Bioresources and Environment 2024, 2(3) 14-23.

Content list available at BioEnv

Bioresources and Environment

Journal homepage: www.bioenvuitm.com

Removal of Chromium (Cr) and Copper (Cu) from Domestic Wastewater Using Eggshells Waste as Adsorbent with Multi Variable Dose and Contact Time

Fauzi Baharudin,[1*] Ain Azreena Ali Abas,[1] Jalina Kassim,[1] Siti Nurulhuda Mohd Imran,[1] Suriati Ghazali,[2]

[1]*School of Civil Engineering, College of Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor Darul Ehsan, Malaysia.*
[2]*Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang Al Sultan Abdullah, Lebuh Persiaran Tun Khalil Yaakob, 26300 Kuantan, Pahang Darul Makmur, Malaysia.*

Received: August 25, 2024, Accepted in revised form: October 20, 2024
Available online: October 21, 2024

ABSTRACT. The removal of Chromium (Cr) and Copper (Cu) from domestic wastewater was investigated using eggshell waste as an adsorbent. The objective of this research was to evaluate the efficacy of eggshell waste in removing these heavy metals and to determine the most optimal conditions for maximum removal efficiency. Adsorption experiments were carried out using the highest values tested, with an adsorbent dosage of 1.5 g and a contact time of 60 minutes. The results showed that both Chromium and Copper removal were promising. The removal efficiency for Chromium was found to be 69.94% at a dosage of 1.5 g, while Copper had a higher removal efficiency of 84.62%. These results highlight the potential of eggshell waste as an effective adsorbent for heavy metal removal from domestic wastewater. Furthermore, an examination of contact time revealed that longer durations significantly enhanced removal efficiencies. Chromium had a removal efficiency of 65.90% at the longest contact time of 60 minutes, while Copper had an impressive removal efficiency of 84.62%. These findings highlight the importance of allowing enough contact time for heavy metal adsorption. The high removal efficiencies at the specified adsorbent dosage and contact time show that eggshell waste has the potential to be a cost-effective and sustainable solution for heavy metal removal in domestic wastewater treatment systems.

Key words: Wastewater treatment, eggshells, heavy metals, Copper, Chromium, adsorption.

INTRODUCTION

Water is a life-sustaining resource required by most living organisms. The demand for water in household and industrial activities continues to rise annually. Today, the world faces a water crisis because of industrialization, increasing residential and commercial areas, and agricultural lands that generate enormous amounts of wastewater (Abdelbasir & Shalan, 2019). Domestic wastewater is water resulting from human activities in the home, such as bathing, laundry, dishwashing, garbage disposal, and toilet use. Even in trace amounts, the presence of non-biodegradable organic compounds in wastewater poses a severe threat to public health because they are endocrine disruptors, toxic to living organisms, and potential carcinogens (Malik et al., 2021).

Heavy metals are among the contaminants that frequently contaminate open streams. However, their presence in water poses grave risks to human and aquatic health. This is because heavy metals tend to accumulate in soil, water, and wastewater, through which they enter the food chain. Even though heavy metals such as Cd, Cr, Zn, Pb, Fe, Cu,

*Corresponding author: Tel.: +60 355437827; fax: +60 355442123.
E-mail address: *fauzi1956@uitm.edu.my* (Fauzi Baharudin)

Mn, and Co are typically present in trace amounts, they are regarded as the most toxic and pervasive components in wastewater effluent (Zhou et al., 2020). This is because these heavy metals are not metabolized by the body, resulting in dangerous accumulation in soft tissues (Sankaran et al., 2020).

Depending on the quality of the wastewater, various of wastewater treatment methods may be utilized. Coagulation, flocculation, biodegradation, adsorption, membrane separation, ion exchange, oxidation and selective bio-adsorbents are some methods that can be used to treat wastewater. It has been discovered that adsorption is an efficient and cost-effective method for wastewater treatment to remove heavy metals (Badrealam et al., 2018). Adsorption is the process of attaching a solute present in a fluid to a porous solid surface known as an adsorbent. It is a process of mass transfer. This method produces high-quality effluent, which is its primary advantage. Therefore, adsorption is an environmentally friendly technique because it is simple to employ and produces no toxic byproducts (Hussain, 2021). Carbon is the most common adsorbent due to its high absorption efficiency. Its exceptional performance is a result of their structural characteristics, which provide them with a large surface area and facilitate chemical modification, rendering them universally acceptable to a broad range of contaminants. There are various adsorbent materials that can be utilized to remove heavy metals from wastewater. Activated carbon is the most popular one among the research for adsorption studies using agricultural or fruit waste (Lewoyehu, 2021). Some of the activated carbons were developed from coconut button waste (Anirudhan & Sreekumari, 2011), banana peels (Baharudin, et al., 2018), orange peels (Elangovan, et al., 2023), and durian rinds (Baharudin, et al., 2021).

It is estimated that approximately 25,000 tonnes of eggshells waste are produced globally and are disposed of in landfills. This waste has a high cost of disposal and is currently accumulating on a landfill site without any pretreatment (Othman et al., 2020). Eggshell waste would have a negative impact on the environment because it can attract rodents such as rats and mice (Saparuddin et al., 2020). Therefore, an alternative way to prevent all of the issues occurred from eggshells waste in landfills is to modify it into a low-cost adsorbent. Thus, as an effort to convert waste into more useful substance, eggshell waste is being investigated in this study as a potential adsorbent for a variety of applications, including heavy metal removal. According to De Oliveira Zonato et al. (2022), eggshells, which are primarily calcium carbonate, have natural adsorption properties that make them suitable for adsorption processes. The porous structure of eggshells offers a large surface area for effective contaminant adsorption. Hence, this study aims to evaluate the efficiency of eggshell waste as low-cost adsorbent in removing Cr and Cu from domestic wastewater.

METHODOLOGY

Sampling Area

This study was conducted in Universiti Teknologi Mara (UiTM) Shah Alam. Generally, there were five Sewage Treatment Plants (STP) that can be found in UiTM Shah Alam. One of them is located at Mawar College with coordinate of 3°04'10.6"N, 101°29'47.9"E. In this study, wastewater sample was collected from STP at Mawar College due to its strategic location and easy to access. The wastewater sample was collected at inlet point of sewage treatment plant (STP) to determine the concentration of Cr and Cu. Grab sampling was used to collect samples, which were then store in water sampling bottles.

Preparation of eggshells waste as an Adsorbent

In this study, eggshells wastes were collected from food outlets at Dataran Cendekia, UiTM Shah Alam. Following the method of Abatan et al. (2020), to remove contaminated particles from the eggshells waste, they were washed several times with deionized water and boiled for 10 minutes. The eggshells were oven-dried at 150 °C for 3 hours before being allowed to cool to 25 °C (ambient temperature) as this is the most optimum temperature to remove moisture content form the eggshells. The dried samples were crushed into small pieces of non-uniform size as size was not considered as the parameter in this study. Then, these eggshells were stored in airtight container for batch adsorption test.

Initial concentration of heavy metals

The initial metal concentration provides a significant driving force to overcome all metal mass transfer resistance between the aqueous and solid phases. In this study, one of the essential parameters that must be measured prior the adsorption process begins is the initial concentration of metal ions, which must be compared to the concentration after treatment of eggshells waste to determine the adsorption capacity of eggshells waste. The wastewater sample which was taken from the STP was measured using DR2800 Spectrophotometer before starting the batch adsorption test.

Batch Adsorption Test

In this stage, a series of batch adsorption tests were conducted to investigate the effects of adsorbent dosage and contact time on the removal of Cr and Cu. Each parameter was tested three times on separate sampling day to obtain an average result for each parameter. The method used in this test were referred from Liu et al. (2013), Badrealam et al. (2018) and Park et al. (2007) and this method were adapted based on suitability of eggshell adsorption capacity. The volume of wastewater sample used for this study was 500 ml for each beaker and stirring rate was set to 120 rpm. The materials used in this study were sample of domestic wastewater, prepared eggshell waste as adsorbent, CuVer® 1 Copper Reagent, and ChromaVer® 3 Chromium Reagent. The apparatus used were beaker, Jar Test apparatus, weighing scale, filter paper, conical flask, filter funnel, Sample Cell: 1" Square Glass 10 mL, and DR2800 Spectrophotometer.

Effect of Adsorbent Dosage on Chromium and Copper

In this test, 0.5 g, 1.0 g and 1.5 g (Liu et al., 2013) of prepared adsorbents were used and set into three distinct 500 mL beaker containing sample of wastewater. Each sample were then stirred at 120 rpm (Park et al., 2007) for 60 minutes (Badrealam et al., 2018).

Effect of Contact Time on Chromium and Copper

To analyse the contact time of Cr and Cu ions, the dosage of adsorbent is fixed to 1.0 g (Badrealam et al., 2018). A batch of adsorption test is carried out at different contact time intervals which were 5 minutes, 30 minutes and 1 hour. After that, each sample was agitated at 120 rpm (Park et al., 2007).

Final concentration of Chromium and Copper

Following the completion of the tests for both parameters, which are the effects of adsorbent dosage and contact time, the samples from each beaker were filtered into Sample Cell 1" Square Glass 10 mL to separate metal ions that had been adsorbed by the prepared eggshells waste using a filter funnel and filter paper. By mixing the filtered sample with CuVer® 1 Copper Reagent for Copper (Cu) and ChromaVer® 3 Chromium Reagent for Chromium (Cr), the concentration of unadsorbed ions in the lasting solution can be measured. Finally, the DR2800 Spectrophotometer was used to analyze the mixture solution. Initial and final concentration of Cr and Cu ions were then to be compared. The removal efficiency of Cr and Cu was obtained using the following expression (Abatan et al., 2020):

$$RE = \frac{C_o - C_f}{C_o} \times 100$$

Where RE is the removal efficiency, C_o is the initial concentration and C_f is the final concentration.

RESULTS AND DISCUSSION

Batch Adsorption Test

The batch adsorption test aimed to evaluate the effectiveness of eggshell waste as an adsorbent for heavy metal removal. The study investigated two key parameters, namely the adsorbent dosage and contact time, by varying the dosage levels and durations. The purpose was to assess the efficiency of eggshell waste under different conditions, including different amounts of adsorbent and varying durations of exposure.

Effect of Adsorbent Dosage on Chromium and Copper

As implied by previous studies (Yahya et al., 2020; Sarin & Pant, 2006), adsorption of all metal ions was reported to be proportional to the adsorbent dosage. This finding is due to the increased contact surface area and the subsequent rise in vacant adsorptions site (Chou et al., 2023). Starting with the findings of this study on chromium removal, the removal efficiency was measured at 23.7% when the adsorbent dosage of eggshell waste was set at 0.5 g. Increasing the adsorbent dosage to 1.5 g has increased the removal efficiency to 69.94% (Table 1). This shows a significant improvement in Chromium removal as the adsorbent dosage increased, demonstrating the advantages of using more eggshell waste as an adsorbent.

Table 1. Effect of Adsorbent dosage in average for 60 minutes contact time

Test	**Adsorbent dosage (g)**	**Initial concentration (mg/l)**		**Final concentration (mg/l)**		**Removal efficiency (%)**	
		Chromium (Cr)	Copper (Cu)	Chromium (Cr)	Copper (Cu)	Chromium (Cr)	Copper (Cu)
1	0.5	0.058	0.04	0.044	0.03	23.70	23.08
2	1			0.030	0.02	47.98	53.85
3	1.5			0.017	0.01	69.94	84.62

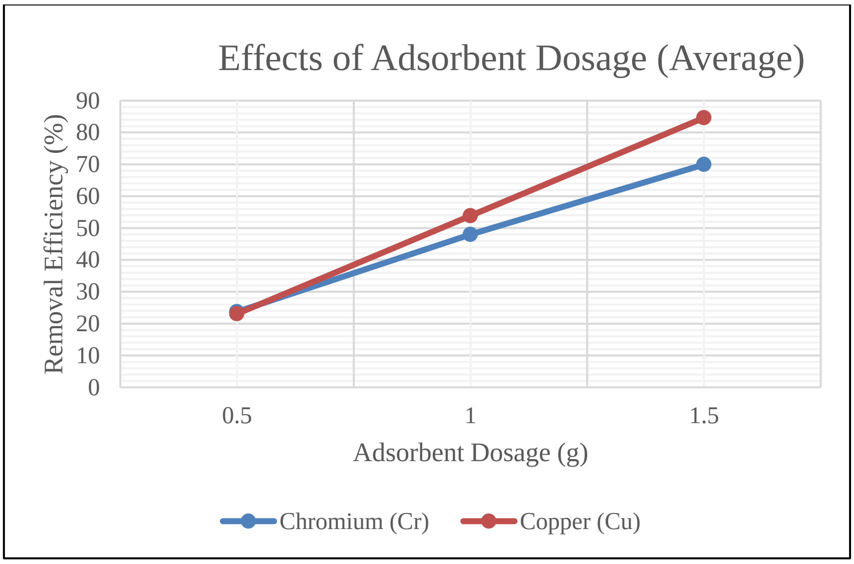

Figure 1. Effect of various adsorbent dosage on Cr and Cu removal

When these findings are compared to other studies, it is clear that there is a consistent trend of increased Chromium removal with higher adsorbent dosages. According to the study conducted by Abatan et al. (2020), the removal efficiency is 44.80% at 5 g of adsorbent dosage and 60.96% at 25 g of dosage. This initial amount was used as to provides support to the concept that increasing the amount of eggshell waste used as an adsorbent correlates with greater Chromium removal, as observed in both this study and other studies. Next is on Copper removal, at 0.5 g adsorbent dosage, the removal efficiency was 23.08%, which increased significantly to 84.62% when the dosage was increased to 1.5 g (Figure 1). These findings show that increasing the adsorbent dosage significantly improves copper removal, highlighting the potential of eggshell waste for effective copper adsorption. Based on these initial findings, it is strongly believed that further improvement study with dose of more than 2.0 g would probably remove close to 100% of Copper.

Comparing Copper removal of this study to Pandey et al. (2017), it is worth noting that both studies show a similar trend of higher removal efficiencies at higher adsorbent dosages. The data from Pandey et al. (2017), show a removal efficiency of 20% at 2.5 g of adsorbent dosage and a significantly higher efficiency of 71% at 15 g of dosage. This consistency supports the positive relationship between increased eggshell waste dosage and improved copper removal. Finally, the comparison of this findings to other researchers emphasises the efficacy of using eggshell waste as an adsorbent for Chromium and Copper removal in wastewater treatment. Both studies show that higher adsorbent dosages result in improved removal efficiencies for both heavy metals, verifying the value and sustainability of eggshell waste for heavy metal adsorption. The consistent trends observed in multiple studies contribute to a better understanding of this novel approach and its practical application in dealing with heavy metal pollution in domestic wastewater.

Effect of Contact Time on Chromium and Copper

The findings of this study have revealed that at 5 minutes of contact time for Chromium removal using eggshell waste as an adsorbent, the removal efficiency was measured at 17.34%. However, increasing the contact time to 60 minutes resulted in a significant improvement in removal efficiency, reaching to 65.9% (Table 2). This suggests that longer contact times with eggshell waste as the adsorbent are more desirable for achieving higher Chromium removal rates.

A comparison with the findings of other studies shows an identical trend. According to the data of Chan & Ngadi (2018), the removal efficiency for Chromium was 10% after 20 minutes of contact time. When the contact time was increased to 120 minutes, the removal efficiency increased significantly, reaching 23%. This consistent finding across studies supports the idea that longer contact times boost the effectiveness of eggshell waste in removing Chromium from wastewater.

Table 2. Effect of Contact time in average for 1.0 g dose

Test	**Contact time (min)**	**Initial concentration (mg/l)**		**Final concentration (mg/l)**		**Removal efficiency (%)**	
		Chromium (Cr)	Copper (Cu)	Chromium (Cr)	Copper (Cu)	Chromium (Cr)	Copper (Cu)
1	5			0.048	0.03	17.34	30.77
2	30	0.058	0.04	0.033	0.02	42.20	53.85
3	60			0.020	0.01	65.90	84.62

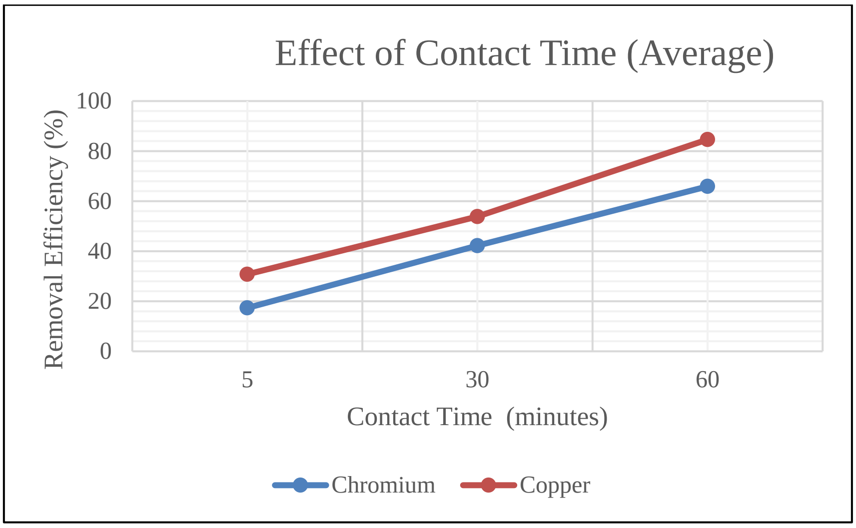

Figure 2. Effect of various contact time on Cr and Cu removal

Regarding the contact time for Copper removal, this study revealed that the removal efficiency was 30.77% after 5 minutes of contact time (Figure 2). The removal efficiency increased to 84.62% with an increase in adsorbent dosage and a longer contact time of 60 minutes. This highlights the significance of adsorbent dosage as well as contact time in achieving higher Copper removal rates using eggshell waste. According to the data of Pandey et al. (2017), it shows that removal efficiency of 20% after 15 minutes of contact time, but this increased dramatically to 70% after 90 minutes. The correlation between studies demonstrates the importance of prolonged contact time in improving the efficiency of eggshell waste as an adsorbent for Copper removal.

The discussion on the results obtained in this study has shown the significance of contact time and adsorbent dosage in removal of Chromium and Copper using eggshell waste in wastewater treatment. Longer contact times and higher adsorbent dosages generally result in more effectively heavy metal pollutant removal rates. However, it will need further improvement study to support the hypothesis as this study only serve as a platform to discover any kind of possibilities on removal of metals using eggshells. These consistent trends in multiple studies can contribute to a better understanding of the optimal operating conditions for using eggshell waste as an effective and sustainable heavy metal adsorption option in domestic wastewater treatment.

CONCLUSION

Overall, the study concludes with a comprehensive conclusion and recommendations based on the findings and analysis of removal of Chromium (Cr) and Copper (Cu) from wastewater. The findings from the experiments provide significant insight into the relationship between adsorbent dosage and heavy metal removal efficiency. It is apparent that increasing the adsorbent dosage increases Chromium and Copper removal significantly. As the findings shows that the removal of chromium (Cr) and Copper (Cu) are 69.94% and 84.62% respectively by utilizing the highest dosage of eggshells which is 1.5 g. The available surface area for adsorption increases with dosage, resulting in a greater number of active sites to capture the metal ions. This phenomenon is especially noticeable in the initial dosage range, where each gradual increase in adsorbent dosage results in a noticeable increase in removal efficiency. With increasing adsorbent dose, the percentage removal of both metal ions increased. The increase in metal ion removal percentage with increasing adsorbent dosage was due to increased surface negative charge and decrease in electrostatic potential near the solid surface, which favors adsorbent adsorbate interaction (Ezeh et al., 2017).

The results have also clearly demonstrated the effect of contact time on the removal of chromium and copper ions. It is evident that increasing contact time resulted in a significant improvement in removal efficiency for both metals. Based on the findings, the removal of chromium and copper is 65.90% and 84.62%, respectively, when the longest contact time is used, which is 60 minutes. As stated by Pandey et al. (2017), that the percentage of heavy metal ion removal increases sharply with increasing contact time for both metal ions due to the large number of vacant sites during the process.

As recommendation for future research, the removal of Chromium and Copper in domestic wastewater using eggshell waste should focus on optimizing the adsorbent dosage, investigating adsorption kinetics for equilibrium time, evaluating the long-term stability and regeneration potential of the adsorbent, and assessing its industrial viability. By understanding the relationship between dosage and removal efficiency, determining optimal contact times, ensuring the sustainability and reusability of eggshell waste, and exploring cost-effective industrial applications, this study can lead to more efficient and eco-friendly wastewater treatment strategies for improved water quality and environmental protection.

ACKNOWLEDGMENTS

The authors would like to thank School of Civil Engineering, UiTM for the support rendered in completing this study.

AUTHOR CONTRIBUTIONS

All authors were involved in sampling and laboratory testing. The contribution in writing for this paper was also done together.

FUNDINGS

Not applicable.

DATA AVAILABILITY

Not applicable.

COMPETING INTEREST

The authors declare that there are no competing interests.

COMPLIANCE OF ETHICAL STANDARDS

Not applicable.

SUPPLEMENTARY MATERIAL

Not applicable.

REFERENCES

Abatan, O.G., Alaba, P.A., Oni, B.A., Akpojevwe, K., Efeovbokhan, V., & Abnisa, F. (2020). Performance of eggshells powder as an adsorbent for adsorption of hexavalent chromium and cadmium from wastewater. *SN Applied Sciences*, *2*(12), 1996 https://doi.org/10.1007/s42452-020-03866-w

Abdelbasir, S.M., & Shalan, A.E. (2019). An overview of nanomaterials for industrial wastewater treatment. *Korean Journal of Chemical Engineering*, *36*(8), 1209–1225. https://doi.org/10.1007/s11814-019-0306-y

Anirudhan, T.S., & Sreekumari, S.S. (2011). Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons. *Journal of Environmental Sciences*, *23*(12), 1989–1998. https://doi.org/10.1016/S1001-0742(10)60515-3

Badrealam, S., Roslan, F.S., Dollah, Z., Bakar, A.A., & Handan, R. (2018). Exploring the eggshell from household waste as alternative adsorbent for heavy metal removal from wastewater. *AIP Conference Proceedings*, *2020*, 020077. https://doi.org/10.1063/1.5062703

Baharudin, F., Mohd Tadza, M.Y., Mohd Imran, S.N., and Jani, J. (2018). Removal of Iron and Manganese in Groundwater using Natural Biosorbent. *IOP Conference Series: Earth and Environmental Science*, *140*(1), 012046. https://doi.org/10.1088/1755-1315/140/1/012046

Baharudin, F., Hamzah, N., Ab Wahab, M., and Wee Kang, C. (2021). Effectiveness of powdered activated carbon from fruit waste in removing heavy metals in groundwater. *IOP Conference Series: Earth and Environmental Science*, *140*(1), 012046. https://doi.org/10.1088/1755-1315/140/1/012046

Chan, J.X., & Ngadi, N. (2018). Biosorption of chromium (vi) ions using sustainable eggshell impregnated pandanus amaryllifolius roxb. Adsorbent. *Perintis eJournal*, *8*(2), 86–101.

Chou, M., Lee, T., Lin, Y., Hsu, S., Wang, M., Li, P., Huang, P., Lu, W., & Ho, J. (2023). On the removal efficiency of copper ions in wastewater using calcined waste eggshells as natural adsorbents. *Scientific Reports*, *13*(1). https://doi.org/10.1038/s41598-023-27682-5

De Oliveira Zonato, R., De Paula Ramos, B., Perez, I. D., Ribeiro, V. a. D.S., & Freire, R. (2022). Eggshell as an adsorbent for removing dyes and metallic ions in aqueous solutions. *Cleaner Chemical Engineering*, *2*, 100023. https://doi.org/10.1016/j.clce.2022.100023

Hussain, A. (2021). Removal of heavy metals from wastewater by adsorption. IntechOpen, London. https://www.intechopen.com/chapters/75491

Lewoyehu, M. (2021). Comprehensive review on synthesis and application of activated carbon from agricultural residues for the remediation of venomous pollutants in wastewater. *Journal of Analytical and Applied Pyrolysis*, *159*, 105279, https://doi.org/10.1016/j.jaap.2021.105279.

Liu, N., Liu, Y., Luan, Y.S., & Hu, X. (2013). The elimination of heavy metal-containing wastewater by eggshells membrane. *Applied Mechanics and Materials*, *299*, 207–210. https://doi.org/10.4028/www.scientific.net/amm.299.207

Malik, S., Prasad, S., Kishore, S., Kumar, A., & Upadhyay, V. (2021). A perspective review on impact and molecular mechanism of environmental carcinogens on human health. *Biotechnology and Genetic Engineering Reviews*, *37*(2), 178-207. https://doi.org/10.1080/02648725.2021.1991715

Othman, S.A., Hasrin, Harun, S.N.I., & Mohd Sufian, A.A. (2020). Application of egg shell. *Asian Journal of Fundamental and Applied Sciences*, *1*(2), 2716–5957. https://www.researchgate.net/publication/343834205_Applications_of_Egg_Shell

Pandey, S.S., Singh, N.B., Shukla, S.P., & Tiwari, M. (2017). Removal of lead and copper from textile wastewater using egg shells. *Iranica Journal of Energy and Environment*, *8*(3), 202-209. https://doi.org/10.5829/ijee.2017.08.03.04

Park, H., Jeong, S.J., Yang, J., Kim, B.S., & Lee, S. (2007). Removal of heavy metals using waste eggshell. *Journal of Environmental Sciences*, *19*(12), 1436–1441. https://doi.org/10.1016/s1001-0742(07)60234-4

Sankaran, R., Show, P.L., Ooi, C.W., Ling, T.C., Shu-Jen, C., Chen, S.Y., & Chang, Y.K. (2020). Feasibility assessment of removal of heavy metals and soluble microbial products from aqueous solutions using eggshell wastes. *Clean Technologies and Environmental Policy*, *22*(4), 773–786. https://doi.org/10.1007/s10098-019-01792-z

Saparuddin, D.I., Mohd Zaid, M.H., Aziz, S.H.A., & Matori, K.A. (2020). Reuse of Eggshell Waste and Recycled Glass in the Fabrication Porous Glass–Ceramics. *Applied Sciences*, *10*(16), 5404. https://doi.org/10.3390/app10165404

Sarin, V. & Pant, K.K. (2006). Removal of chromium from industrial waste by using eucalyptus bark. *Bioresource Technology*, *97*(1), 15-20. https://doi.org/10.1016/j.biortech.2005.02.010

Yahya, M.D., Abubakar, H., Obayomi, K.S., Iyaka, Y.A. & Suleiman, B. (2020). Simultaneous and continuous biosorption of Cr and Cu (II) ions from industrial tannery effluent using almond shell in a fixed bed column. *Results in Engineering*, *6*, 100113. https://doi.org/10.1016/j.rineng.2020.100113

Zhou, Q., Yang, N., Li, Y., Ren, B., Ding, X., Bian, H., & Yao, X. (2020). Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017. *Global Ecology and Conservation*, *22*, e00925. https://doi.org/10.1016/j.gecco.2020.e00925