Efficiency of Coconut Husk as Agricultural Adsorbent in Removal of Chromium and Nickel Ions from Aqueous Solution

IOP Conf. Series: Earth and Environmental Science **596** (2020) 012048 doi:10.1088/1755-1315/596/1/012048

Efficiency of Coconut Husk as Agricultural Adsorbent in Removal of Chromium and Nickel Ions from Aqueous Solution

S F M Hanafiah[1], N F M Salleh[1]*, N A Ghafar[1], N M Shukri[1], N H N Kamarudin[2], M Hapani[1], R Jusoh[3]

[1]School of Health Sciences, Universiti Sains Malaysia, Health Campus, 16150 Kubang Kerian, Kelantan, Malaysia.
[2]Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.
[3]Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia

E-mail: nurfatiensalleh@usm.my

Abstract. Coconut husk is categorized as the agriculture waste product that can act as biosorbent material. In this study, coconut husk was used as an adsorbent to investigate the ability of this agricultural by-product to adsorb nickel and chromium. In this experiment, nickel and chromium ion were adsorbed in batch adsorption experiment using different parameters; effect of contact time (30, 60, 90, 120, 150) minutes, pH (3, 5, 7, 9,11), adsorbent dosage (1.0, 1.5, 2.0, 2.5, 3.0) g. An optimum level of adsorption for chromium by using raw coconut husk occurred at 90 minutes of contact time, pH 3, and dosage of adsorbent of 1.5g. Meanwhile, optimum adsorption of nickel occurred at contact time of 90 minutes, with pH 5, adsorbent dosage of 1.5g. Statistical analysis showed that there was a significant mean difference between percent removal of chromium (Cr) and nickel (Ni). There was a significant mean difference between dosage and percent removal of chromium ions. In conclusion, both raw and acid-treated coconut husk can adsorb nickel and chromium ions from aqueous solutions.

1. Introduction

Water pollution has affected the lives of humans and animals in all aspects. Most of the sources of water pollution are caused by human activity, in spite the fact that a few of them emanate from natural sources of pollution [1]. Example of sources of pollution from industry include energy and fuel production, mining and smelting of metalliferous, surface finishing industry, iron and steel, electroplating, electrolysis, metallurgy, leather working, fertilizer and pesticide industry, photography, and aerospace [2,3].

Chromium (Cr) and Nickel (Ni) are used primarily in metallurgic industries for producing alloys and in electroplating industry for making batteries and paints [4]. Heavy metals are highly toxic and non-biodegradable. It withal considered carcinogenic to human and cause many health effects on human. The excessive exposure toward Ni may lead to a few types of cancer including lungs, nose, and bone [5]. Hence, Ni and Cr should be treated at their permissible level before it is ready to be discharged to the environment.

IOP Conf. Series: Earth and Environmental Science **596** (2020) 012048 doi:10.1088/1755-1315/596/1/012048

Currently, conventional methods were used to remove heavy metals. These methods include chemical precipitation [6], ion exchange [7], membrane filtration, coagulation, and flocculation. However, adsorption method is the most common method as compared to other techniques due to its capability in adsorbing heavy metal efficiently, simple in design, easy to handle and several adsorbents are readily available [5,8]. Physical or chemical interactions were the concepts lied behind the adsorption process whereby a substance is transferred from liquid phase to the surface of a solid and were bound together [9].

According to previous study, there are various low-cost adsorbents of the natural waste product that proven to be suitable adsorbent which could be modified to treat wastewater such as plant origin, sawdust, agricultural by-products of coconut husk, rice husk, and oil palm shell, cork biomass, etc. [10-17]. Beside the composition of lignin and cellulose as major constituents, the agricultural adsorbent also includes other polar functional groups of lignin; alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. Process of electron pair donating would lead to the binding of heavy metals to form complexes with the metal ions in solution [8].

Coconut husk is a type of agricultural byproduct that found in abundance in Malaysia. Coconut husk is the outer layer of coconut and consists of 33–35% of husk. Using coconut husk is another effective way to adsorb heavy metal in wastewater because it can be modified into suitable adsorbent. Besides, since Malaysia is the major producer of coconut husk, this type of biomass is easy to get in large quantity. Thus, this can reduce the waste management problems besides increasing the demand of the coconut by-product to be fully utilized. In this study, different parameters such as contact time, pH, dosage and initial concentration, were used to determine the adsorption efficiency of coconut husk toward Ni and Cr adsorption in aqueous solution.

2. Methodology

2.1. Materials

Coconut husks were collected from Kedai Mulong market, Kota Bharu, Kelantan. Hydrochloric acid, nickel, chromium, and sodium hydroxide were purchased from Merck, Germany.

2.2 Preparation of coconut husk

The coconut husks were crushed and dried in the microwave. Then, the dried coconut husk was divided into two samples. First sample was raw dried coconut husk that was used as control. Second sample was treated with hydrochloric acid as can be seen in Figure.1 (a) and (b). After that, the samples were dried at 100 °C to remove the chemical residue [8,11].

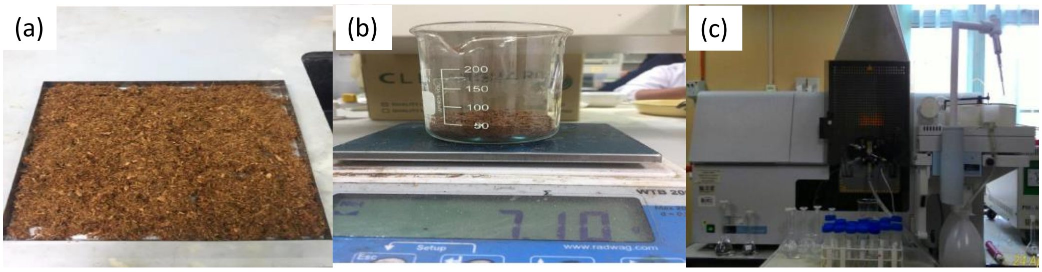

Figure 1. (a) raw coconut husk; (b) treated coconut husk; (c) FAAS instrument

2.3 Characterization of adsorbents

Flame Atomic Absorption Spectrophotometer (FAAS) by Perkin Elmer was used to determine the concentration of Cr and Ni in the adsorption process (Figure. 1(c)). Fourier-Transform Infrared Spectroscopy (FT-IR) was used to detect the presence of functional groups in a coconut husk beside to analyze the content of carbon, hydrogen, oxygen, and sulphur. The FT-IR absorbance data were collected in the range of wave number 400-4000cm^{-1}.

IOP Conf. Series: Earth and Environmental Science **596** (2020) 012048 doi:10.1088/1755-1315/596/1/012048

2.4 Batch adsorption study
Stock solution of 1000 mg/L was prepared by dissolving nickel sulphate, $NiSO_4$ and chromium oxide, CrO_2 in deionized water that contains Cr(VI) metal ions. The aqueous solution of CrO_2 solution were prepared from in five concentrations: 10, 20, 30, 40 and 50 mg/L using serial dilution of the stock solution. Flame Atomic Absorption Spectroscopy (FAAS) was utilised to determine the concentration of the aqueous solution.

During the experiment, four parameters were measured; effect of contact time, pH, adsorbent dosage and the initial concentration of Cr (VI) towards adsorption process. Firstly, 1.0g of adsorbent was added in 250 mL beaker containing 100 mL of 10 mg/L Cr(VI) solution. Then, the solution was stirred at 400 rpm using magnetic stirrer until it reached equilibrium. During the process, 10 mL was withdrawn from the solution at pre-determined time interval and was centrifuged before the concentration of Cr(VI) being analysed by FAAS. The different contact time was carried out at 30, 60, 90, 120, and 150 minutes. To study the effect of pH, the sample pH (3, 5, 7, 9, 11) was adjusted with 0.1 M NaOH and 1. 0 M HCl. Various amounts of adsorbents (1.0, 1.5, 2.0, 2.5, 3.0) g were used to study the effect of adsorbent dosage. The experiment was performed in triplicate.

2.5 Percentage of removal of Cr (VI)and Ni
The removal percentage was calculated by using the following equation.
Removal (%) $= \frac{C_0 - C_e}{C_0} x100$, where C_0 and C_e are the concentration of initial and after adsorption respectively.

2.6 Data analysis
Statistical Package of Social Science (SPSS) software was used to analyze the data. The frequency and percentage were obtained through descriptive statistics. Non-parametric test (Mann Whitney) was performed to determine if there is significant difference between the percent removal of heavy metal by raw and acid-treated coconut husk.

3. Result and discussion

3.1 Effect of contact time
Figure. 2 displayed on how the adsorption occurred with different time for Cr and Ni solution using 1 g dosage of adsorbent and 10 mg/L initial concentration. For raw coconut husk, it was observed that the removal percentage of both ions in aqueous solution were increasing for the first 30 minutes, are increasing. Then, the trend becomes constant afterward. Between contact times of 90 to 150 minutes, the percent removal of Cr ions ranged 60% to 65%, meanwhile for Ni ions range 80% to 100%. The explanation behind this is due to the vacant adsorbent sites of the coconut husk. At minute 90, the absolute concentration peaked and the removal of Cr and Ni become constant. Meanwhile, acid-treated coconut husk has lower percent removal of Cr and Ni as compared to raw coconut husk. The acidic pH of the coconut husk was contributed by the acid. This was due to the electrostatic interaction between Cr and Ni ions and the raw coconut husk structure and composition [21]. This equilibrium state of time at 30 minutes was due to all of the active sites of acid treated coconut husk had been occupied led to less efficiency in adsorbing Cr and Ni ions after 30 minutes [18]. Thus, for the next procedure of determining optimum level, 90 minutes of contact time was chosen for removing Cr and Ni ions using raw coconut husk.

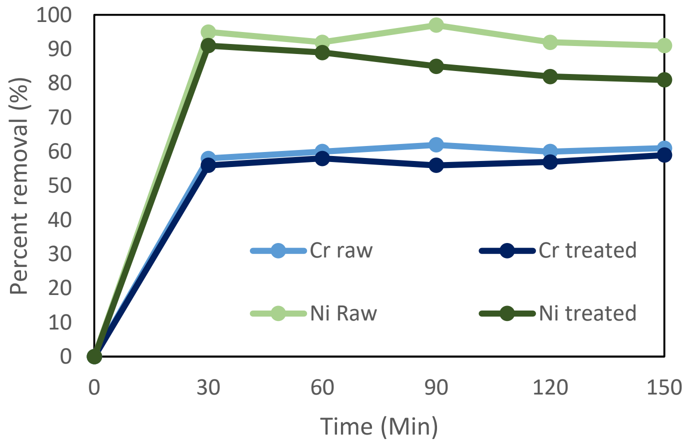

Figure 2. Raw coconut husk performance towards removal of both ions with different time

3.2 Effect of pH

The adsorption behaviour of both ions upon the change of pH is portrayed in Figure 3. As the pH affects the degree of ionization of the adsorbate during reaction, concentration of the counter ions on the functional groups of the adsorbent, and the solubility of the metal ions, is it an important parameter to be considered in the adsorption process [22]. From Figure.2, the highest percent removal of the Cr by the coconut husk is at pH 3 (86%). The Cr showed low affinity for electrostatic interaction with the positively charged composite, hence the lowest removal of Cr was observed at pH 7 [23]. This is almost similar to the previous report, which stated that pH 4 is the optimum pH for the maximum removal of both ions but significantly decreased at pH 5–6. However, their pattern slightly increased at higher pH values [24]. In this study, the removal was decreased after pH changed to 10 and onwards.

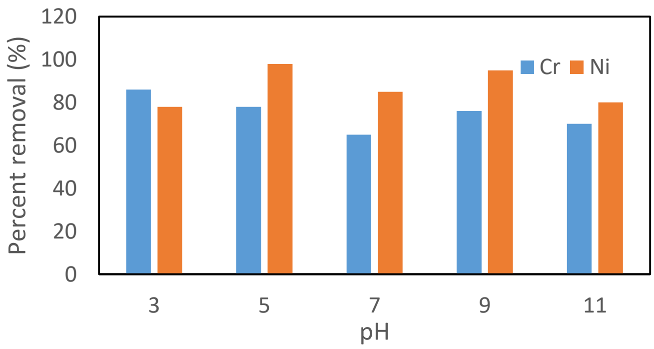

Figure 3. Effect of pH for adsorption of Cr and Ni using raw coconut husk

In addition, based on Figure. 3 it was found that the highest removal of Ni ions was at pH 5 which had 99% percentage of removal. This indicated that pH 5 was the most suitable pH for the adsorption of Ni on the raw coconut husk. At pH more than 5, the Ni precipitated due to hydroxide anions forming a nickel hydroxide precipitate. As reported by the previous study, H+ ions competed with Ni on the surface of the adsorbent in pH less than 3. The repulsive forces exist caused the Ni to be rendered from reaching the binding sites of the sorbent [25]. Thus, the optimal pH value was selected to be 5 [26].

IOP Conf. Series: Earth and Environmental Science **596** (2020) 012048 doi:10.1088/1755-1315/596/1/012048

3.3 Effect of adsorbent dosage

Figure. 4 illustrates the percentage removal of Cr and Ni ions increased with increase of dosage of adsorbent until reaching 1.5 g of adsorbent. According to the graph, 1.5 g of adsorbent had the highest percent removal of Cr and Ni ions. After 1.5 g, the percent removal of Cr and Ni became constant and decreased because the adsorbent was saturated and it decreased the surface area [27]. In agreement with previous study, more availability of adsorption sites resulted to the increase of adsorption [20, 25]. In this study, the removal of Cr and Ni was achieved at 1.5g of raw coconut husk.

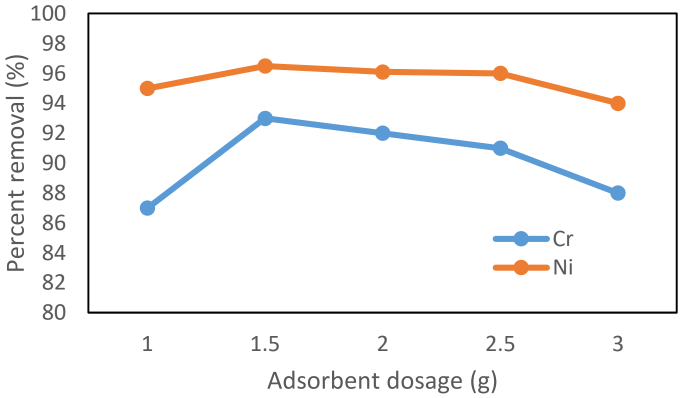

Figure 4. Effect of adsorbent dosage for adsorption of Cr and Ni using raw coconut husk

3.4 Characterisation of coconut husk

FTIR spectra in Figure. 5A shows that raw coconut husk had a higher peak at 3363.71 cm^{-1} indicated the presence of bonded hydroxyl group in stretching mode (O-H group). Acid-treated coconut husk had a lower peak at 3336.21 cm^{-1} because during acid hydrolysis, major components of the functional group were removed because hydrochloric acid changes the structural and composition of the adsorbent. From the Figureure, peaks of (C-H), (C-O), and (C-O-C) for raw coconut husk were higher than acid-treated coconut husk which at 2912.46 cm^{-1}, 1606.64 cm^{-1}, and 1033.80 cm^{-1} respectively.

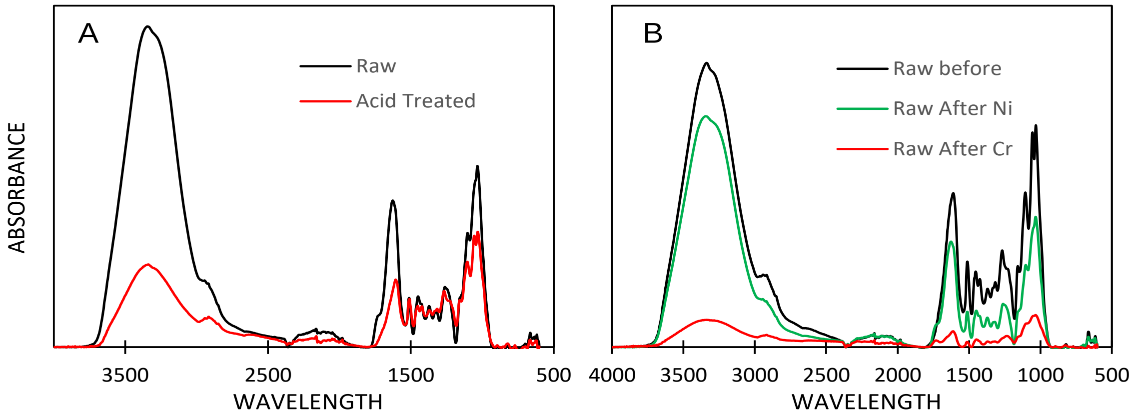

Figure 5. (A) FTIR spectra of raw and acid treated coconut husk; (B) FTIR spectra of before and after adsorption of Cr and Ni using raw coconut husk

Figure. 5B shows the FTIR spectral analysis for the raw coconut husk before and after adsorption of Cr and Ni. From Figure. 5B, after adsorption process of Cr, O-H group shifted from peak 3363.71 cm^{-1} to 3232.56 cm^{-1}, C-H group from 2912.46 cm^{-1} to 2873.81 cm^{-1}, and C-O group from 1606.64 cm^{-1} to 1595.06 cm^{-1}. The decrease of peak after the adsorption of raw coconut husk on the Cr and Ni indicated that the raw coconut husk efficiently can adsorb the Cr. This was due to the interaction force

IOP Conf. Series: Earth and Environmental Science **596** (2020) 012048 doi:10.1088/1755-1315/596/1/012048

between the functional group of coconut husk and Cr/Ni [19]. After adsorption, the peaks of the functional group shifted to a lower wavelength. This also indicated that the raw coconut husk adsorbs the metal ions efficiently and has a high adsorption capacity. From this study, the percentage of adsorption varies non-linearly with pH, on the contrary, the adsorption varied linearly with the amount of adsorbent and concentration with time but [20].

3.5 Comparison of mean difference between percent removal of heavy metal adsorbed by raw and acid treated coconut husk

Mann-Whitney test was used to compare the mean difference of percent removal of Cr and Ni between raw and acid-treated coconut husk, since the data was not normally distributed. Based on Table 1, the p-value was 0.016 indicating that there was a significant difference in the amount of metals reduced by raw and acid-treated coconut husk. Raw coconut husk had higher percent removal as compared to acid-treated coconut husk.

Table 1. Comparison of percent removal of Cr and Ni using raw and acid-treated coconut husk

Variable	**n**	**Median (IQR)% removal**	**Z statistic**	**p-value***
		Cr		
Raw	15	64 (4)	-2.402	0.016[a]
Acid-treated	15	58 (8)		
		Ni		
Raw	15	95 (2)	-2.61	<0.009[a]
Acid-treated	15	86 (8)		

[a]Mann Whitney Test

For Ni, the p-value was 0.009. The result again shown significant difference in the amount of the metal reduced using raw and acid-treated coconut husk. Raw coconut husk recorded a higher percent removal as compared to acid treated coconut husk.

4. Conclusion

In summary, coconut husk was the adsorbent that has a high ability to adsorb metal ions. This was due to the surface of coconut husk that contain functional groups which can bind to the metal ion. Coconut husk has a good adsorption as all the parameters achieve their optimum state. In this study, the optimum conditions for adsorption of Cr using raw coconut husk were 90 minutes contact time, pH 3, 1.5g adsorbent dosage at 20 mg/L initial concentration of Cr aqueous solution. Meanwhile, the optimum conditions for adsorption of Ni were 90 minutes of contact time, pH 5, and at 1.5g adsorbent dosage. Statistical analysis shown that there was a significant mean difference of percent removal of Cr and Ni between raw and acid-treated coconut husk, whereby raw coconut husk has a higher ability to adsorb Ni and Cr. In conclusion, raw and acid-treated coconut husk had a good ability to adsorb heavy metals especially Cr and Ni using method of adsorption.

5. Acknowledgement

The authors greatly appreciate the financial support received from the Universiti Sains Malaysia (USM) under the Short Term Grant Scheme (304/PPSK/6315124).

References

[1] Akhtar, R., Water Pollution Challenges and Future Direction for Water Resource Management Policies in Malaysia. 2014. *Environ. Urban. Asia*, **5**, pp.63–81.

[2] Wang, J. and Chen, C., Biosorbents for heavy metals removal and their future. 2009. *Biotechnol. Adv.*, **27**(2), pp.195–226.
[3] Congeevaram, S. et al., Biosorption of nicke and nickel by heavy metal resistant fungal and bacterial isolates. 2007. *J. Hazard. Mater.*, **146**(1–2), pp.270–277.
[4] Jacobs, J. A., & Testa, S. M. 2005. Overview of chromium (VI) in the environment: background and history. Chromium (VI) handbook, 1-21.
[5] Katsou, E., Malamis, S., Haralambous, K.J. and Loizidou, M., Use of ultrafiltration membranes and aluminosilicate minerals for nickel removal from industrial wastewater. 2010. *J. Membr. Sci.,* **360**(1–2), pp.234–249.
[6] Fu, F. and Wang, Q., Removal of heavy metal ions from wastewaters: A review. 2011. *J. Environ. Manage.*, **92**(3), pp.407–418.
[7] Alyüz, B., & Veli, S. Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. (2009). *J. Hazard. Mater.,* **167**(1-3), 482-488.
[8] Demirbas, A., Heavy metal adsorption onto agro-based waste materials: A review. 2008. *J. Hazard. Mater.,* **157**(2–3), pp.220–229. 63
[9] Bhatti, H.N., Nasir, A.W. and Hanif, M.A., Efficacy of Daucus carota L. waste biomass for the removal of chromium from aqueous solutions. 2010. *Desalination*, 253(1), pp.78–87.
[10] Barakat, M.A., New trends in removing heavy metals from industrial wastewater. 2011. *Arab. J. Chem.*, **4**(4), pp.361–377.
[11] Vinod, V.T.P., Sashidhar, R.B. and Sreedhar, B., Biosorption of nickel and total chromium from aqueous solution by gum kondagogu (Cochlospermum gossypium): A carbohydrate biopolymer. 2010. *J. Hazard. Mater.*, **178**(1), pp.851–860.
[12] Tan, I.A.W., Ahmad, A.L. and Hameed, B.H., Adsorption of basic dye on high surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies. 2008. *J. Hazard. Mater.*, **154**(1–3), pp.337–346.
[13] Guo, J., & Lua, A. C. Preparation of activated carbons from oil-palm-stone chars by microwave-induced carbon dioxide activation. 2000. *Carbon*, **38**(14), 1985-1993.
[14] Srinivasakannan, C., & Bakar, M. Z. A. Production of activated carbon from rubber wood sawdust. 2004. *Biomass Bioenergy*, **27**(1), 89-96.
[15] Prahas, D., Kartika, Y., Indraswati, N., & Ismadji, S. Activated carbon from jackfruit peel waste by H3PO4 chemical activation: pore structure and surface chemistry characterization. 2008. *Chem. Eng. J.,* **140**(1-3), 32-42.
[16] Demiral, H., Demiral, I., Tümsek, F., & Karabacakoğlu, B. Adsorption of chromium (VI) from aqueous solution by activated carbon derived from olive bagasse and applicability of different adsorption models. 2008. *Chem. Eng. J.*, **144**(2), 188-196.
[17] Lima, I., & Marshall, W. E. Utilization of turkey manure as granular activated carbon: Physical, chemical and adsorptive properties. 2005. *J. Waste Manag.*, **25**(7), 726-732.
[18] Salleh, N. F. M., Jalil, A. A., Triwahyono, S., Ripin, A., Sidik, S. M., Fatah, N. A. A., & Hassim, M. H. New direct consecutive formation of spinel phase in (Fe, Co, Ni) Al2O4 composites for enhanced Pd (II) ions removal. 2017. *J. Alloys Compd.*, **727**, 744-756.
[19] Fahma, F. et al., Effect of pre-acid-hydrolysis treatment on morphology and properties of cellulose nanowhiskers from coconut husk. 2011. *Cellulose*, **18**(2), pp.443–450.
[20] Etim, U.J., Umoren, S.A. and Eduok, U.M., Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution. 2016. *J. Saudi Chem. Soc.*, **20**, pp.S67–S76.
[21] Nomanbhay, S.M. and Palanisamy, K., Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. 2005. *Electron. J. Biotechn.*, **8**(1).
[22] Amuda, O.S., Giwa, A.A. and Bello, I.A., Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. 2007. *Biochem. Eng. J.*, **36**(2), pp.174–181.
[23] Gupta, V.K., Agarwal, S. and Saleh, T.A., Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes. 2011. *Water. Res.,* **45**(6), pp.2207–2212.

[24] Rahmani, A., Mousavi, H.Z. and Fazli, M., Effect of nanostructure alumina on adsorption of heavy metals. 2010. *Desalination*, **253**(1–3), pp.94–100.
[25] Jain, R. and Shrivastava, M., Adsorptive studies of hazardous dye Tropaeoline from an aqueous phase on to coconut-husk. 2008. *J. Hazard. Mater.*, **158**(2–3), pp.549–556.
[25] Hasar, H., Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk. 2003. *J. Hazard. Mater.*, **97**(1–3), pp.49–57.
[27] Radnia, H., Ghoreyshi, A.A., Younesi, H. and Najafpour, G.D., Adsorption of Fe(II) ions from aqueous phase by chitosan adsorbent: equilibrium, kinetic, and thermodynamic studies. 2012. *Desalin. Water. Treat.*, **50**(1–3), pp.348–359.