

## Active Capping Treatment of Copper and Chromium Contaminated Sediment with Bentonite Kaolin and Sand to Inhibit their Release to the Overlying Water

Mohammed Kabir Aliyu<sup>1\*</sup>, Ahmad Tarmizi Bn Abd Karim<sup>1</sup>, Chee Ming Chan<sup>2</sup>, Aeslina Abdulkadir<sup>1</sup>, Zawawi Bin Daud<sup>1</sup>, Adeleke Abdulrahman Oyekanmi<sup>3</sup>

<sup>1</sup> Faculty of Civil Engineering and Built Environment, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia

<sup>2</sup> Department of Civil Engineering, Faculty of Engineering Technology, Pagoh Higher Education Hub, 84600 Pagoh, Muar, Johor, Malaysia

<sup>3</sup> Department of Earth Science and Environment, Faculty of Science and Technology, The National University of Malaysia, Bangi, Selangor, Malaysia

\* Corresponding author's email: mk4aliyu@gmail.com

### ABSTRACT

The public concern over sediment contamination brought on by mining operations, excessive use of chemical fertilisers or pesticides, industrial, agricultural, and municipal effluent, is increasing. Dredging is a more expensive treatment option than in situ capping of polluted sediment for immobilising pollutants in sediments on site. In order to stop the release of Cr and Cu from chemically contaminated sediments, this study aimed to evaluate the efficiency of utilising active capping materials such as bentonite (B), kaolin (K), and a 1:1 combination of bentonite and kaolin (BK) as capping materials. In a 90-day laboratory experiment carried out in glass tanks with a 1 cm thickness cover of capped material plus sand spread over the polluted sediment, the efficacy of B, K, and BK in inhibiting trace metal leachability was examined. The findings demonstrated that B and BK decreased the ability of sediments to leach Cr and Cu. The results suggest that BK and B should be considered as a suitable active material for capping treatment of polluted sediment sites because of their high Cu and Cr trapping. According to an analysis of adsorption kinetics, chemisorption was the adsorption process. The outcomes of this study demonstrated the potential for using kaolin, a bentonite-kaolin clay mixture covered with sand, and bentonite as capping materials for the in-situ treatment of Cr and Cu polluted coastal sediments.

**Keywords:** in situ capping, polluted sediment, bentonite, kaolin, chromium, copper.

### INTRODUCTION

Chemical contaminants such as heavy metals continue to damage coastal areas in the marine environment as a result of lithogenic and anthropogenic activity (Belin, 2013). Streams and water reservoirs naturally become enriched in heavy metals due to rock weathering and volcanic activity, a process known as “lithogenic” (Sany, 2011). On the other hand, through rivers and canals, human activities like industry, agriculture, and urban development structures add pollutants to the sea (Sany, 2011). Chemical pollution has an

influence on both the marine environment and the human population (Belin, 2013).

These contaminants pose a threat to the environment, human health, and food safety. Therefore, heavy metals-contaminated sediment needs to be cleaned up as soon as possible (Benami et al., 2013; Wang et al., 2013b; Zeng et al., 2015; Cheng et al., 2016b). Recent media attention has focused heavily on the hot topic of sediment pollution. Many strategies have been used to reduce and avoid pollution. (Xu et al. 2012; Zhang et al. 2013a; Cheng et al. 2016a; Gerhardt et al. 2009; Peng et al. 2009). The two major categories that

remediation technologies fall into are in-situ and ex-situ remediation.

In situ remediation is the process of treating a contaminant in its actual environment. Without needing to transfer the sediment, this method seeks to eliminate contaminants from sediment. Ex-situ remediation involves excavating contaminated sediment and treating it elsewhere, away from the site. When compared to other treatments, in-situ cleanup provides a variety of potential technical, financial, and environmental benefits (Kuppusamy et al., 2016; Bardos et al., 2000). In situ remediation may be the only option for treating pollutants once the size of the polluted region and cost-benefit are taken into account.

In-situ remediation is preferred for sizable contaminated soil or sediment, because it harms the environment less, is relatively easy to carry out, and costs less compared to the ex-situ treatment (Guiwei et al., 2008; Velimirovic et al., 2014; Carberry and Wik, 2001). In order to prevent surface water and biota from being permanently contaminated, polluted sediments can be covered with a capping material using an in-situ remediation technique called capping. A subaqueous layer over polluted sediments stabilises the sediments, prevents resuspension and transport, and lessens the transmission of dissolved pollutants into surface waters. It is a method for controlling the discharge of pollutants from the sediments through adsorption or binding keeping the amount of pollutants in the water above the sediments at an acceptable level (Ghosh et al., 2011; Gomez et al., 2013).

Additionally, compared to other types of sediment remediation, capping treatment has less of an effect on aquatic ecology (Beckingham et al., 2013; Ghosh et al., 2011). In addition to being expensive, dredging disturbs sediments that could lead to secondary contamination (Nayar et al., 2004; Knox et al., 2012). According to numerous studies (Föstner and Apitz 2007; Perelo 2010; Sun et al. 2015), in comparison to dredging, capping is expected to be far less expensive and a highly effective means of limiting the spread of pollution.

While several researchers have examined the use of reactive capping materials for inorganic and organic-contaminated sediments, the heavy metals in sediments have received little attention. The knowledge about in-situ capping is inadequate for heavy metal contaminated sediments (Akcil, 2015). Clay, gravel, zeolites, and

activated carbon are the main materials used in today's capping remediation techniques (Fadaei et al., 2015; Jacobs and Förstner, 1999).

This main objective of the study was to determine how to use kaolin, bentonite, and sand as capping materials to prevent contaminants (Cr and Cu) from migrating from the sediment to the water below. In order to determine if the active ingredients are effective at treating polluted sediments, the study will examine their performance. For the prevention and management of contaminated sediment risk, this study is anticipated to offer useful information. All of the experiments in this study were carried out in a flow condition with an impeller attached to the tank to simulate ocean waves, in contrast to the vast majority of prior research that was done under batch experimental conditions without flows, which appears to have limitations in field application.

## MATERIALS AND METHODS

The sample of the excavated sediment for this experiment was taken at the sungai shoreline of Kuala Perlis estuary as shown in Figure 1.

With permission from the Malaysian Marine Department and the Dredging Contractor (Malaysian Maritime Dredging Company Sdn Bhd), the sample was taken at random using the Backhoe dredger at depths of 4–6 metres below sea level. The collected sediment was transported to the UTHM laboratory for analysis in sealed plastic containers. Any debris was collected, dried at room temperature, and then crushed using a porcelain mortar and pestle and a 1 mm sieve before sifting. After the samples were acid-digested according to Edgell (1989) (USEPA System 3050B), inductively coupled plasma mass spectrometry (ICP-MS) (ELAN 9000, Perkin Elmer, USA) was used to measure the content of chromium and copper in the sediments. An X-ray fluorescence (XRF) spectrometer was used to evaluate the chemical composition of sediments, bentonite and kaolin.

### The experimental setup for capping

A laboratory-scale capping experiment was used to measure the amount of heavy metals in the saltwater that was above the contaminated sediment. The experiment was conducted at the Faculty of Civil Engineering and Built Environment,



Figure 1. The satellite image of the dredging site in Kuala Perlis, Malaysia, where sediment samples were taken

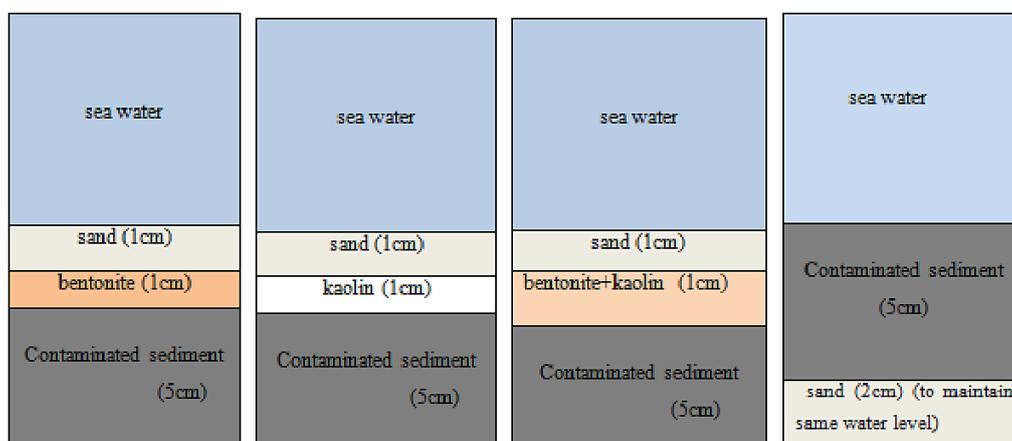


Figure 2. An illustration of the experimental setup showing the sand, sediment, and capping material depths)

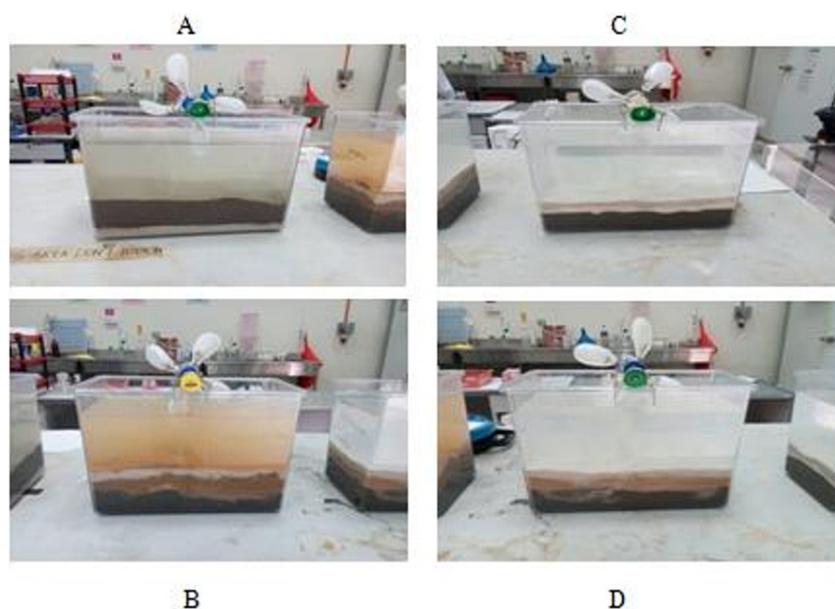


Figure 3. Experimental setup for sediment capping: A is the uncapped, polluted sediment (Control), B is sediment that has been covered in bentonite and sand (Sed+B+S), while C is sediment that has kaolin and sand on top (Sed+K+S) and D is sediment that has a composite cap (50/50) made of bentonite by kaolin and sand

Universiti Tun Hussein Onn Malaysia. The goal of this study was to determine how the active materials for capping (kaolin, bentonite and sand) affected the Cr and Cu release from contaminated coastal sediment. For this purpose, four glass tank models with similar dimensions ( $25 \times 20 \times 35$  cm) were used. Each 5 cm thick layer of glass tank models had about 3.5 kg of polluted sediment at the bottom, followed by a 1 cm thick cover (700 g) of bentonite, kaolin, or sand. Each model was gently and carefully filled with sea water. A total of 7 litres of saltwater were utilised in each experiment.

The depth of each layer of contaminated sediment and capping materials is shown schematically in Figure 2. To imitate ocean wave turbulence, an impeller was placed at the upper mid of the glass tank, as illustrated in Figure 3.

To replicate sea wave turbulence and to stimulate mass transfer of pollutants from the sediment, the impeller was turned at a 100 revolutions speed per minute (rpm) for the period of 8 hours every day. A tachometer was used to measure the rpm. Four separate experimental setups were established to test the efficacy of the active materials used: bentonite, kaolin, and sand in preventing metal migration or release, as illustrated in Figure 3.

To test the effectiveness of kaolin, bentonite and sand in preventing metal migration or release, four separate experimental setups were developed. (i) Control (No capping) (ii) Bentonite cap of 1cm thickness + sand cap of 1cm thickness (iii) 1cm kaolin thickness cap + 1cm sand thickness cap (iv) 1cm thick cap of a 1:1 mixture of kaolin + bentonite + 1 cm thick sand capping layer over the

polluted sediment as presented in Figure 3. Each of the four models was carefully filled with approximately 7 litres of uncontaminated synthetic seawater. An aliquot part of 20 mL of the overlying water was randomly obtained from various sections of the glass tanks using a plastic syringe attached with a plastic tubing on every second day after the test began and then once a week throughout the length of the 90-day test duration.

The concentration of each Cr and Cu element in the surrounding water was examined for the entire period of 90 days of the experiment. To preserve the sample, it was filtered through a 0.45 m membrane filter and treated with 0.2 percent (v/v) concentrated HNO<sub>3</sub>. Using inductively coupled plasma optical emission spectroscopy (ICP-OES), the amounts of heavy metals in the samples were assessed.

### The diagram of the capping experiment

Figures 4–7 shows the diagrams of experimental set-up measurements. This method can be used to assess the impact of capping materials on the release and transformation of hazardous metals. Both sizes are in millimeters (mm).

## RESULTS AND DISCUSSION

### The release of Cu and Cr to the water column above the contaminated sediment

Table 1 displays the average concentration release of the Cu and Cr obtained from the overlying

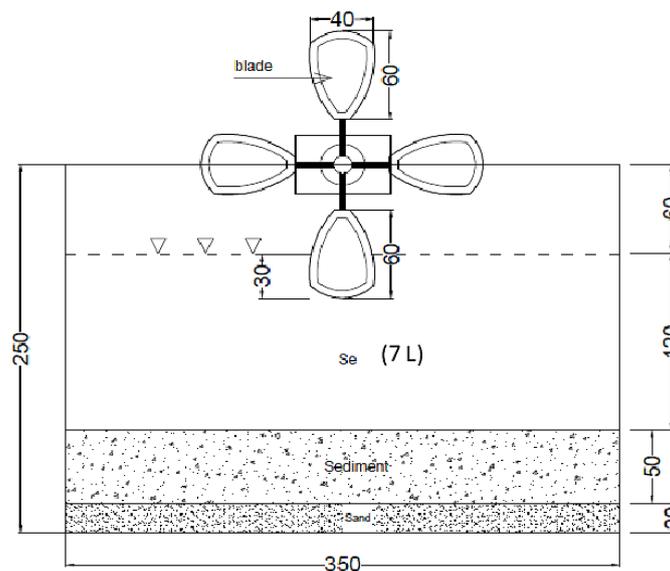


Figure 4. The frontal view of the control sample (without the capping layer)

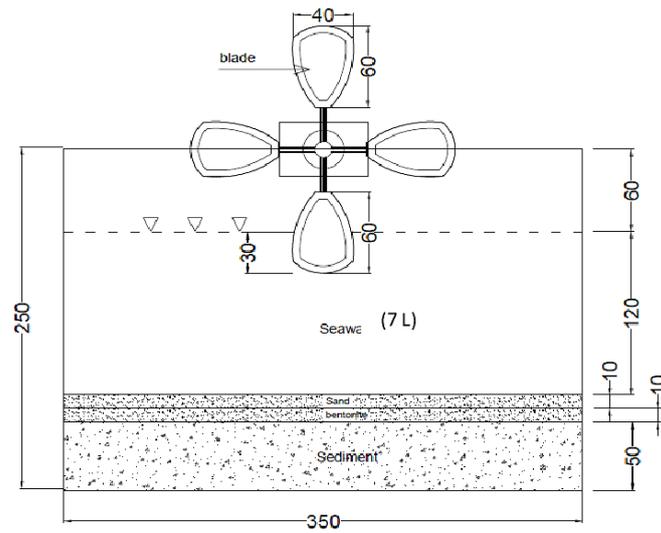


Figure 5. The image of the frontal view of bentonite + sand capping layer

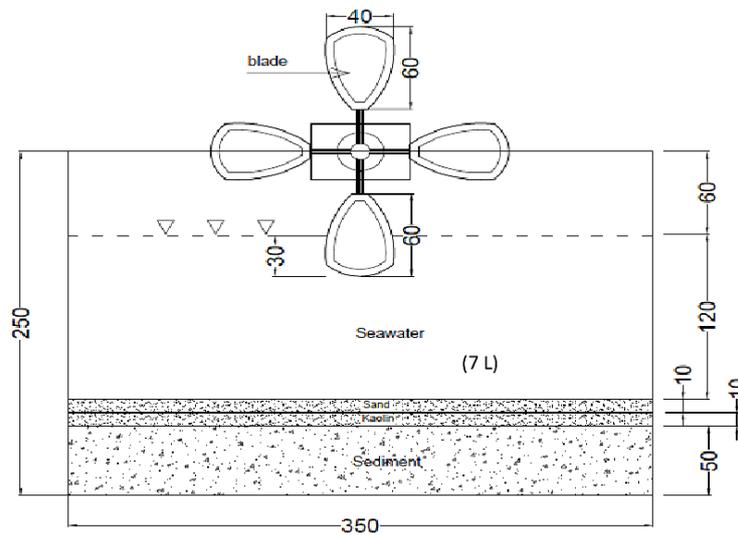


Figure 6. The image of the frontal view of kaolin + sand capping layer

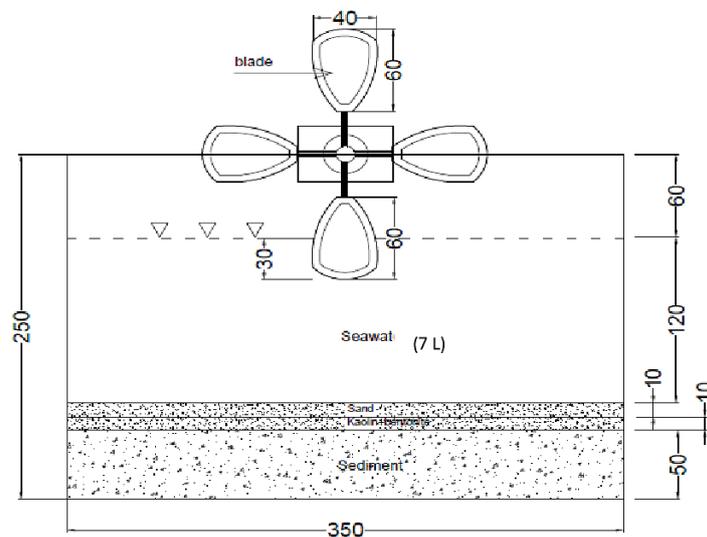


Figure 7. The image of the frontal view of kaolin + bentonite (50:50) + sand capping layer

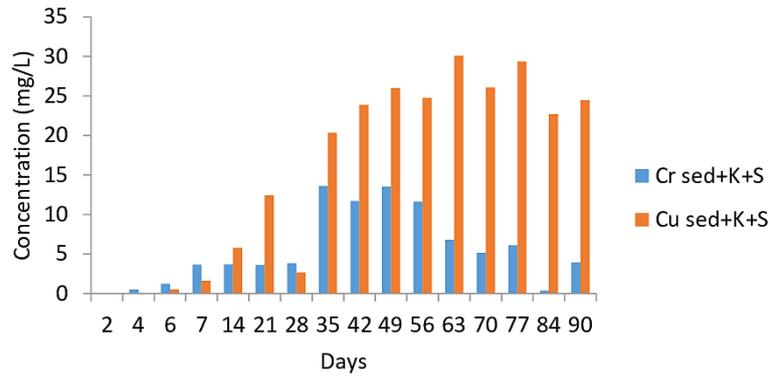


Figure 8. Release of Cr and Cu during the course of a 90-day period in the control sample

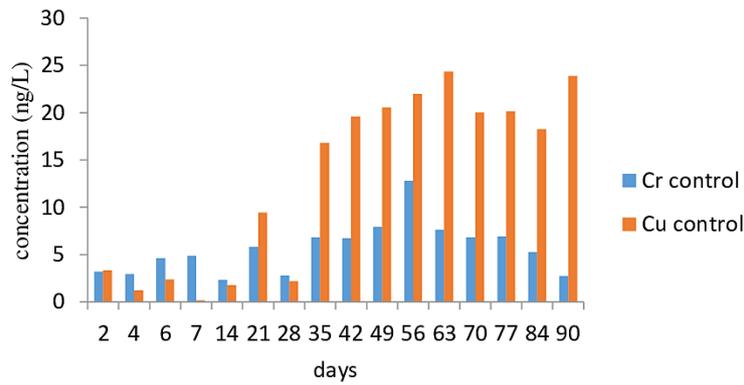


Figure 9. Release of Cr and Cu during a 90 day period in the bentonite treated sample

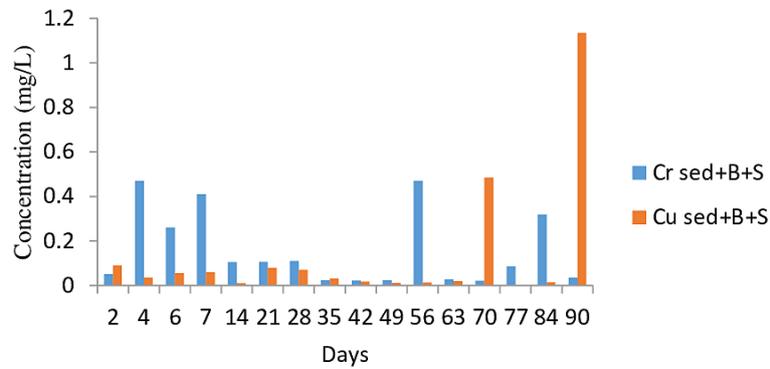


Figure 10. Release of Cr and Cu during a 90-day period in the kaolin + sand treated sample

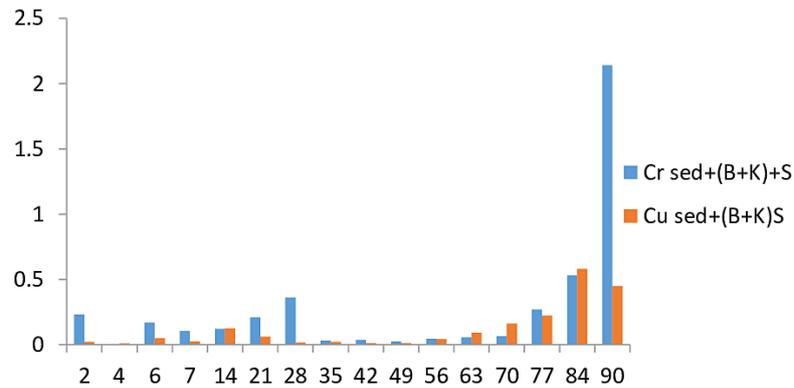


Figure 11. Release of Cr and Cu over a period of 90 days in the bentonite, kaolin and sand-treated sample

water column of the uncapped and capped sediment during the 90 days of experiment in relation to time. The overall release from the sediment of each pollutant constituted a modest percentage of the spiked material when taking into account the concentration of Cr and Cu observed in the sediment sample after its artificial contamination (3000 ppm). Only a small amount of chromium and copper were detected in the bentonite-capped sediment (Sed+B+S) and the mixture of bentonite and kaolin (Sed+(B+K)+S) over the course of the 90-day period. These concentrations were 0.158 mg/l and 0.293 mg/l for chromium and 0.145 mg/l and 0.118 mg/L for copper, respectively. Similarly Figures 8–11 illustrate the average concentration release of the trace metals (Cr and Cu) obtained from the overlying water column of the uncapped and capped sediment during the course of the 90 days experiment duration as a function of time.

Though the concentration of the kaolin-treated sample is slightly higher than that of the other two treatments, when compared to the control sample, it is still lower as shown in table 1. Because kaolinite has a low percentage and a poor ability to adsorb metal ions, bentonite and/or mixtures of bentonite and kaolin (Sed+(B+K)+S) effectively contained the two Cr & Cu contaminants during the entire experiment. One of the factors contributing to its poor ability to adsorb metal ions was the low percentage of kaolinite (Jiang et al., 2010). Additionally, the prominent peaks found in the kaolinite clay as shown in Figure 12 appears at  $2\theta$  of  $19.86^\circ$ ,  $50.98^\circ$ ,  $59.81^\circ$ ,  $69.44^\circ$  Halite at  $2\theta$  of  $12.31^\circ$ ,  $19.94^\circ$ ,  $35.68^\circ$ ,  $62.59^\circ$ , dickite at  $2\theta$  of  $12.31^\circ$ ,  $25.88^\circ$ ,  $38.61^\circ$ ,  $54.22^\circ$ ,  $69.44^\circ$  and Muscovite at  $2\theta$  of  $28.60^\circ$ ,  $45.40^\circ$ .

This kaolin mineral has a lower percentage of kaolinite clay than Turkish kaolinite clay, which

has a higher purity of 83.0% kaolinite and a peak FWHM of 0.651 nm with an intensity of 1056. The basal spacing is 6.54, and the peak FWHM is 0.651 nm with this intensity (Sari et al., 2007). The basal spacing is 6.54 Å, and peak FWHM is 0.651 nm with an intensity of 1056, which indicates that a low percentage of kaolinite clay presented in this kaolin mineral compared to with a correspondingly upper purity of 83.0% kaolinite in the Turkish kaolinite clay (Sari et al., 2007).

The alkaline pH conditions were also a factor in the high rate of Cr and Cu immobilisation by bentonite and the mix of bentonite and kaolin covered sediment. Since negative surface charges predominate at neutral to alkaline pH, increasing the electrostatic attraction of cationic pollutants to surfaces of minerals, the adsorption of cations (Cr and Cu) in the surfaces of the clay mineral is maximum. On the adsorption surface sites, protons and cations compete when the pH is low. Because hydroxyl ions (OH<sup>-</sup>) are more prevalent, a high pH lowers competition and increases the number of binding sites (Huifen et al., 2011; Duan and Su, 2014). Cr and Cu hydroxides may also precipitate at extremely alkaline pH levels in addition to adsorption. Due to its abundance, great adsorption capacity, chemical and mechanical durability, and exceptional structural features, bentonite has a lot of potential as a cheap and efficient adsorbent for the application to remove heavy metals from sediments (Shi et al. 2011). Furthermore, according to Shi et al. (2011), the removal of metal ions from bentonite depends on ion exchange and adsorption mechanisms since the material has a high cation exchange capacity (CEC) and a large specific surface area. Combining clay minerals with kaolin may enable for the use of each individual adsorption properties (Han et al., 2019).

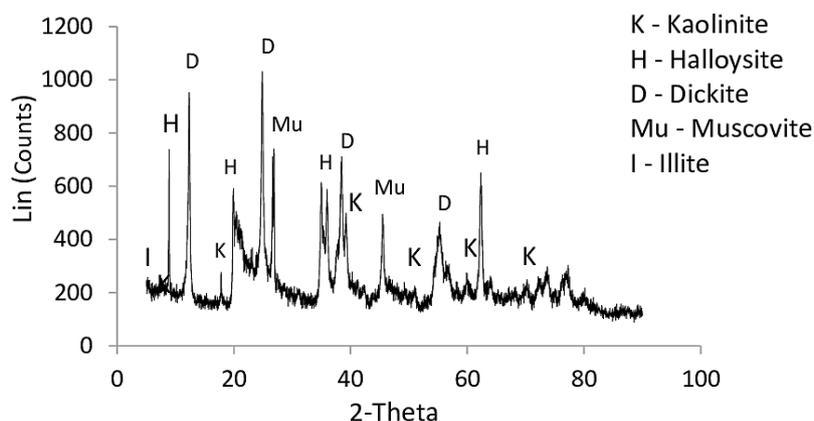


Figure 12. X-ray diffraction patterns of Kaolin clay

## CONCLUSIONS

According to the findings of the study, bentonite and a bentonite-kaolin mixture greatly decreased the release of the contaminants under investigation. The release of Cu and Cr from the polluted sediments. This study examined the viability of utilising bentonite, kaolin, or a combination of the two as materials for capping polluted sediment for in-situ remediation. In order to treat the Cu and Cr in the sediment, it was discovered that bentonite (B) and a mixture of bentonite and kaolin (BK) (1:1) were both successful. The pollutants are released from the polluted sediment in descending order as follows: Cu > Cr into the overlying water. Particularly, the cases of Cr and Cu, B and BK were successful in reducing the leachability of the contaminants from the sediments. The outcomes of capping treatment suggested that because of their significant Cu and Cr entrapment, B and BK might be used as promising materials for active capping treatment of polluted sites.

## Acknowledgements

The authors would like to acknowledge Universiti Tun Hussein Onn Malaysia (UTHM) for funding this research through GPPS Grant Vote Number U574 and UTHM Publisher's Office via Publication Fund E15216.

## REFERENCES

1. Akcil, A., Erust, C., Ozdemiroglu, S., Fonti, V., Beolchini, F. 2015. A review of approaches and techniques used in aquatic contaminated sediments: metal removal and stabilization by chemical and biotechnological processes. *Journal of Cleaner Production*, 86, 24–36.
2. Bardos, R.P., Morgan, P., Swannell, R.P. 2000. Application of in situ Remediation. *Land Contamination & Reclamation*, 8(4), 4.
3. Beckingham, B., Buys, D., Vandewalker, H., Ghosh, U. 2013. Observations of limited secondary effects to benthic invertebrates and macrophytes with activated carbon amendment in river sediments. *Environmental toxicology and chemistry*, 32(7), 1504–1515.
4. Belin, S, Sany, S.B.T., Salleh, A., Rezayi, M., Saadati, N., Narimany, L., Tehrani, G.M. 2013. Distribution and contamination of heavy metal in the coastal sediments of Port Klang, Selangor, Malaysia. *Water, Air, & Soil Pollution*, 224(4), 1476.
5. Benami, M., Gross, A., Herzberg, M., Orlofsky, E., Vonshak, A., Gillor, O. 2013. Assessment of pathogenic bacteria in treated graywater and irrigated soils. *Sci. Total Environ.*, 458–460, 298–302.
6. Carberry, J.B., Wik, J. 2001. Comparison of ex situ and in situ bioremediation of unsaturated soils contaminated by petroleum. *Journal of Environmental Science and Health, Part A*, 36(8), 1491–1503.
7. Cheng, M., Zeng, G., Huang, D., Lai, C., Xu, P., Zhang, C., et al. 2016b. Degradation of atrazine by a novel Fenton-like process and assessment the influence on the treated soil. *J. Hazard. Mater.*, 312, 184–191.
8. Cheng, M., Zeng, G., Huang, D., Lai, C., Xu, P., Zhang, C., et al. 2016a. Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: a review. *Chem. Eng. J.*, 284, 582–598.
9. Duan, J., Su, B. 2014. Removal characteristics of Cd (II) from acidic aqueous solution by modified steel-making slag. *Chemical Engineering Journal*, 246, 160–167.
10. Fadaei, H., Watson, A., Place, A., Connolly, J., Ghosh, U. 2015. Effect of PCB bioavailability changes in sediments on bioaccumulation in fish. *Environmental science & technology*, 49(20), 12405–12413.
11. Förstner, U., Aplitz, S.E. 2007. Sediment remediation: US focus on capping and monitored natural recovery. *Journal of Soils and Sediments*, 7(6), 351–358.
12. Gerhardt, K.E., Huang, X.D., Glick, B.R., Greenberg, B.M. 2009. Phytoremediation and rhizoremediation of organic soil contaminants: potential and challenges. *Plant Sci.*, 176(1), 20–30
13. Ghosh, U., Luthy, R.G., Cornelissen, G., Werner, D., Menzie, C.A. 2011. In-situ Sorbent Amendments: A New Direction in Contaminated Sediment Management. *Environmental Science & Technology*, 45(4), 1163–1168.
14. Gomez-Eyles, J.L., Yupanqui, C., Beckingham, B., Riedel, G., Gilmour, C., Ghosh, U. 2013. Evaluation of biochars and activated carbons for in situ remediation of sediments impacted with organics, mercury, and methylmercury. *Environmental science & technology*, 47(23), 13721–13729.
15. Guiwei, Q., De Varennes, A., Cunha-Queda, C. 2008. Remediation of a mine soil with insoluble polyacrylate polymers enhances soil quality and plant growth. *Soil Use and Management*, 24(4), 350–356.
16. Han, H., Rafiq, M. K., Zhou, T., Xu, R., Mašek, O., Li, X. 2019. A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants. *Journal of hazardous materials*, 369, 780–796.

17. Huifen, Y., Wen, M., Weina, Z., Zhiyong, W. 2011. Steel slag as multi-functional material for removal of heavy metal ions in wastewater. In 2011 International Conference on Computer Distributed Control and Intelligent Environmental Monitoring, IEEE, 1287–1290.
18. Jacobs, P.H., Förstner, U. 1999. Concept of subaqueous capping of contaminated sediments with active barrier systems (ABS) using natural and modified zeolites. *Water Research*, 33(9), 2083–2087.
19. Jiang, M.Q., Jin, X.Y., Lu, X.Q., Chen, Z.L. 2010. Adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) onto natural kaolinite clay. *Desalination*, 252(1–3), 33–39.
20. Knox, A.S., Paller, M.H., Roberts, J. 2012. Active capping technology—new approaches for in situ remediation of contaminated sediments. *Remediation Journal*, 22(2), 93–117.
21. Kuppusamy, S., Palanisami, T., Megharaj, M., Venkateswarlu, K., Naidu, R. 2016. In-situ remediation approaches for the management of contaminated sites: a comprehensive overview. In *Reviews of Environmental Contamination and Toxicology*. Springer, Cham, 236, 1–115.
22. Nayar, S., Goh, B., Chou, L. 2004. Environmental impact of heavy metals from dredged and resuspended sediments on phytoplankton and bacteria assessed in in situ mesocosms. *Ecotoxicol Environ Saf*, 59, 349–369.
23. Peng, J.F., Song, Y.H., Yuan, P., Cui, X.Y., Qiu, G.L. 2009. The remediation of heavy metals contaminated sediment. *J. Hazard. Mater.*, 161(2–3), 633–640.
24. Perelo, L.W. 2010. Review: in situ and bioremediation of organic pollutants in aquatic sediments. *Journal of Hazardous Materials*, 177(1), 81–89.
25. Sany, B.T., Sulaiman, A.H., Monazami, G.H., Salleh, A. 2011. Assessment of sediment quality according to heavy metal status in the West Port of Malaysia. *World Academy of Science, Engineering and Technology*, 74, 639–643.
26. Sari, A., Tuzen, M., Citak, D., Soylak, M. 2007. Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay. *Journal of hazardous materials*, 149(2), 283–291.
27. Shi, L. N., Lin, Y. M., Zhang, X., Chen, Z.L. 2011. Synthesis, characterization and kinetics of bentonite supported nZVI for the removal of Cr (VI) from aqueous solution. *Chemical Engineering Journal*, 171(2), 612–617.
28. Sun, Y., Li, Y., Xu, Y., Liang, X., Wang, L. 2015. In situ stabilization remediation of cadmium (Cd) and lead (Pb) co-contaminated paddy soil using bentonite. *Appl. Clay Sci.*, 105-106, 200–206.
29. Velimirovic, M., Tosco, T., Uyttebroeck, M., Luna, M., Gastone, F., De Boer, C., Braun, J. (2014). Field assessment of guar gum stabilized microscale zerovalent iron particles for in-situ remediation of 1, 1, 1-trichloroethane. *Journal of contaminant hydrology*, 164, 88–99.
30. Wang, X.T., Miao, Y., Zhang, Y., Li, Y.C., Wu, M.H., Yu, G. 2013b. Polycyclic aromatic hydrocarbons (PAHs) in urban soils of the megacity shanghai: occurrence, source apportionment and potential human health risk. *Sci. Total Environ.*, 447, 80–89.
31. Xu, P., Zeng, G.M., Huang, D.L., Feng, C.L., Hu, S., Zhao, M.H., et al., 2012. Use of iron oxide nanomaterials in wastewater treatment: a review. *Sci. Total Environ.*, 424, 1–10.
32. Zeng, G., Cheng, M., Huang, D., Lai, C., Xu, P., Wei, Z., et al. 2015. Study of the degradation of methylene blue by semi-solid-state fermentation of agricultural residues with *Phanerochaete chrysosporium* and reutilization of fermented residues. *Waste Manag.*, 38, 424–430.
33. Zhang, Y., Dong, X., Jiang, Z., Cao, B., Ge, S., Hu, M., 2013a. Assessment of the ecological security of immobilized enzyme remediation process with biological indicators of soil health. *Environ. Sci. Pollut. Res.*, 20(8), 5773–5780.