



Synthesis of geopolymer using fly ash and kaolin to remove copper from synthetic water

Javed Ahmed*, Khadija Qureshi, Zulfiqar Ali Bhatti and Abdul Qadeer Laghari
Department of Chemical Engineering, Mehran University of Science and
Technology, Jamshoro.

*Corresponding author email: javed5807382@gmail.com

ABSTRACT

The aim of this study is to synthesize geopolymer for the removal of copper Cu^{2+} from water, utilizing kaolin and fly ash. The resulting geopolymer demonstrates promising efficacy as an absorbent for heavy metals such as copper, arsenic, and lead. Enhanced elimination efficiency is observed with increasing geopolymer dosage, contact time, and temperature, coupled with a decrease in the initial concentration of Cu^{2+} . The highest removal efficiency is achieved at a pH value of 6.

In this investigation, kaolin is transformed into metakaolin, a widely used aluminosilicate material employed in the production of geopolymers. However, its suboptimal rheological properties, processing challenges, high water demand, and rapid hydration response constrain its applicability. Conversely, industrial waste serves as a viable source of aluminosilicate material, boasting diverse components. By utilizing industrial waste, geopolymer adsorbents with enhanced ion-exchangeability and increased active sites on the surface can be developed. Geopolymers yield promising results for heavy metal removal from synthetic water at a cost-effective rate.

Keywords:

*Geopolymer,
Heavy metals,
Copper removal,
Wastewater treatment*

1. Introduction

There are notable concentrations of heavy metal ions in the effluent of the engineering, papermaking, fine chemicals, dyes, paints, pharmaceutical, petrochemical, and textile industries due to the extensive usage of heavy metals in these industries. Elements with an atomic weight between 63.5 and 200.6 g/mol and a specific density greater than 5.0 g/cm³ are classified as heavy metals (Abdelwahab et al, 2007, Ahalya et al, 2003). The most hazardous heavy metals include arsenic (As), copper (Cu), mercury (Hg), nickel (Ni), cadmium (Cd), lead (Pb), and chromium (Cr), according to the US Environmental Protection Agency (Ahmaruzzam et al, 2010, Al-subu et al, 2001). These heavy metal ions pose a major risk to human health and the environment due to their mutagenic, carcinogenic, teratogenic,

and bioaccumulative characteristics. Consequently, before being released back into the environment, these heavy metal ions must be extracted from the effluent. In the past, heavy metals from wastewater have been removed using a variety of techniques (Al-zboon et al, 2011, Annadurai et al, 2008).

According to Clark (1989) and Tumin et al. (2008), copper is regarded as the second harmful metal to aquatic organisms after mercury since it is a persistent, bioaccumulative, and toxic chemical. Through ingestion or uptake, it may accumulate in the ecological or human food chain and pose a risk to the ecosystem and public health (Tumin et al., 2008). Man's absorption of excess copper causes nervous system damage, cancer, nausea, vomiting, headaches, diarrhea, respiratory problems, liver and kidney failure, and death (Bokris, 1978, Tumin et al., 2008, Wahi et al., 2009).

According to Stoplić et al. (2007), the traditional techniques for removing copper from industrial effluent typically entail a chemical precipitation process. Ion exchange, reverse osmosis, electrochemical treatment, evaporative recovery, and adsorption are possible additional efficient techniques (Abdelwahab, 2007).

The investigations that were carried out looked into how various factors, such as pH, contact time, starting concentration, and adsorbent dosage, affected adsorption capacity. Heavy metals can be extracted from wastewater via chemical precipitation, ion exchange, electrocoagulation, membrane filtration, and adsorption techniques (Al-zboon et al, 2011, Annadurai et al, 2008). Adsorption is one of the heavy metal treatment techniques that has drawn the most attention due to its simplicity of use, low energy consumption, little secondary contamination, high cost-effectiveness, and speedy removal of heavy metals from aqueous solution. The most crucial element in the adsorption process is the adsorbent. Among the well-known adsorbents are activated carbon (AC), charcoal, carbon nanotubes (CNT), zeolite, geopolymer, and clay minerals (Arivoli et al, 2009, Baskaran et al, 2010). AC is one of these adsorbents; it is an amorphous, carbonaceous substance with a large surface area that has a greater range of applications in the water remediation process (Bassi et al., 1999). Carbon-rich organic materials such as wood, coal, peat, coconut shells, and other materials can be processed to create AC. Because of its wide surface area and porous structure, AC is widely used in wastewater treatment (Bokris et al, 1978). It did not, however, achieve the required adsorption capacity for the removal of heavy metals (Buasi et al, 2008). This is due to the fact that basic research and structural optimization for enhanced removal performance are hampered by the disordered structure of amorphous carbon (Bulgariu et al., 2008). Moreover, its costly synthesis and difficult regeneration limit its application in large-

scale wastewater treatment. Because geopolymer has superior adsorption qualities over other adsorbents, researchers are interested in using it to create more affordable adsorbents. Geopolymer made of a three-dimensional (3D) network structure with pores of a predetermined size and routes that only permit the passage of specific heavy metals. The composition of geopolymer is a polymeric silicon-oxygen-aluminum (Si-O-Al) framework that shares all bridging oxygen atoms and alternately links silicon (SiO₄) and aluminum (AlO₄) tetrahedra (Cetin et al, 2007). An exothermal chemical reaction between silica and alumina-rich precursors and alkaline activators at low temperature produces geopolymers, which have semi-crystalline to amorphous structures (Chu, K.H et al, 2002). Because the geopolymer's negatively charged alumina-silicate framework allows for ion exchangeability between heavy metal ions and cations in alkaline activators, it is a valuable adsorbent for treating contaminated water. Furthermore, cyclic molecular chains with a "crystal-like" structure make up geopolymer (Danis, U. et al., 2010). Because geopolymer materials use less energy, heat, and carbon dioxide during production, they are thought to be environmentally beneficial. Furthermore, geopolymers offer notable benefits such low cost, simple synthesis, and local raw material availability (Fengi et al., 2004).

Recycling waste materials and turning them into valuable and useable commodities is a big trend. Coal fly ash is one of these waste items. Fly ash removal has grown to be a significant environmental and financial issue (Li et al., 2006, Ahmaruzzaman, 2010). Using fly ash to create geopolymers is one of the most crucial solutions to the problem. This method helps to solve the issue of ash accumulation as an industrial waste product in addition to being successful in removing heavy metals from wastewater.

This work's primary goal is to ascertain whether fly ash and meta-kaolin based geopolymer are capable of extracting copper from aqueous solutions. Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray analysis (EDX), and scanning electron microscopy (SEM) were used to evaluate the geopolymer both before and after. The investigation focused on the behavior of the process under various parameters, including temperature, pH, contact time, initial concentration of copper, and dosage of geopolymer.

2. Materials and Methods

2.1. Materials

Fly ash (FA) and kaolin (K) were the basic materials employed in this investigation. Fly ash from coal and kaolin were acquired from the department of metallurgy. To create an alkaline activator, fumed silica (SiO₂) and sodium hydroxide (NaOH) were utilized. Different concentrations of copper solutions were made using a standard 1000 ppm solution of (Cu²⁺).

2.2. Preparation of geopolymer adsorbent

The process of creating geopolymer adsorbent is multi-step. First step we will convert kaolin into meta-kaolin through process we heat kaolin up to 750-800C* for 2 hours. In the second step, we'll make an alkaline solution using fume silica (SiO₂) and sodium hydroxide (NaOH). While any alkali might theoretically be utilized in geopolymerization reactions, the majority of research has concentrated on the effects of potassium (K⁺) and sodium (Na⁺) ions (van Jaarsveld et al., 2002). Both NaOH and KOH could be used in the activation process, but using NaOH led to a greater degree of dissolution. This is because Na⁺ has a smaller size than KOH, which makes it easier to stabilize the silicate monomers and dimers in the solution and accelerates the rate at which minerals dissolve (Bakharev, 2006). NaOH is utilized in this study's geopolymer synthesis as a result. Process of alkaline solution start with deionized water in beaker and outside fill with ice when we add Sodium hydroxide (NaOH), Ice because of heat release when we add Sodium hydroxide (NaOH) after dissolved of Sodium hydroxide then add Fumed silica (SiO₂) mix through magnetic stirrer for 24 hr when it look like viscous and transparent. Third step alkaline solution put in beaker add metakaolin mix with homogenizer after mixing we add fly ash mix again when it reach like gum type material its mean geopolymer obtained after this we put geopolymer in oven for 24 hr.

3. Results and discussion

3.1. Characterization of Geopolymer Samples

FT-IR Analysis

The composition of the adsorbent mixture and the development of functional groups were investigated through FT-IR analysis. Prior to adsorption, various functional groups were identified. Initially, prominent O-H stretching bonds were detected at 3360.64 cm⁻¹, indicating strong bonds. Subsequently, the presence of C=N stretching bonds at 1646.72 cm⁻¹ was observed, characterized by a medium bond intensity. Additionally, medium intensity C-H bending bonds were detected, followed by strong C=C bending bonds at 980 cm⁻¹. These findings are illustrated in Fig. 1.

After adsorption, it exhibits various functional groups, the O-H stretching is observed at 3566.93 cm⁻¹, representing a strong bond. The C=H stretching occurs at 1646.86 cm⁻¹, indicating a medium bond, while the N-O stretching is noted at 1507.85 cm⁻¹, also signifying a strong bond. Additionally, the C=C bending is detected at 988.46 cm⁻¹, and the C-I bending falls within the range of 611.52 cm⁻¹, as illustrated in Fig. 2.

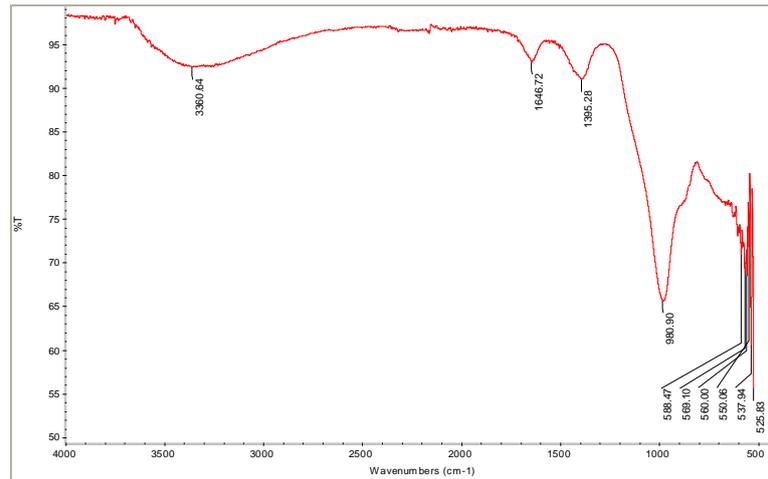


Fig. 1: FT-IR Spectra

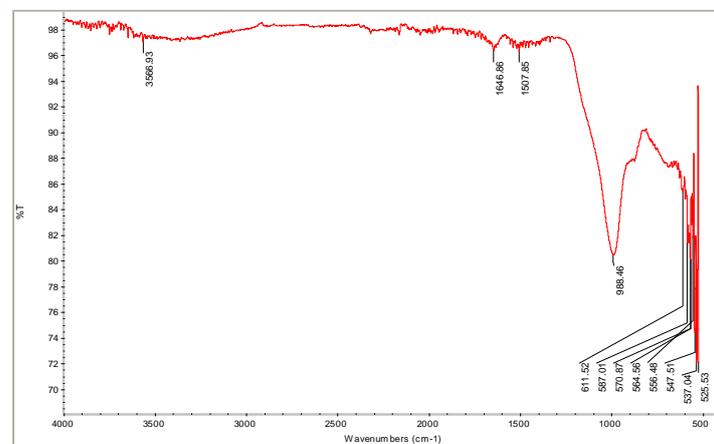


Fig. 2: FT-IR Spectra

Scanning Electron Microscopy (SEM)

In this study, SEM was performed to investigate the surface morphology of geopolymer adsorbent. To carefully study the adsorbent surface, the diagrams below were obtained at various magnifications. Figs. 3(a) and 3(b) show before absorption and after absorption respectively.

Energy Dispersive X-ray Analysis (EDX)

In order to ascertain the elemental makeup of the adsorbent, Energy Dispersive X-Ray analysis and chemical characterization were performed. It uses X-rays to reveal the elemental concentrations of a substance and is based on the fundamental principles of spectroscopy, which include spectra exhibiting distinct peaks that are accurate to the elements and supplying the true elemental composition data. Its main objective is the evaluation of qualitative materials, while it also does quantitative analysis on occasion. Figs. 4 (a) and (b) show EDX analysis before adsorption and after adsorption.

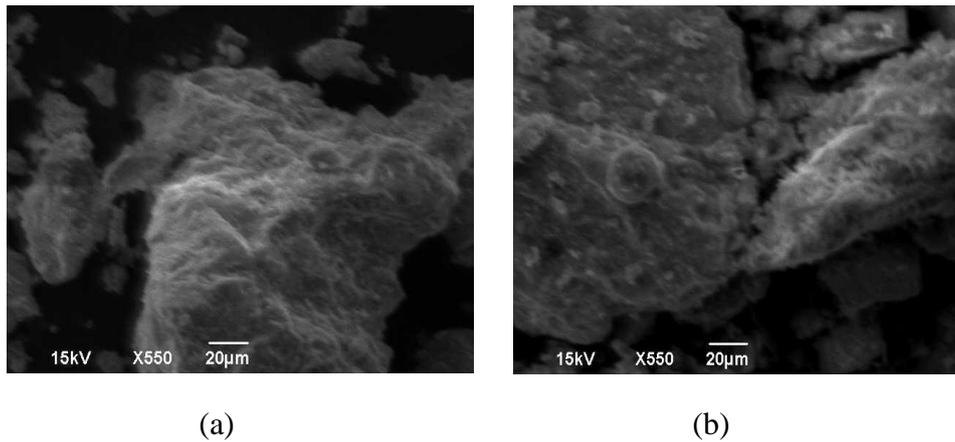


Fig. 3: SEM analysis, before adsorption (a) and after adsorption

3.2. Parametric study of Cu^{2+} Adsorption

Effect of geopolymer dosage

Fig. 5 illustrates how the dosage of the geopolymer affects the Cu^{2+} removal. The findings demonstrate that with increasing dose from 0.1 g to 3 g, the removal efficiency increased from 50.30% to 87.40%. We utilize varying dosages ranging from 0.1 g to 3 g, observing the highest removal efficiency of copper from water at 3 g, reaching a percentage of 87.40%. It is evident in Fig. 5 that the removal efficiency was at its minimum at 0.1 g and peaks at 3 g. Additionally, beyond 3 g, the efficiency remained constant, aligning with the conclusions drawn from this study (Muhammad S. AL-Harashseh et al, 2015)

Effect of pH

The results (Fig. 6) show that when pH rises from 2 to 9, efficiency increased from 23.12% to 90.20%. Positive H_3O^+ ions were abundant in the solution at low pH levels, and they compete with Cu^{2+} positive ions for the accessible active sites on the geopolymer surface. Protons and Cu^{2+} had less competition for active sites when pH rose, making the active sites more accessible to Cu^{2+} ions (Tumin et al., 2008). The predicted pattern for the relationship between pH and metal sorption was that, up to a certain point, sorption increased with rising pH values, after which it declined (Ahmaruzzaman, 2010). It was well known that elevating pH above 6 promoted Cu^{2+} precipitation as $\text{Cu}(\text{OH})_2$ (Goyal et al., 2001).

Effect of Contact Time

Cu^{2+} ion removal's time-dependent behavior was investigated by adjusting the contact duration from 30 to 130 minutes. Cu^{2+} ion concentration was maintained at 100 ppm using a fixed dosage of 1 g/L of geopolymer and an initial pH of 6. The results are shown in Fig. 7. The similar result patterns were obtained previously (Muhammad S.AL-Harashseh et al, 2015).

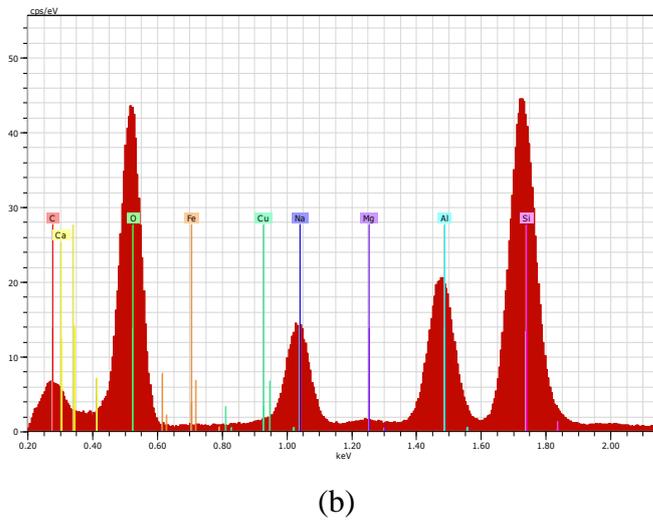
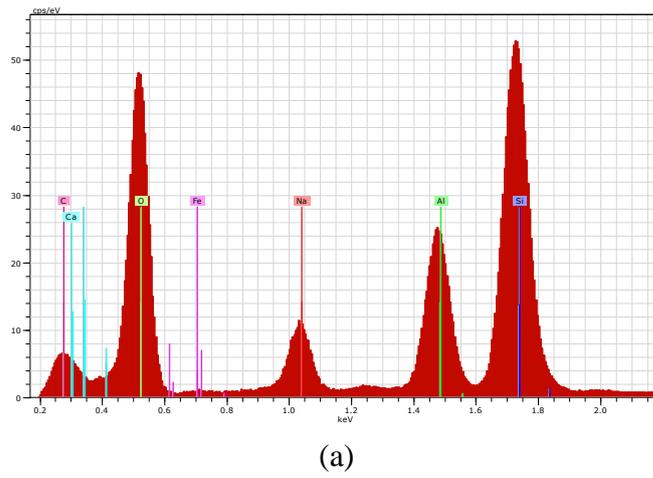


Fig. 4: EDX spectra, before adsorption (a) and after adsorption(b)

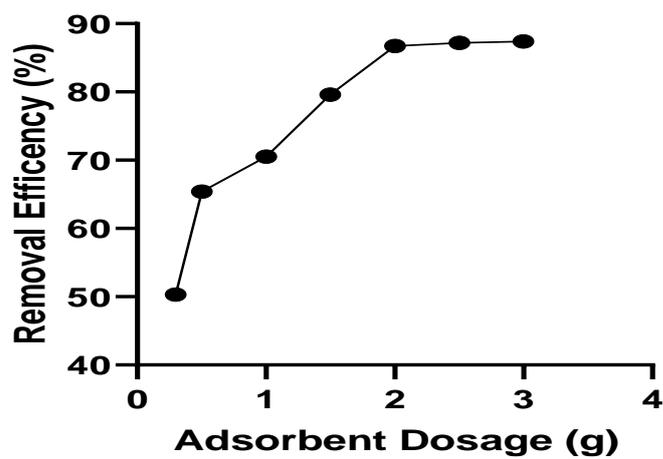


Fig. 5: Effect of adsorbent dosage on removal efficiency

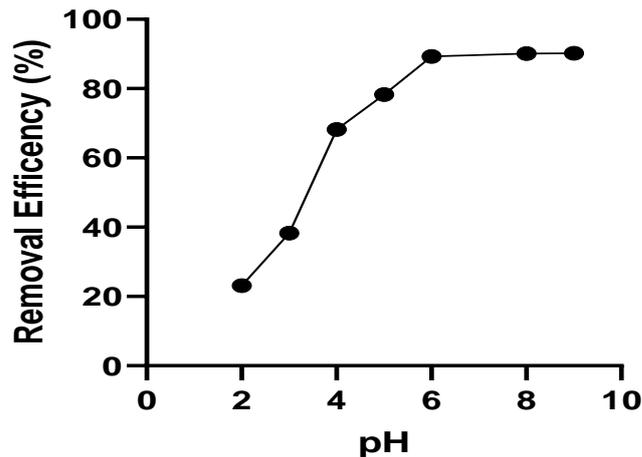


Fig. 5: Effect of pH on removal efficiency

Effect of Initial Cu^{2+} Concentration

The impact of the initial concentration of Cu^{2+} on the removal efficiency is depicted in Fig. 8. It is observed that as the initial concentration is increased beyond 50 ppm, the removal efficiency first stayed high at lower initial concentrations before declining. At 50 ppm, the efficiency might range from 83.66% to 45.20%. Numerous studies have demonstrated that the effectiveness of heavy metal removal depends on their initial concentration. Present results are consistent with findings of Wang et al. (2006).

Effect of Shaking Time

Cu^{2+} ion removal's shaking time dependent behavior was investigated by altering the speed between 50 and 300 rpm. Maximum removal efficiency of copper from water at 300 rpm it was 93.20%. The minimum and maximum efficiencies were found at 50 rpm and at 300 rpm respectively, and above 300 rpm it remained constant (Fig. 9).

4. Conclusions

The current study focused on the creation of fly ash and kaolin-based geopolymers, as well as their adsorption properties toward Cu^{2+} removal. It was found that the generated geopolymer was highly amorphous. Through a batch method, the properties of Cu^{2+} ions from synthetic water were investigated across various experimental scenarios. The following conclusions were drawn:

The geopolymer synthesized for this investigation exhibited a high efficiency in removing copper from artificial water.

The impact of the synthesized geopolymer dosage on the uptake of Cu^{2+} metal ions revealed an increase in uptake with higher doses of produced geopolymer.

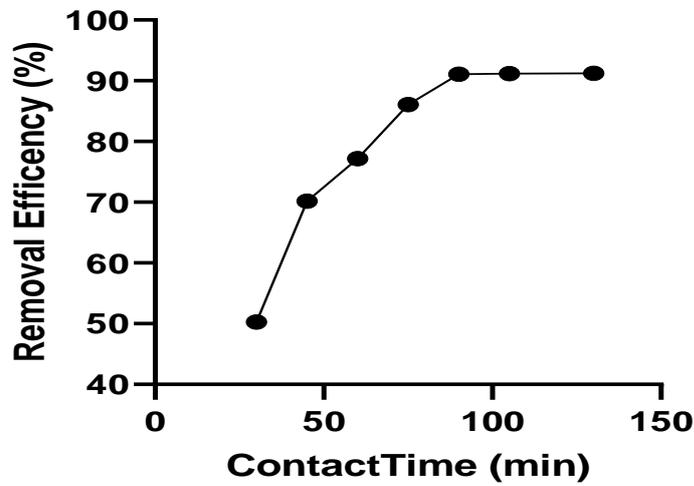


Fig. 7: Effect of contact time on removal efficiency

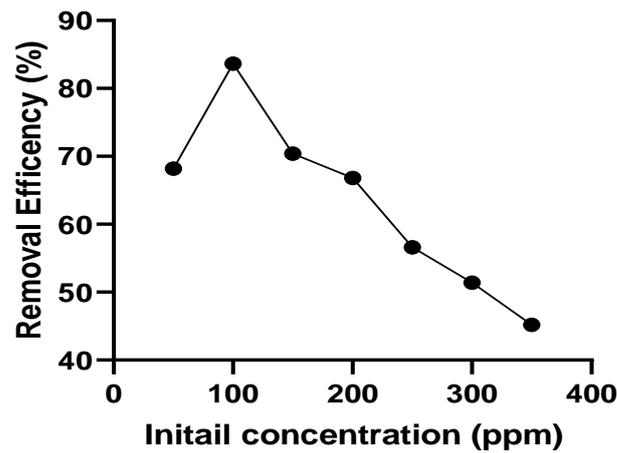


Fig. 8: Effect of Initial concentration on removal efficiency

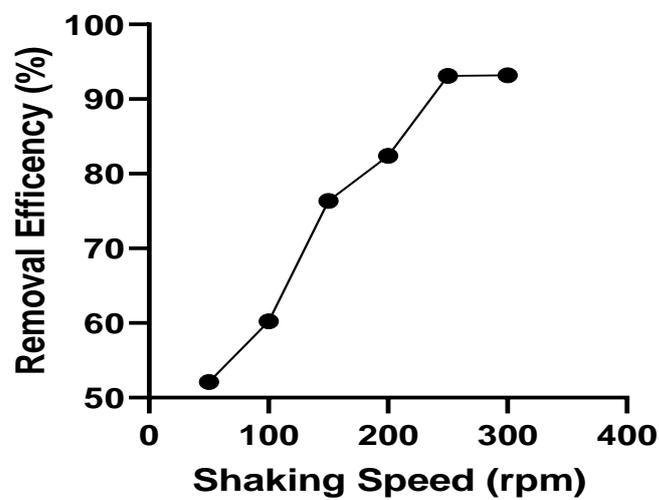


Fig. 9: Effect of shaking speed on removal efficiency

At a pH of 8, the highest removal effectiveness was observed in the experimental setup (25°C, 30 minutes of contact time, 1 g/L dosage).

The greatest removal effectiveness, at a temperature of 25°C and a pH of 6, was achieved after 130 minutes of contact time (dose: 1 g/L).

The highest removal efficiency was attained at the starting concentration of 100 ppm and under experimental conditions (temperature: 25°C, pH: 6, dose: 1 g/L, contact time: 30 minutes).

Under experimental conditions (temperature: 25°C, pH: 6, dose: 1 g/L, contact time: 30 minutes), the greatest removal effectiveness was reached at a shaking speed of 300 rpm.

Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX), Fourier Transform Infrared Spectroscopy (FT-IR), and Acid Solution Sensitivity (ASS) analyses demonstrated that the geopolymer functions efficiently as an adsorbent for removing heavy metals from water. This technique proves to be economically viable.

References

- Abdelwahab, O. (2007). "Kinetic and isotherm studies of copper (II) removal from wastewater using various adsorbents." *Egypt J. Aquat. Res.* **33**(1): 125-143.
- Ahalya, N., T. V. I. Ramachandra and R. D. Kanamadi (2003). "Biosorption of Heavy Metals" *Res. J. Chem. Environ.* **7**(4): 71-79.
- Ahmaruzzaman, M. (2010). "A review on the utilization of fly ash." *Prog. Energy Comb. Sci.* **36**(3): 327-363.
- Al-Subu, M. M., R. Salim, I. Abu-Shqair and K. M. Swaileh (2001). "Removal of dissolved copper from polluted water using plant leaves: 1. Effect of acidity and plant species." *Rev. Int. Contam. Ambeint* **7**(2): 91-96.
- Al-Zboon, K., M. S. Al-Harashsheh and F. B. Hani (2011). "Fly ash-based geopolymer for Pb removal from aqueous solution." *J. Hazard. Mater.* **188**(1-3): 414-421.
- Allen, S. J. and P. A. Brown (1995). "Isotherm analysis for single component and multi-component metal sorption onto lignite 17-24." *J. Chem. Technol. Biotechnol.* **62**: 17-24.
- Annadurai, G., L. Y. Ling and J.-F. Lee (2008). "Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis." *J. Hazard. Mater.* **152**(1): 337-346.
- Arivoli, S., V. Nandhakumar, S. Saravanan and S. Nagarajan (2009). "Adsorption dynamics of copper ion by low cost activated carbon." *The Arabian J. Sci. Eng.* **34**(1A): 1-12.

- Bakharev, T. (2006). "Thermal behaviour of geopolymers prepared using class F fly ash and elevated temperature curing." Cement and Concrete Research **36**(6): 1134-1147.
- Baskaran, P. K., B. R. Venkatraman, M. Hema and S. Arivoli (2010). "Adsorption studies of copper ion by low cost activated carbon." J. Chem. Pharm. Res. **2**(5): 642-655.
- Bassi, R., S. O. Prasher and B. K. Simpson (1999). "Removal of selected metal ions from aqueous solutions using chitosan flakes" Separ. Sci. Technol. **35**(4): 547-560.
- Bokris, J. O. M. (1978). Environmental Chemistry. New York, Plenum Press.
- Buasri, A., N. Chaiyut, K. Phattarasirichot, P. Yongbut and L. Nammueng (2008). "Use of Natural Clinoptilolite for the Removal of Lead (II) from Wastewater in Batch Experiment" Chiang Mai J. Sci. **35**(3): 447-456.
- Bulgariu, L., M. Rățoi, D. Bulgariu and M. Macoveanu (2008). "Equilibrium study of Pb(II) and Hg(II) sorption from aqueous solutions by moss peat." Environ. Eng. Manage. J. **7**(5): 511-516.
- H.H. Murray (Ed.), Developments in Clay Science, Elsevier (2006), pp. 85-10
- Cetin, S. and E. Pehlivan (2007). "The use of fly ash as a low cost, environmentally friendly alternative to activated carbon for the removal of heavy metals from aqueous solutions." Colloids Surface A **298**(1-2): 83-87.
- Chu, K. H. (2002). "Removal of copper from aqueous solution by chitosan in prawn shell: adsorption equilibrium and kinetics." J. Hazard. Mater. **90**(1): 77-95.
- Clark, C. (1989). Marine Pollution. New York, Oxford University Press.
- Danis, U. (2010). "Biosorption of copper(II) from aqueous solutions by *Pleurotus cornucopiae*." Desalin. Water Treat. **22**(1-3): 117-126.
- Donat, R., A. Akdogan, E. Erdem and H. Cetisli (2005). "Thermodynamics of Pb²⁺ and Ni²⁺ adsorption onto natural bentonite from aqueous solutions." J. Colloid Interface Sci. **286**(1): 43-52.
- Feng, Q., Q. Lin, F. Gong, S. Sugita and M. Shoya (2004). "Adsorption of lead and mercury by rice husk ash." J. Colloid Interface Sci. **278**(1): 1-8.
- Gabai, B., N. A. A. dos Santos, D. C. S. Azevêdo, S. Brandani and C. L. Cavalcante Jr (1997). "Removal of copper electrolyte contaminants by adsorption." Braz. J. Chem. Eng. **14**(3).
- Goyal, M., V. K. Rattan, D. Aggarwal and R. C. Bansal (2001). "Removal of copper from aqueous solutions by adsorption on activated carbons." Colloids Surface A **190**(3): 229-238.
- Li, L., S. Wang and Z. Zhu (2006). "Geopolymeric adsorbents from fly ash for dye removal from aqueous solution." J. Colloid Interface Sci. **300**(1): 52-59.

Stopić, S., B. Friedrich and A. Widigdo (2007). "Electrolytic recovery of copper from highly contaminated wastewaters " Metalurgia **13**(1): 27-34.

Tumin, N. D., A. L. Chuan, Z. Zawani and S. Abdul Rashid (2008). "Adsorption of copper from aqueous solution by Elais Guineensis kernel activated carbon." J. Eng. Sci. Technol. **3**(2): 180-189.

Wahi, R., Z. Ngaini and V. U. Jok (2009). "Removal of Mercury, Lead and Copper from Aqueous Solution by Activated Carbon of Palm Oil Empty Fruit Bunch." W. Appl. Sci. J. **5**: 84-91.

Mohammad S.Al-Harashsheha, Kamel Al Zboonb, Leema Al-Makhadmehc ,Muhannad Hararaha , Mehaysen Mahasnehb "Fly ash based geopolymer for heavy metal removal: A case study on 2 copper removal" J. Environ. Chem. Eng. (2015) 1–9.

Shaobin Wang , Lin Li , Z.H. Zhu "Solid-state conversion of fly ash to effective adsorbents for Cu removal from wastewater" Journal of Hazardous Materials B139 (2007) 254–259.