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Assessment of Heavy Metal Adsorption Efficiency of Shells from Groundnut Grown in KauraNamoda – Zamfara State, Nigeria

Emmanuel Onoja*,
Clifford .C. Odenigbo,
Comfort Onoja
Shaibu Momoh
Department of Science Laboratory Technology, School of Science and Technology, The Federal Polytechnic, KauraNamoda, P.M.B. 1012, Zamfara State, Nigeria.

Abstract:

Groundnut is one of the major agricultural products of farmers in KauraNamoda. Yearly, a large quantity of groundnut shells are produced as biomass from groundnut processing sites and disposed indiscriminately into the ecosystem, leading to environmental pollution as just small percentage is utilized for agricultural purposes. The present study investigated the adsorbent efficiency of shells generated from groundnut farms in Kaura Namoda on heavy metals. Findings of this study indicated that a contact time of 60 minutes was sufficient to remove 95.2% and 93.0% of lead (Pb) and chromium (Cr) respectively, while Ni, Cu and Zn require a minimum of 120 minutes contact time to reduce their concentrations by 94.9%, 90.1% and 94.1% respectively. It was revealed from this study that the adsorbent efficacy of groundnut shell was pH sensitive as it works best in alkaline medium. At pH of 10.0, the efficiency of the groundnut shell adsorbent was 96.1%, 95.3%, 87.7%, 94.8% and 96 8% for Pb, Ni, Cu, Cr and Zn respectively, relative to acid medium that gave 94.6%, 93.0%, 84.0%, 91.0% and 94.6% for Pb, Ni, Cu, Cr and Zn respectively. The optimum dose of 10.0g/100cm3 water solution of 6 ppm heavy metal concentration was achieved in this study. The study demonstrated a significant difference ($p<0.05$) in the adsorption efficiency of groundnut shell for all the water samples analyzed at varying concentrations, an observation attributed to sufficient adsorption site being available for more adsorption at lower concentrationsof heavy metal ions. The study concludes that shells from groundnut grown in Kaura Namoda could serve as alternative cost-effective, ecofriendly and renewable bio-adsorbent for removal of heavy metals from wastewater.

Keywords: Adsorbent; Efficiency; Groundnut; Heavy metal; Wastewater.

Introduction

Heavy metal refers to a group of metals and metal like elements with density greater that 5gm and atomic number above 20 g/mol. It also refers to any metallic chemical element that has relatively high atomic weight and is toxic or poisonous at low concentration (Amal*et al.*, 2012). These include nickel (Ni), copper (Cu), zinc (Zn), lead (Pb), chromium (Cr), mercury (Hg), cadmium (Cd) etc. Heavy metals ion have been excessively release into environment due to rapid industrialization, causing major pollution of the environment (Beliles, 2007). Copper (Cu) is highly toxic because it is non-biodegradable and carcinogenic.The effect of Nickel (Ni) exposure very from skin irritation to damage of the lungs nervous system; and mucous membrane. While Zinc (Zn) exposure causes depression, lethargy, neurological signs and increase thirst. Chromium (Cr) has been considered as one of the top 18th toxic pollutant and because of its carcinogenic characteristics, it has become a serious health concern (Khan *et al.*, 2001). Nickel and chromium which are widely used are extremely toxic in relatively low dosages, the main pathway through which nickel and chromium enter the body is through wastes from industrial processes (Alluri, 2007). Industrial wastewater comes from activities from metal plating, mining activities, smelting, battery, manufacturing, pesticides, pigment, petroleum refining, paint manufacturing, printing and photographic industries etc.

The pollution of water bodies with heavy metals and other particles resulting from human activities and channeling of industrial effluents as well as hospital wastewater into them is becoming a serious matter of global concern. Worthy of note also is the generation of heavy metals from other industrial processes such as mining, mineral processing and metallurgical operations that consistently find their way into both surface and underground water. These heavy metals are soluble in aquatic environment, thus can be easily absorbed by living cells. The heavy metals, if absorbed above the permissible levels, could lead to serious health disorders (Beni and Esmaeili, 2020).

In light of the above, treatment of heavy metals containing industrial effluent and heavy metals from other human and industrial activities becomes sacrosanct before discharging them into the ecosystem. Development of adsorbents from renewable agricultural biomass for the treatment of wastewater should be given top priority, as this would not only be cost effective but also leads to solving environmental pollution by clearing off these biomass from the ecosystem (Mohan *et al.*, 2014; Sowmya*et al.*, 2018).

Over the years, metal ions have been removed from wastewater using several synthetic adsorbents (Salgot and Folch, 2018). Conventional methods such as chemical precipitation, chemical oxidation, ion exchange, membrane separation, reverse osmosis, electro dialysis etc, have been widely used for treatment of wastewater. However, these methods are laborious, expensive and require high energy input as well as technical expertise to make them effective. Additionally, the conventional methods are associated with generation of toxic sludge that are non-ecofriendly and disposing these sludge into the ecosystem could cause more damage to the environment. One of the conventional adsorbent, activated carbon has been extensively

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used in many applications. However, the high cost of producing activated carbon limits its usage in wastewater treatment processes.
Groundnut is one of the major agricultural products of farmers in KauraNamoda. Yearly, a large quantity of groundnut shells are produced as biomass and disposed indiscriminately into the ecosystem, leading to environmental pollution. The application of low cost natural adsorbent including carbonaceous material, agricultural products and biomass has been investigated in many previous studies (Bhatnagar and Sillanpaa, 2010; Wani and Patil, 2017). Utilization of biomass as adsorbent for removing heavy metals from wastewater has been reported as potential alternative to the conventional technologies such as precipitation, ion exchange, solvent extraction and liquid membrane (Jeyaseelan and Chauhan, 2015).However, findings of research work showing the utilization of shells of groundnut grown within KauraNamoda Local Government Area of Zamfara state as adsorbent is yet to be seen.
The present study is aimed at developing an ecofriendly, cost effective and renewable natural adsorbent (Lema*et al.*, 2016; Ajala and Ali, 2020; Shrivastava*et al.*, 2021) from locally and highly abundant agricultural biomass that is produced in large quantities in KauraNamoda. Transforming these highly abundant agricultural biomass into ecofriendly adsorbent and its utilization for removing heavy metals from wastewater is worth investigating, as this will not only produce cleaner environment but would generate more funds to the locals and would improve their living standard.

Figure 1: a) groundnut pods b) groundnut shells

2.0 Experimental

2.1 Sample Collection/Preparation

The groundnut shells were collected from KauraNamoda groundnut processing site and taken to the laboratory. The groundnut shell sample was sorted manually to remove dirt and sound particles. It was washed with distilled water and dried it in a laboratory oven at 100^oC for 24 hours to remove adhered water molecules. The dried sample was pulverized into powderusing laboratory blender and was sieved with a standard shell sieved to obtain the desired particle size while the unwanted particles were discarded. The sample was used directly as the adsorbent without further treatment in the experiment.

2.2 Preparation of Stock Solutions

$CuSO_4.5H_2O$, $NiSO_4.6H_2O$, $Cr_2(SO_4)_3.6H_2O$, $PbSO_4.8H_2O$,$ZnSO_4.7H_2O$,were obtained in analytical grade and used without further purification to prepare 10ppm stock solution for each metal as outlined below.

i. **Copper Solution**: 10.048g of $CuSO_4.5H_2O$ was carefully weighed and dissolved in a beaker containing 100cm^3 ofdistilled. The solution was transferred into 1000 cm^3 volumetric flask and made up to mark with distilled water with gentle swirling. The prepared stock solution was transferred into reagent bottle and stored for further analysis.

ii. **Nickel Solution:** It was prepared as described above by weighing 9.504g of $NiSO_4.6H_2O$and dissolving in 100cm^3 ofdistilled water in a beaker. The resulting solution was transferred into 1000 cm^{3}volumetric flask and made up to mark with distilled water.

iii. **Zinc Solution:**10.004g of $ZnSO_4.7H_2O$ was added in the 100cm^3 ofdistilled water in in a beaker and transferred into 1000 cm^{3}volumetric flask and made up to mark with distilled water.

iv. **Lead Solution:** 17.622g of $PbSO_4.8H_2O$ was dissolved in the 100cm^3 of distilled water ina beaker and transferred into 1000 cm^3 of volumetric flask. It was made up to mark by adding distilled water.

v. **Chromium Solution**: 10.006g of $Cr_2(SO_4)_3.7H_2O$ was added in the 100cm^{3}of distilled water in a beaker. The resulting solution was transferred into a 1000 cm^3 volumetric flask and made up to mark with further addition of distilled water.

Lower concentration of 2, 4, 6 and 8 ppm were prepared from the stock solutions using serial dilution.

2.3 Analysis of Adsorbent Efficiency of Shells of Groundnut Grown in Kaura Namoda

i.Effect of Contact Time of Adsorbent with Heavy Metals:

The adsorbent (5.0g) was weighed and equilibrated with 100cm^{3}of each metal(Zn, Cu, Cr, Pb and Ni) using 6 ppm concentration of each metal solution in a stoppered glass flask at room temperature in an orbital shaker for a time interval ranging from 15 – 240min. At the end of the specified time, aliquot of each sample (10 cm^3) was withdrawn from each flask and centrifuged to remove the adsorbent from the solution. The resultant clear solution was analyzed for heavy metal concentration using AAS.

ii.Effect of pH of Solution on Adsorbent Efficiency:

Effect of pH of solution on the adsorbent efficiency of was investigated by examining its efficiency under very acidic, mildly acidic, neutral and alkaline media. Four pH range (pH 2, 5, 7 and 10) were examined by placing few drops of HCl in 100 cm^3 of the various sample solution (6 ppm) until the desired pH of 2 and 5 were obtained. In a similar fashion, few drops of NaOH were also placed into 100 cm^{3}separate sample solution (6 ppm) until a pH of 10 was obtained. To each, 5.0g of the adsorbent was added and allowed to stand for 120 min. The adsorbent was removed from the solution by centrifugation and the clear solution was analyzed for heavy metal concentration using AAS.

iii.Effect of Dose of Adsorbent on Heavy Metal Adsorption:

This was carried out by varying the quantity of the adsorbent in the range of 2.5, 5.0, 7.5, 10.0 and 12.5 g using 100cm^3 heavy metal solutions (6 ppm) for a period of 120 min. At the end of 120 min, the adsorbent was separated from the mixture via centrifugation and the clear solution was subjected to AAS analysis to ascertain the concentration of heavy metals present after analysis.

iv. Effect of Initial Concentration of Heavy Metals on Adsorbent Efficiency:

The effect of initial concentrations of the various metal samples on the efficiency of the adsorbent was investigated by placing equal amount of the adsorbent (10.0g) in 100cm^3 solutions of varying concentrations of 5, 10, 15, 20 and 25 ppm respectively for a period of 120 min. At the end of the analysis, the adsorbent was removed from the mixture by centrifugation and 10cm^3 of the clear solution was analyzed using AAS.

v. Effect of Adsorbent on Heavy Metal Removal

The adsorbent efficiency of ground shell was investigated by analyzing the various heavy metal solutions (6 ppm) in AAS without the groundnut shell and with 5.0g of groundnut shell.

2.4 Statistical Analysis:

Statistical analyses were performed using the IBM SPSS version 20.0 software, whereby significant differences among groups, was based on a level of significance of 0.05 ($P < 0.05$), if any using ANOVA repeated measurement for parametric test. In this study, unless specified otherwise, the data meant for statistical inference are presented as mean ± standard deviation.

3.0 Results and Discussion

3.1 Effect of Contact Time of Adsorbent on Heavy Metals

Findings of this study shows that the adsorbent efficiency of groundnut shell increases with increase in contact time (Fig. 1). For Pb and Cr, a contact time of 60 minutes was sufficient to reduce their concentrations from 6.00 ppm to 0.29 and 0.42 ppm, translating into 95.2% and 93.0% efficiency respectively. However, Ni, Cu and Zn require a minimum of 120 minutes contact time to reduce their concentrations from 6.00 ppm to 0.31, 0.59 and 0.35 ppm, translating into 94.8%, 90.2% and 94.2% efficiency respectively.

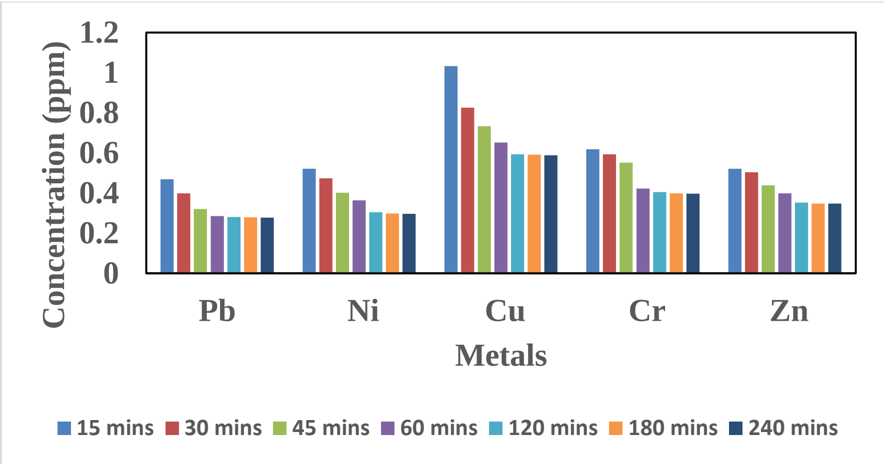

Fig. 1: Effect of Contact time of groundnut shells with heavy metals on its adsorptive efficiency

It was observed that there was no significant difference ($p<0.05$) for contact time beyond 60 minutes in percentage efficiency of the groundnut shell adsorbent for Pb and Cr (Fig. 1). The findings also revealed that prolonging the contact time beyond 120 minutes for Ni, Cu and Zn was counterproductive as there was no appreciable change in the percentage efficiency of the adsorbent beyond this time. It can be inferred from the present study that that the optimum contact time for Pb and Cr removal from wastewater is 60 minutes while that of Ni, Cu and Zn is 120 minutes. The findings of this study demonstrates an improvement to those reported by Lema and Mwegoha (2016) and it is in congruence with those of Ajala and Ali (2020) that studied the effect of activation time of groundnut shell adsorbent on heavy metal removal.

3.2 Effect of pH of Water Samples on Heavy Metals

The result of the effect of pH of the water sample on the efficacy of groundnut shell adsorbent on heavy metal removal is displayed in Fig. 2.

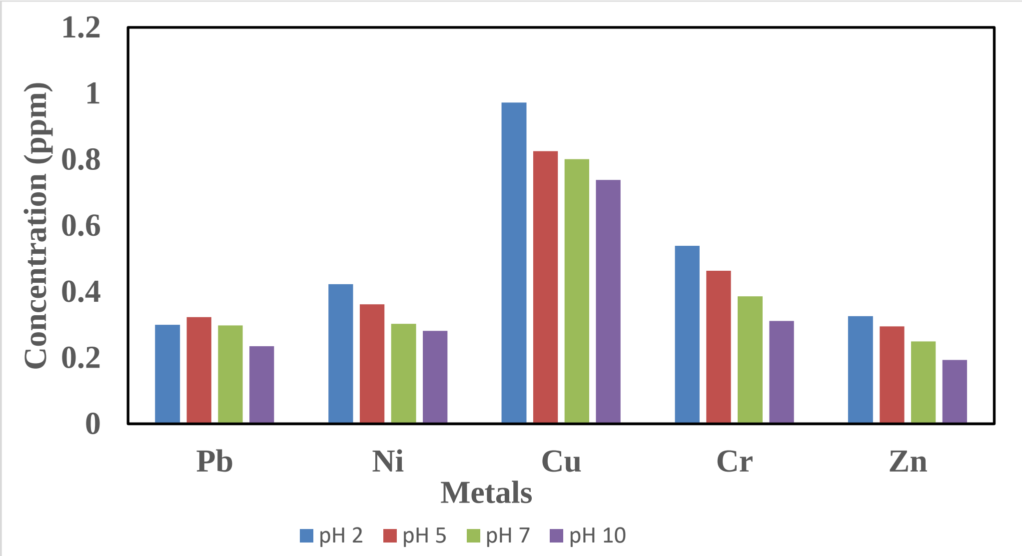

Fig. 2: Effect of pH of heavy metal solutions on adsorption efficiency of groundnut shells

It was observed that as the pH of the water samples increases from strongly acid through neutral to slightly alkaline (pH = 2 to 10), there was a corresponding decrease in the concentration of all the heavy metals tested in this study. As shown in Fig. 2, at pH 10, the percentage efficiency of groundnut shell adsorbent was 96.0%, 95.3%, 87.7%, 94.8% and 96 6% for Pb, Ni, Cu, Cr and Zn, as their concentrations were reduced from 6.00 ppm to 0.24, 0.28, 0.74, 0.31 and 0.20 ppm respectively. However, in the acidic medium, the groundnut shell adsorbent showed percentage efficiency of 95.0%, 93.0%, 83.8%, 91.0% and 94.5% for Pb, Ni, Cu, Cr and Zn, demonstrating the reduction of their initial concentrations of 6.00 ppm to 0.30, 0.42, 0.97, 0.54 and 0.33 ppm respectively. ANOVA results showed that there was a significant difference ($p<0.05$) in the adsorbent efficiency as the pH changes from strongly acidic to alkaline. Results of the present study suggest that groundnut shell adsorbent is more effective at removing or reducing heavy metals from wastewater or aqueous solutions in alkaline medium that in acidic medium. The results of this study corroborates the findings of Kinuthia*et al.,* (2020). However, the result obtained in the present study slightly disagrees with those of Lema and Mwegoha (2016) that reported that the best pH for removing Cr from wastewater is pH 4.

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3.3 Effect of Adsorbent Dose on Heavy Metals

Fig. 3 shows the effect of varying the weight of groundnut shell on its adsorption activity. Findings of the present study revealed that heavy metal removal efficiency of groundnut shell adsorbent is dose dependent for all the metals tested.

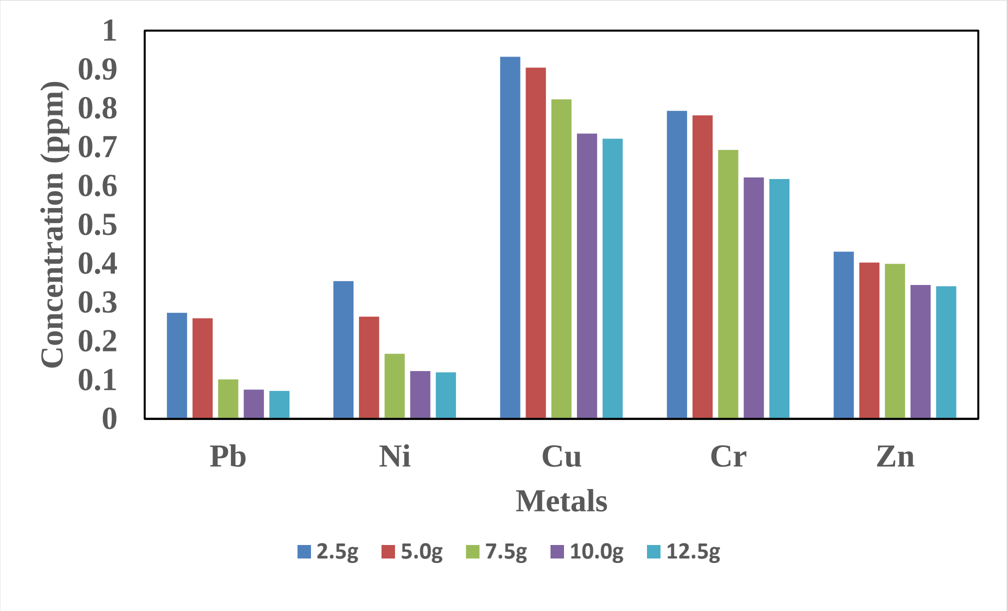

Fig. 3: Effect of dose of adsorbent on its heavy metals adsorption efficiency

The finding shows that as the adsorbent dose increases from 2.0g to 10.0g, there was a significant increase ($p<0.05$) in the percentage removal of all the heavy metals; Pb (95.5% to 98.8%), Ni (94.4% to 98.0%), Cr (86.8% to 89.7%), Zn (92.8% to 94.3%). However, Cu displayed a slightly different trend as the percentage removal increases continuously with increase in adsorbent dose (Fig. 3). The increase in the adsorption capacity of groundnut shell adsorbent with increase in adsorbent dose could be attributable to availability of more adsorptive active sites to accommodate more heavy metals. The present study therefore revealed that the optimum dose of groundnut shell adsorbent required to effectively reduce the concentration of Pb, Cr, Ni and Zn from 6.00 ppm to its bearable level of 0.07, 0.12, 0.62 and 0.34 ppm respectively that translated to the highest percentage efficacy shown above is 10.0g per 100 cm^3(6 ppm) heavy metal solution. The finding of this study is in agreement with those of Gautam*et al.*, (2014).

3.4 Effect of Initial Concentration of Heavy Metals

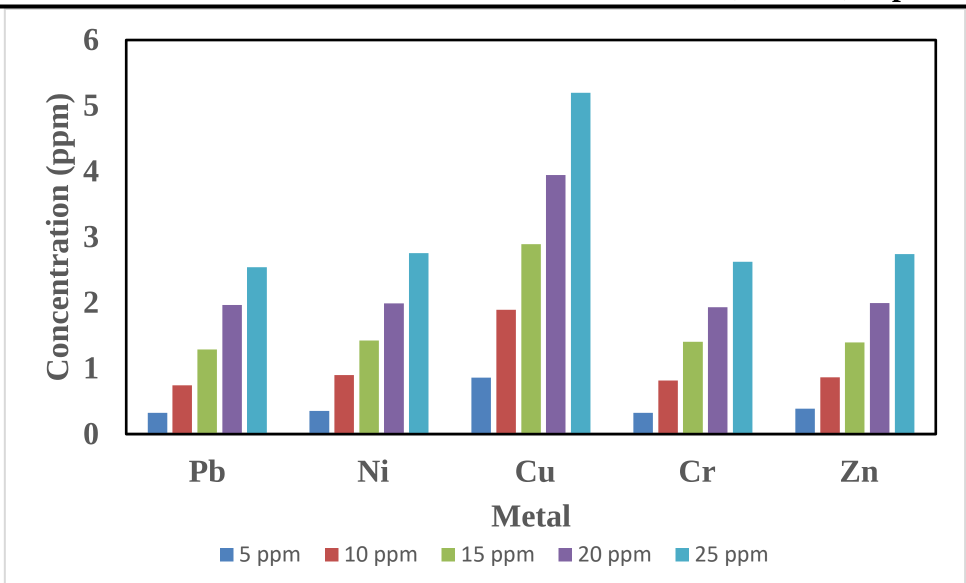

Fig. 4: Effect of initial concentration of heavy metals on the efficiency of the adsorbent.

Fig. 4 shows the effect of concentration of heavy metals on the adsorbent efficiency using water samples of heavy metal initial concentrations of 5, 10, 15, 20 and 25 ppm with 10g/100cm^{3}adsorbent dose for 120 minutes. The adsorbent efficiency of groundnut shells on heavy metal removal decreases with the increase in initial concentration of heavy metal for all the metal tested. For the lowest concentration of 5 ppm and the highest concentration of 25 ppm for all the metals investigated, groundnut shell adsorbent was able to reduce their concentrations to 0.33 and 2.54 ppm for Pb, 0.35 and 2.76 ppm for Ni, 0.86 and 5.20 ppm for Cu, 0.32 and 2.63 ppm for Cr, 0.39 and 2.74 ppm for Zn, translating into 93.4% and 89.8%, 93.0% and 89.0%, 82.8% and 79.2%, 93.6% and 89.5%, 92.2% and 89.0% of Pb, Ni, Cu, Cr and Zn respectively. There was significant difference ($p<0.05$) in the adsorption efficiency of groundnut shell for all the water samples analyzed.The observation here could be attributed to the fact that at lower initial metal concentration, sufficient adsorption site were available for adsorption of the heavy metal ions. However, as the initial concentration of the metal ions increases, the number of heavy metal ions were relatively too high for the available adsorption site, hence the observed decrease in the adsorption capacity. Findings of the present study agree closely with those of Allure, (2007) who investigated the effect of bio-sorption and ecofriendly alternative for heavy metal removal.

3.5 Effect of Groundnut Shell Adsorbent on Heavy Metals

Fig. 5 shows the concentrations of the metal ions in the various water samples before and after treatment with groundnut shell adsorbent. The experiment was carried out with the initial concentration of each metal set at 6.00 ppm using 5.0g of adsorbent dosage and a volume of 100 cm^3 heavy metal solution, at a contact time of 120 minutes. The result indicated that Pb, Ni, Cu, Cr and Zn were reduced from the initial concentration of 6.00 ppm to 0.45, 0.51, 1.79, 0.62 and 0.53 respectively.

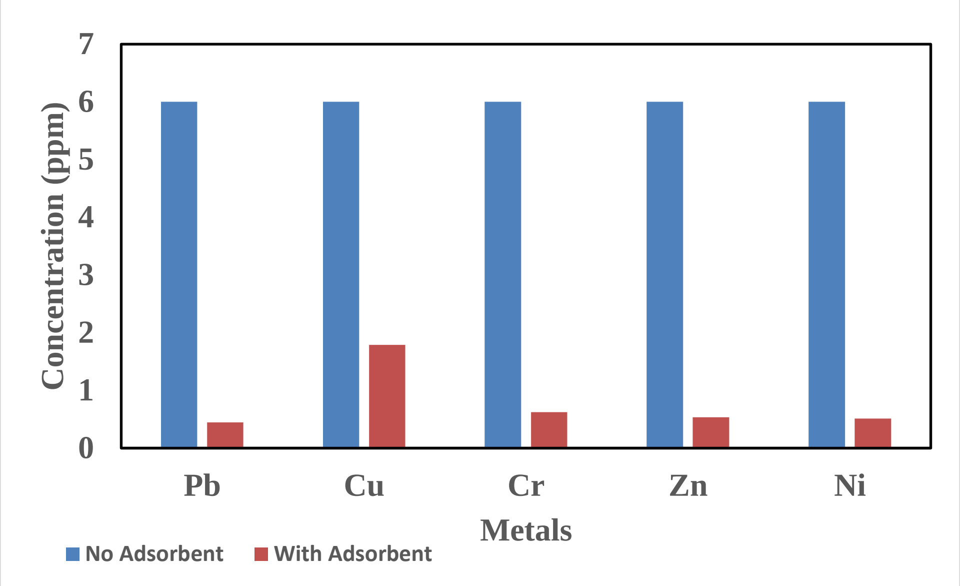

Fig. 5: Effect of adsorbent on heavy metals removal

The highest effect of the adsorbent was recorded for Pb with 92.5% reduction. Cu, Cr, Ni and Zn had their initial concentrations reduced by 70.2%, 89.7%, 91.5% and 91.2% respectively. The results suggest that adsorbent developed from groundnut shells is more effective in removing Pb, Cr, Ni and Zn ions from wastewater compared to Cu. This could be associated to high affinity between the surface of the adsorbent and these metal ions. The findings of this study is agreement with those ofGautam*et al.*, (2014).

CONCLUSION

The present research had demonstrated that groundnut shell is a good natural adsorbent for reducing the concentration of heavy metals in wastewater to a bearable level. In this study, groundnut shell effectively reduced the concentration of Cu, Zn, Ni, Pb, and Cr from aqueous solutions. The study also highlights the effect of different parameters such as, contact time, pH, initial concentration, and adsorbent dose, in removal of metal ions from wastewater. A contact time of 60 and 120 minutes were established to be sufficient to drastically reduce the concentration of Pb, Cr and Ni, Cu, Zn respectively. Also an adsorbent dose of 10.0g/100cm^3 was set as optimum for considerable reduction of a 6 ppm heavy metal solution of wastewater. The study concludes that shells from groundnut grown in KauraNamoda could serve as alternative cost-effective, ecofriendly and renewable bio-adsorbent for removal of heavy metals from wastewater.

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