



Research Article

Thermally modified laterite soil by means of an adsorptive material for copper and chromium elimination from polluted water

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Abstract

Recent research focuses on the effectiveness of particular laterite grain sizes of thermally modified laterite soil as an adsorptive material for getting rid of copper and chromium subatomic particles out of polluted water in lab settings. By auger drilling, the pure laterite soil was extracted from tropical weathering conditions. Collected soil samples were washed and dried by air. Soil was crumpled to create 2 mm and 0.5 mm grain sizes. By heating the laterite at 100 °C, 200 °C, 300 °C, and 400 °C for three hours in a muffle furnace, thermally activated soil was arranged. Batch studies were carried out at an ambient temperature and the natural pH was used to determine the adsorption states of copper and chromium ions for the thermally activated laterite soil. According to the findings, 200°C thermal-activated laterite soil has higher removal efficiencies. The maximum removal efficiency of copper and chromium ions was given at 90 minutes of optimal contact time for both 2 mm and 0.5 mm grain sizes. However, the optimum dosage of 0.50 g of thermally activated soil of 2 mm and 0.5 mm grain sizes was responsible for significant removal efficiency. Thus, thermal-activated laterite soil can remarkably remove copper and chromium from water at natural pH levels.

Keywords: Adsorption, Thermally modified Laterite, Copper, Chromium, Optimum conditions

Introduction

The principal cause of considerable heavy metal discharge into the environment is massive industrial development. Due to their inherent poisonousness along with harmful effects, heavy metals (namely Cu, Zn, Pb, Cd, Cr, and Hg) in industrial wastes are currently the biggest cause for concern. Overall, copper and chromium are poisonous substances whose presence in water causes serious health issues in people. Getting rid of heavy metals from aqueous solutions is necessary for environmental aspects for the reason that, heavy metals can extremely harm human well-being through water resources.

There is a high concentration of copper in the discharges from the manufacturing of fertilizer, paper and pulp, brass, mining, smelting, electroplating, and metal plating (Lopez & Fred Lee, 1977). Leather tanning, the metal plating industry, electroplating, metal mining, battery manufacturing, finishing,

and the glass industry are the leading causes of chromium water pollution (Wang et al., 2011; Yang et al., 2014).

Although copper is a known micronutrient for plants and animals as well as an important micronutrient for the human body, it is poisonous if consumed in excess. When chromium concentrations in wastewater exceed acceptable limits, it exhibits extremely undesirable behavior in people, animals, and vegetation. Copper poisoning can result in nausea, vomiting, diarrhea, stomach cramps, coma, jaundice, and gastrointestinal distress. DNA damage, non-healing skin ulcers, nasal septum rupture, ulceration of the digestive and respiratory tracts, and lung cancer are some of the health effects.

The WHO recommends 1.3 mg/L of Cu and, 0.05 mg/L of Cr in drinking water. However, the samples from 2944 family units in Berlin, Germany, revealed maximum copper concentrations of 3.5 mg/L and 4.2 mg/L (Zietz et al., 2003). Copper concentration was 2 mg/L in 7307 domestic samples

in the United States. It was in 10% of the samples were higher than 5 mg/L, and 1% were above 10 mg/L (Council, 2000). About 18% of Americans are exposed to chromium contamination in their drinking water, and the contamination level is 60 µg/L. A minor percentage of people is vulnerable to levels ranging from 60 - 120 µg/L (Council, 2000).

As a consequence, treating contaminated water before throwing it into the environment is crucial. Water quality declines as a result of inadequate treatment of industrial wastewater, particularly in developing nations. Due to this serious environmental issue, effective and efficient treatment technologies are required.

For the elimination of copper and chromium, several ways and means, such as precipitation, ion exchange, electro-coagulation (Rengaraj et al., 2001), ultra-filtration, bio-filtration, and reverse-osmosis were suggested (Bailey et al., 1999; Fu & Wang, 2011; Yoon et al., 2009). One of these methods that is applied the most commonly to remove heavy metal ions is adsorption. Several adsorbents are coupled to extract copper and chromium from water solution using adsorption methods. Carbon foam, chemically activated sawdust, activated carbon, biochar, modified coal fly ash, tree bark, polypyrrole conducting polymer and, multi-adsorbent system are among the materials used (Radian et al., 2010). However, activated carbon and metal oxides are effective heavy metal ion adsorbents (Faur-Brasquet et al., 2002; Visa et al., 2010).

The current approaches have drawbacks like high costs, challenges in producing adsorbents, low efficiency, and the production of hazardous byproducts (Faur-Brasquet et al., 2002). In order to enhance the financial potential and usability, it is critical to produce low-cost adsorbents in developing countries. In tropical and subtropical regions, laterite is a common type of soil. The primary components of the material are Fe, Al, and Si, which together form a positive surface charge that facilitates the adsorption of anionic metals (Van Dang et al., 2008). Due to its positive charge in neutral and acidic media, laterite has been extensively used to remove many toxic anionic ions, including anionic heavy metals (Mitra et al., 2016).

The recent study was conducted in which the abundant and inexpensive laterite was used as an adsorbent material. The focus of this research was to examine in the making of laterite soil as per a cheap, accessible adsorbent for the removal of Cu and Cr from contaminated water. Numerous batch adsorption analysis was conducted in various settings.

Methods and Materials

Collection and preparation of samples

The raw laterite was obtained as combined samples from a local location in the Gampaha district of southwest Sri Lanka. Samples were taken in Sri Lanka's wet zone, which has less contaminated in situ weathered laterites. To get rid of the excess moisture content, the laterite was gently cleaned with

deionised water and dried up at ambient temperature for around 24-48 hours. To separate the 0.5 mm and 2 mm sized particles from the dried laterite, it was crushed and sieved. The soil samples were heated at 100°C, 200°C, 300°C, and 400°C for three hours in a muffle furnace to prepare the thermally activated laterite samples. The samples were then put in safekeeping in polyethylene baggage to escape contaminants.

Physiochemical evaluation for raw laterite

The outward geomorphology and arrangement of the laterite sample were investigated using field emission Hitachi S-4200 scanning electron microscopy. Gold-stumbled raw laterite soil samples were ascended on the SEM specimen holder using a two-sided conductive carbon band for the analysis. Gold was successfully sputtered onto ground soil at a constant current of 25 mA (Mitra et al., 2016).

A Rigaku TTRAX III X-Ray diffractometer was used to examine crystallographic structure of the laterite soil. The fine-grained samples were studied by means of Cu K (alpha) radiation with a wavelength of 1.54 Å over 2 (theta) of 5-700 and a step size of 0.020/sec (Beauvais, 1999).

FT-IR analysis (FTIR Thermo Nicolet iS10) was used to investigate the behaviour of adsorption sites in laterite soil sample. The soil was deposited on the instrument's ZnSe crystal with 16 scans and a resolution of 2 cm⁻¹ in the 4000-400 cm⁻¹ spectral band (Mitra et al., 2016).

Chemical experimentation

All of the chemicals were of analytical reagent grade and, 1000 ppm standard copper and chromium solution were used as the stock solution. Subsequent dilutions were made using distilled water to prepare 5 ppm copper and 1 ppm chromium solutions. The adsorption assimilation of copper and chromium along laterite soil were conducted with a volume of 50.0 mL of these solutions, which were used in batch experiments. Eq. 1 below was used to calculate the percentage deduction of copper and chromium from aqueous solutions at equilibrium.

$$\text{Percentage Removal efficiency} = \frac{(C_0 - C_e) \times 100}{C_0}$$

C₀ – Initial copper or chromium (ppm) concentration

C_e – Equilibrium concentration of the copper or chromium (ppm)

Batch tests for adsorption study

Identification of the optimal temperature for activated laterite soil

50 mL of copper solution was combined with 1.00 g of 100°C, 200°C, 300°C, and 400°C thermally modified laterite soil in order to test the most favorable temperatures for thermally modifying soil. The 0.5mm and 2mm soil sample solutions were then shaken at 120 rpm for 3 hours at ambient

temperature and natural pH. Then, solid-phase separation was done by centrifuging for 10 minutes at 4000 rpm. The 0.22 mm pore size millex-GP syringe filter unit was used to filter the centrifuged solutions. Hach DR900 Multiparameter Portable Colorimeter was used to determine the remaining copper concentration in the supernatants. For samples containing chromium, the process was repeated, and the supernatants' concentrations were calculated.

Identification of the optimum contact time

Volume of 50.0 mL of 5 ppm copper solution and 1.00 g of 0.5 mm and 2 mm of 200°C thermally modified laterite soil was used to study the impact of contact time for the laterite. The contact time was recorded at various intervals, including 10, 20, 30, 60, 90, 120, 150, and 180 mins. The experiment was carried out in a way alike to that defined in the preceding section, and the Hach DR900 Multiparameter Portable Colorimeter was used to determine the remaining copper concentration in the supernatants. The process was performed on chromium samples, and the supernatants' concentrations were determined.

Identification of the optimum thermal activated laterite soil dosage

To determine the optimal laterite dosage, 0.5 mm and 2 mm of 0.10, 0.25, 0.50, 0.75, and 1.00 g of 200°C laterite soils were added to 50.0 mL of 5 ppm copper and 1 ppm chromium solutions. At ambient temperature and their natural pH, the solutions were shaken for 90 minutes at 120 rpm. The Hach

DR900 Multiparameter Portable Colorimeter was used to measure the remaining copper and chromium concentration in the supernatants by following the above-mentioned procedure.

Results and Discussion

Adsorbent characteristics

Fig. 1 depicts the XRD pattern of raw laterite soil and, the peaks are denoted by the clay minerals of kaolinite, goethite, gibbsite, hematite, and quartz. For laterite soil, these bands have been described with a slight deviation (Dissanayake, 1980; Dissanayake et al., 2022; Nayanthika et al., 2018). Fig. 2 represents the FTIR spectra of raw laterite. The being of Fe, Al, and Si oxides or hydroxides is confirmed by reviewing spectral peaks. The bands at 3,688.97 and 3,619.38 cm^{-1} indicate the existence of the OH group of Si and Al (Dissanayake et al., 2022; Maiti et al., 2013). The band at 1,645.28 cm^{-1} denotes the attendance of inner layer water molecules. The bands at 1,024.62, 998.76, 908.74, and 788.68 cm^{-1} are due to the presence of Si-O-Fe, Al-OH, Fe-OH vibrations. The bands at 541.24, 467.25, and 531.07 cm^{-1} be a sign of the presence of Hematite (Fe-O stretching) (Dissanayake et al., 2022; Mitra et al., 2016).

The SEM is made use of to investigate the morphology of the apparent adsorbent. The SEM image is shown in Fig. 3, revealing that the surface is heterogenous (Dissanayake et al., 2022; Rani et al., 2019) and has flaky-shaped constituent parts with blocky structures.

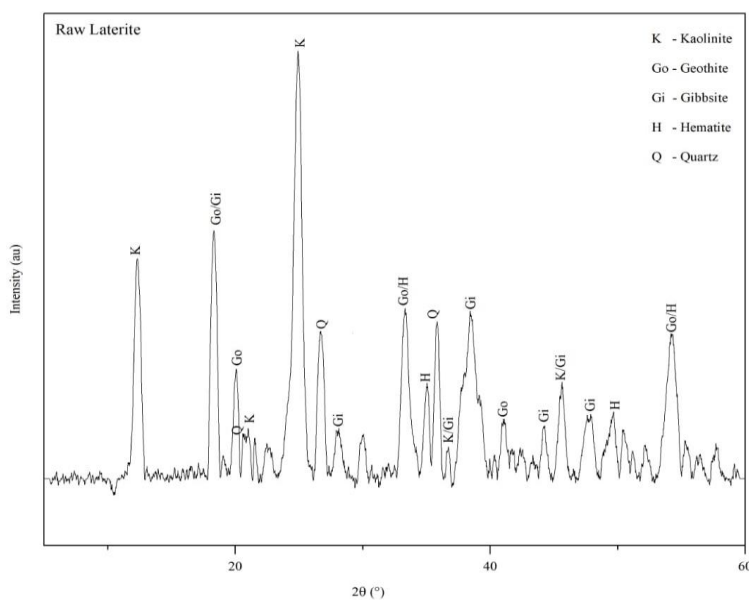


Fig. 1 XRD Patterns of Raw Laterite

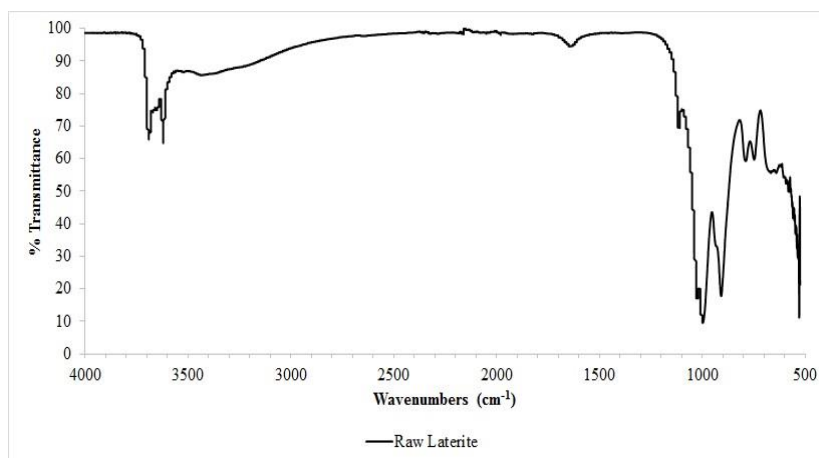


Fig. 2 FTIR Spectra of Raw Laterite

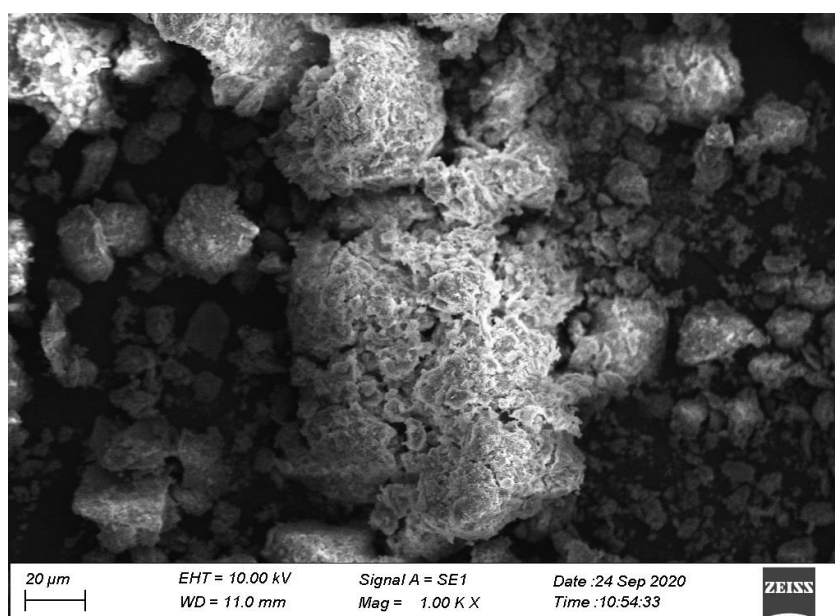


Fig. 3 Photomicrographs by SEM of Raw Laterite

Effect of optimal soil activation temperature

Possibly as a result of the laterite's positive charge in the acidic and neutral media (Mitra et al., 2016) the solid electrostatic repulsive force makes the removal of cations quite difficult (Pham et al., 2017). The maximum chromium removal effectiveness was seen in 200 °C activated laterite soil on both 2 mm and 0.5 mm particle sizes as $84.67 \pm 0.5\%$ and $96.67 \pm 1.5\%$, respectively (Fig. 4). Chromium ions removal efficiencies were increased from 100 °C to 200 °C and dropped from 300 °C and 400 °C activated temperature. Priyantha & Bandaranayaka (2011) discovered that Cr (VI) adsorption by fired brick clay was highly reliant on firing high temperature, with maximum adsorption occurring at 200 °C. Rani et al., (2019) observed that the temperature significantly influenced adsorption, and the adsorption rate increased when

the temperature increased from 200 °C to 300 °C and decreased at 400 °C during the chromium removal by modified laterite.

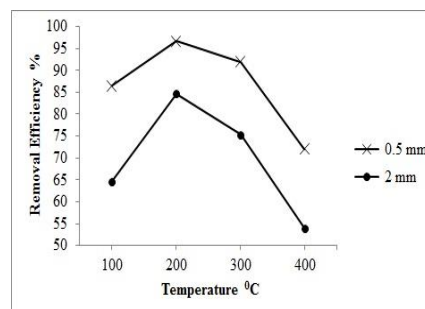


Fig. 4 Determination of Optimum Temperature of Chromium

Copper removal efficiency is slightly increased when increasing the activation temperature (Fig. 5). When

increasing the activation temperature, removal efficiencies slightly increase from $12.07 \pm 0.37\%$ to $14.13 \pm 0.41\%$ and $15.07 \pm 0.41\%$ to $17.07 \pm 2.47\%$ of 2 mm and 0.5 mm grain sizes correspondingly. The highest copper removal ability of 2 mm and 0.5 mm were measured at 200 °C and were $14.53 \pm 0.58\%$ and $17.33 \pm 0.64\%$, respectively. (Mahagodage et al., 2018) showed that thermally activated laterite has high Cu removal efficiency from an aqueous solution. Rani et al., (2019) revealed that the amount of copper absorbed by treated laterite greater than before with increasing temperature from 200 °C to 400 °C.

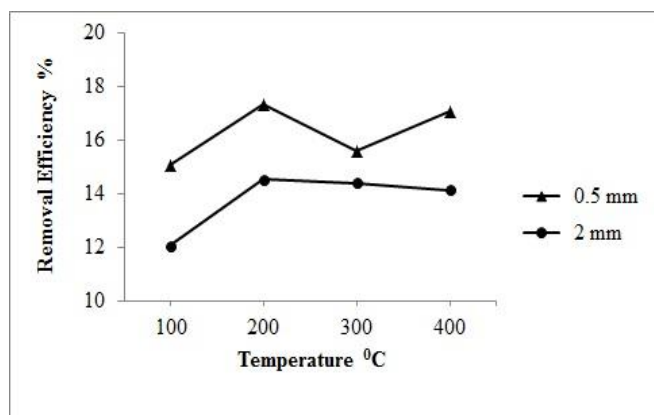


Fig. 5 Determination of Optimum Temperature of Copper

The adsorption percentage was increased initially, and the optimal removal efficiency was achieved in 200°C thermally activated laterite soil for both cations and grain sizes. 200°C thermally activated laterite soil was taken for further experiments.

Impact of optimal time

The impact of interaction time on chromium and copper adsorption was studied (Fig. 6 & 7) with an adsorbent dose of 1.00 g of 200 °C thermally activated 0.5mm and 2mm laterite soil. In 2 mm and 0.5 mm grain sizes, the amount of chromium removed increases from $47.00 \pm 1.06\%$ to $77.00 \pm 0.69\%$ and 77.00 ± 0.69 percent to 89.00 ± 0.47 percent, respectively, when the interaction time with laterite soil is increased from 10 minutes to 180 minutes. The adsorption potential of thermally activated laterite soil for removing the above ions was found to be rapid in the early stages of contact time. It can be observed that the increasing trend of adsorption, in the initial stages, has become slower near the equilibrium. The main reason for this rapid adsorption pattern may be the accessibility of a higher amount of accessible active sites on the exterior of the adsorbent at the initial stages of adsorption. At 90 mins, the chromium removal efficiencies in 2 mm and 0.5 mm were $73.00 \pm 1.29\%$ and $86.00 \pm 0.40\%$, respectively. Mitra et al. (2016) revealed that at the start, the percent deduction of Cr (VI) metal rises rapidly with time, and afterwards that, it increases step by step and to end with

reaches an equilibrium value. Rani et al. (2019) discovered that the percentage of chromium adsorption by modified laterite increased gradually and reached a maximum at 20 minutes of interaction time.

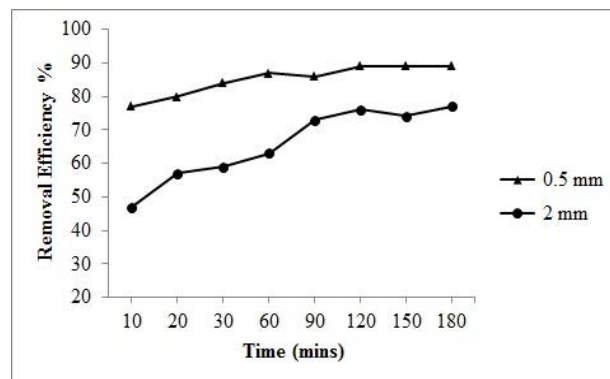


Fig. 6 Determination of Optimum Contact Time of Chromium

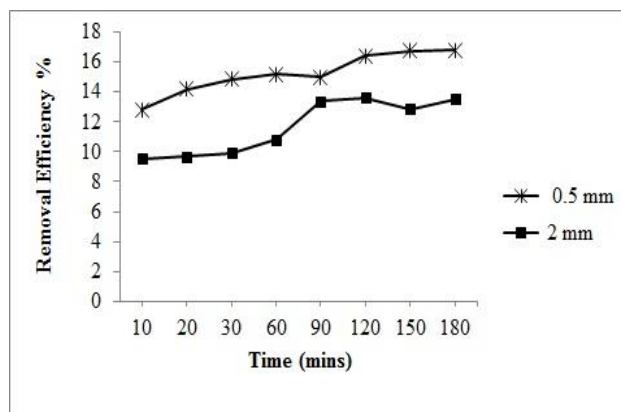


Fig. 7 Determination of Optimum Contact Time of Copper

When the exposure time with laterite soil is increased from 10 minutes to 180 minutes, the amount of copper removed increases from $9.53 \pm 0.37\%$ to $13.53 \pm 0.88\%$ and 12.80 ± 0.40 percent to 16.80 ± 0.50 percent in 2 mm and 0.5 mm grain sizes, respectively. The copper removal efficiencies in 2 mm and 0.5 mm at 90 minutes were $13.40 \pm 0.42\%$ and $15.00 \pm 0.29\%$, respectively. Pham et al. (2017) demonstrated that the removal ability of Cu^{2+} from aqueous solution by modified laterite increases over time. Rani et al. (2018) discovered that, in the treated laterite solution, the copper concentration decreased gradually and remained constant after 120 minutes. Conferring to the experiment outcomes, there is no statistically significant difference between 90 minutes and other longer contact times. Based on the data received, the best possible contact time for further analysis was determined to be 90 minutes.

Effect of optimum soil dosage

Fig. 8 & 9 explain that the percentage removal of chromium and copper rises with an increase in adsorbent dose. The

chromium removal capability increases starting from $97.67 \pm 0.88\%$ to $99.00 \pm 1.00\%$ when the laterite soil amount is added from 0.10 g to 0.50 g in 0.5 mm grain size, and decreases from $99.00 \pm 1.00\%$ to $96.67 \pm 0.33\%$ when the soil amount is added from 0.50 g to 1.00 g.

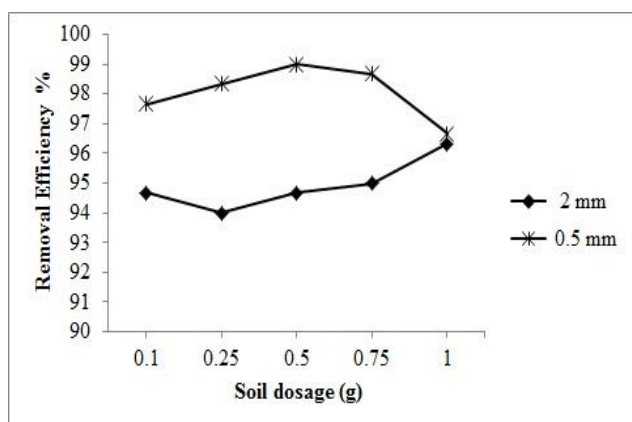


Fig. 8 Determination of Optimum Soil Dosage of Chromium

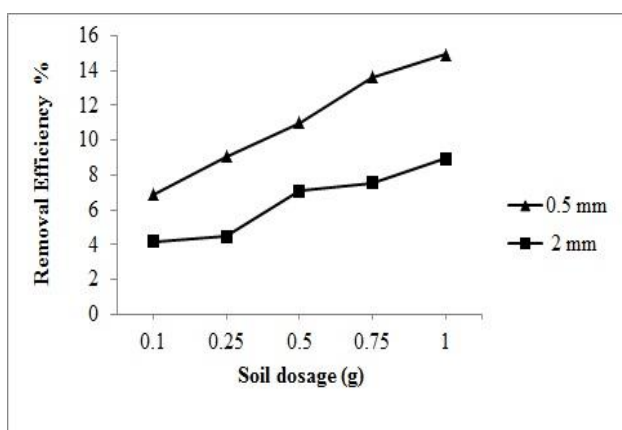


Fig. 9 Determination of Optimum Soil Dosage of Copper

This decrease results from 0.5 mm soil colliding and reducing the surface area. Chromium removal efficiency rises from 94.67 ± 0.33 percent to 96.33 ± 0.33 percent as the dosage of laterite soil is increased from 0.10 g to 1.00 g in 2 mm grain size. When the laterite soil dosage is added from 0.10 g to 1.00 g in 0.5 mm and 2 mm grain size, the copper removal efficiency increases from $6.87 \pm 0.13\%$ to $14.93 \pm 0.18\%$ and $4.17 \pm 0.59\%$ to $8.93 \pm 0.55\%$ respectively. Adsorption initially increased as the amount of adsorbent is increased because, additional active sites are added to the solution. The most of the metal ions are then adsorbed. The key factor (concentration gradient) carries metal ions from the solution to the adsorbent surface, but it is less powerful (Jayaram et al., 2009; Mitra et al., 2016). As a reason, increasing the adsorbent dose doesn't appreciably rise the percentage removal. Mitra et al. (2016) revealed that percentage removals of Cr (VI) by laterite soil rise with the

increase in adsorbent dose and remain constant above the more adsorbent dose. Pham et al. (2017) investigated the removal of Cu^{2+} by improved laterite, while Rani et al. (2018) proved the elimination of copper by activated laterite. Both confirmed that increasing adsorbent dose remains constant with increasing adsorbent mass, and that partial grouping among the remaining active binding sites may account for a lower amount of copper removal at high doses. As well, due to the inadequate of active binding sites, a lesser reduction was found at little adsorbent doses. Rani et al. (2019) investigated Cr adsorption was most significant at 0.50 g of modified laterite. According to Rani et al. (2018) the exclusion of copper by treated laterite was most significant at 1.00 g of adsorbent. Pham et al. (2017) determined that the optimal adsorbent dosage for copper removal using surfactant-modified laterite soil is 5 mg/mL.

The test results showed no significant difference in percentage chromium removal efficiencies when the dosage was increased beyond 0.10 g. However, when the dosage was increased above 0.50 g, there was no significant difference in percentage of copper removal efficiencies. As a result, 0.50 g of copper and chromium was used as an appropriate dosage for both grain sizes.

Conclusions

Adsorption experiments were performed to investigate the laterite's capacity for adsorption under different conditions. The results show that 200°C is the optimum temperature for laterite soil activation, 90 min is the optimum contact time, and 0.50 g is the optimum adsorbent dosage. Large quantities of laterite are easily accessible, and the adsorption treatment method seemed to be reasonably priced. According to the findings, heat activation of laterite allowed for the elimination of copper and chromium ions from the water. As a result, the material can be used to treat wastewater without altering the pH of the water.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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