of contact time on percent removal of Ni(II). (1.0 g of adsorbent dosage, 10 mg/L of initial concentration).

Figure 7 Effect of pH on percent removal of Ni(II). (90 minutes, 1.0 g acid-treated OP dosage, 10 mg/L initial solution).

From the trends presented in Figure 4 and 5, the adsorptions of the heavy metals were predicted to occur quite rapidly initially, and most were adsorbed in under one hour 30 minutes. The adsorption rate becomes slower over time, in the range of 1 to 30 minutes and above. In this study, the faster removal efficiency during the first hour could initially be attributed to adsorbent availability of the uncovered surface area. A slightly higher removal efficiency of metal ions using OP could be due to increased functional groups on the modified adsorbents and chemical pre-treatment of these adsorbents.

3.2.2 Effect of pH

The effects of pH (3, 5, 7, 9, 11) on the adsorption of Cr(VI) and Ni(II) by the adsorbents are shown in Figure 6 and 7. Based on Figure 6, the adsorption of Cr(VI) on the acid-treated OP decreased with increasing pH, with the highest uptake at a pH of 3 where the percent removal was 68.65%. In Figure 7, it showed that the percentage removal of Ni(II) was increased with an increased in pH of the solution. However, there are no significant increase was observed in the pH higher than 7. The highest removal recorded at pH 7 with the percent removal 88% in the Ni(II) solution.
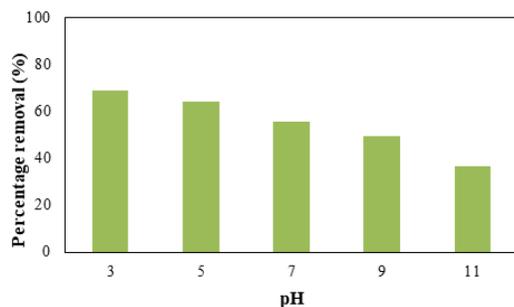
The effect of pH on the biosorption process is possibly due to interactions between the Cr(VI) in solution and adsorbent surface charge contaminants. At lower pH value, the surface of adsorbent would be surrounded by hydronium ions makes the biomaterial surface more positive which enhanced the Cr (VI) interaction with the binding site of the adsorbent [5]. The decreased of biosorption at higher pH value (pH > 5.0) because of competitiveness of the oxyanions of Cr(VI) and OH^{-1}.

For removal of Ni(II), at lower pH value, the H^+ ions compete with metal cation for the exchange sites in the system thereby partially releasing the latter. The heavy metal cations are completely released under circumstances of extreme acidic conditions. Furthermore, the adsorption decreased when pH is increased further because high numbers of OH^-.

3.2.3 Effect of adsorbent dosage

The effect of the dosage was investigated by using 1.0, 1.5, 2.0, 2.5 and 3.0 g of prepared OP. Based on the Figure 8 and 9, it showed that the pattern of percentage removal of Cr(VI) and Ni(II) were inconsistent. The highest percent of removal of Cr(VI) was 35.65% by using 1.5 g of adsorbent dosage, meanwhile the highest percentage removal of Ni(II) was recorded to be 66.15% with application of 1.0 g of adsorbent dosage.

Figure 6 Effect of pH on percent removal of Cr(VI). (90 minutes, 1.0 g acid-treated OP dosage, 10 mg/L initial solution).

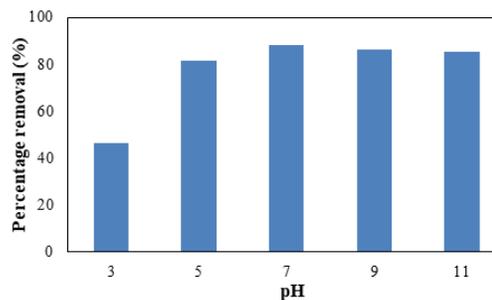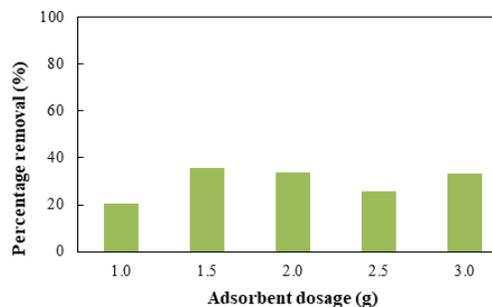**Figure 8** Effect of adsorbent dosage on removal of Cr (VI). (90 minutes, pH 3, 10 mg/L initial concentration).
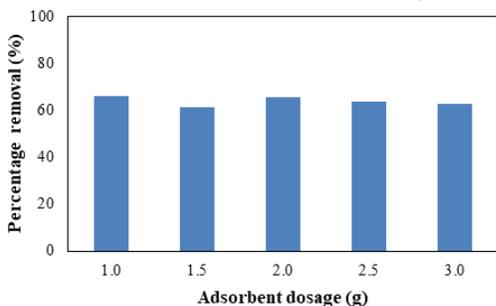
Figure 9 Effect of adsorbent dosage on removal of Ni (II). (90 minutes, pH 3, 10 mg/L initial concentration)

Generally, the increase in the percentage of metallic ion removed with increasing adsorbent doses could be attributed to increased adsorbent surface area, which could increase the number of adsorption sites available [6]. It can be observed also the adsorption decreased with increase in adsorbent dose. This may be attributed to overlapping or aggregation of adsorbent surface area available to ion and an increase in diffusion path length [7].

3.2.4   Effect of initial concentration of Cr(VI) and Ni(II)

In this study, biosorption of Cr(VI) and Ni(II) was investigated by change the initial concentration of the heavy metal solution (10, 20, 30, 40, 50 mg/L). As shown in Figure 10, the percentage of Cr (VI) ions uptake for biosorbent was increased with the initial metal concentrations. However, after 40 mg/L of Cr(VI), the percentage removal gradually decreased. The highest percentage removal recorded to be 47.45% at 20 mg/L of initial concentration of Cr(VI). The result in Figure 11 showed that the percentage of removal of Ni(II) was increased with the increased in the initial concentrations. However, after 40 mg/L of initial Ni(II) concentration, the percentage of removal was gradually declined. The highest removal recorded was 83.85% at 40 mg/L of Ni(II) aqueous solution.
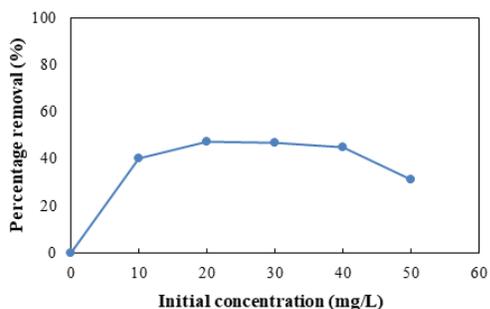

Figure 10 Effect of difference initial concentration of Cr(VI) onto acid-treated orange peel. (90 minutes, 1.5 g adsorbent dosage, pH 3).
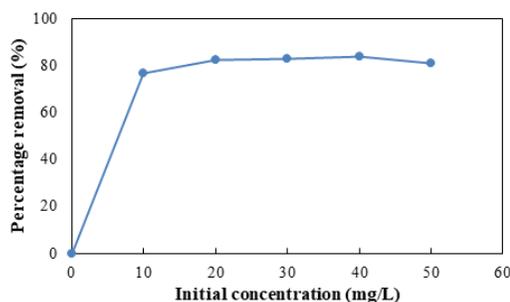

Figure 11 Effect of difference initial concentration of Ni (II) onto acid-treated orange peel. (90 minutes, 1.0 g adsorbent dosage, pH 7).

At lower Cr(VI) concentrations, the ratio of the initial number of moles of metal ions to the available surface area is smaller and subsequently the fractional adsorption process becomes independent of the initial concentrations. The extent of adsorption was rapid in the initial stages and became slow in later stages till saturation was attained. This is obvious from the fact that a large number of surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to be occupied because of repulsion between the solute molecules of the solid and bulk phases [7]. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions depends upon the initial concentration [8].

3.3   Comparison of mean different between percent removal of heavy metal adsorb by raw and acid-treated orange peel.

Since the data is not normally distributed, the Mann-Whitney test was used to compare differences between raw and acid-treated orange peel with percent removal of Cr(VI) and Ni(II) from aqueous solution. Based on Table 1, for removal of Cr(VI), the p value was 0.076. The result showed no significant mean different ($p>0.05$) in the amount of metal reduced using raw and acid-treated orange peel. Therefore, null hypothesis is accepted. There is no significant mean different of percent removal of Cr(VI) between raw and acid-treated orange peel. Meanwhile for removal of Ni(II), the p value for Ni(II) was 0.009. The result showed significant mean different ($p<0.05$) in the amount of metal reduced using raw and acid-treated orange peel. Therefore, null hypothesis is rejected. There is significant mean different of percent removal of Ni(II) between raw and acid-treated orange peel. Acid-treated orange peel has a higher percent removal compared to raw orange peel.

Table 1: The comparison of mean different between percent removal of Cr(VI) and Ni(II) using raw and acid-treated orange peel.

Heavy Metal	Variable	n	Median (IQR % removal)	Z statistic	P value*
Cr(VI)	Raw	15	37(13)	-1.776	<0.076
	Acid-treated	15	54(15)		
Ni(II)	Raw	15	70(17	-2.611	<0.009
	Acid-treated	15	95(10)		

Mann Whitney test

Table 2: Relationship of percent removal of Cr(VI) and Ni(II) with different adsorption dosage.

Parameter	Heavy metal	Percentage removal (%)		
		n	r	P value
Dosage	Cr(VI)	15	0.100	0.873[a]
	Ni(II)	15	-0.400	0.505[a]

Spearman's correlation

For Mann Whitney test, the Z statistic of Cr(VI) was -1.776 and p value is >0.05. Therefore, the null hypothesis is accepted, and the result is no significant. The Z statistic of Ni(II) was -2.611and p value is <0.05. Therefore, the null hypothesis is rejected, and the result is significant. Meanwhile, for Spearman's correlation, there is no significant correlation between dosage and percent removal. There is a weak positive correlation relationship (r=0.100, p>0.05). There is no significant correlation between dosage and percent removal. There is a good positive correlation relationship (r=-0.400, p>0.05).

3.4 Relationship between different dosage of orange peel with percent removal of heavy metal in aqueous solution

Since the data is not normally distributed, the Spearman's correlation test was used to measure the strength and direction of association between percent removal of Cr(VI) and Ni(II) with different adsorbent dosage. Based on Table 2, the p value for Cr(VI) and Ni(II) were 0.873 and 0.505, respectively. The result showed a significant relationship (p>0.05) in the percent removal of both heavy metals with addition of adsorbent dosage. Therefore, null hypothesis is accepted. There is no significant relationship between dosage and percent removal of from aqueous solution.

4. CONCLUSION

From this study, the highest removal efficiency for Cr(VI) were achieved when using 1.5 g of acid-treated orange peel at pH 3 in 20 ppm of initial Cr(VI) concentration which successfully removed 47.45% of Cr(VI) from aqueous solution within 90 min of contact time. Meanwhile, the highest removal effciciency for Ni(II) were achieved when using 1.0 g acid-treated orange peels at pH 7, with 40 mg/L of initial Ni(II) concentration which removed 83.85% Ni (II) from aqueous solution within 90 min of adsorption time. For the removal of Ni(II) and Cr(VI) from aqueous solution, acid-treated orange peel was found to be better adsorbent than raw orange peel. From the statistical analysis,

it can be said that there was a significant mean different between percent removal of heavy metal adsorb by raw and acid-treated orange peel. it can be concluded that there was no significant relationship between dosage and percent removal of Ni(II) from aqueous solution. The relationship was found very strong negative relationship (r = -0.400). However, there is no significant relationship between dosage and percent removal of Cr (VI) from aqueous solution.

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CONFLICT OF INTEREST

The authors confirm that there are no known conflicts of interest associated with this publication.

REFERENCES

[1] P. Rajasulochana, V. Preethy, Resource-Efficient Technol. 2 (2016) 175–184.
[2] M. Mahurpawar, Int. J. Res. Granthaalayah. 0530 (2015) 1-7.
[3] A. Gupta, P.S.R. Mote, Chem. Process. Eng. Res. 19 (2014) 47–56.
[4] M.T. Amin, A.A. Alazba, M.N. Amin, Pol. J. Environ. Stud. 26 (2017) 543–557.
[5] E. Pehlivan, H.T. Kahraman, Food. Chem. 133 (2012)1478–1484.
[6] J. Sáez, M. Lloréns, A.B.P. Marín, M.I. Aguilar, V.F. Meseguer, J.F. Ortu, Chem. Eng. J. 155 (2009) 199–206.
[7] F. Gönen, D.S. Serin, Afr. J. Biotechnol. 11 (2012) 1250–1258.
[8] S. Mandina, F. Chigondo, M. Shumba, B.C. Nyamunda, E. Sebata, J. Appl. Chem. 6 (2013) 66–75.