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Efficiency of Chemically Modified Activated Carbon Derived from Banana Peel for Removal of Pb^{2+} and Zn^{2+} from Aqueous Solution

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Abstract
Natural and anthropogenic activities generally result to large production of heavy metals. These heavy metals produced are indiscriminately discharged into rivers and other water bodies. Wastewater treatment of industrial effluents become very necessary due to toxic effect of heavy metal pollutants and its indirect effect pose to human health. Banana peel, an agricultural waste biomass can be used to produce bio-sorbent for adsorption of heavy metals from industrial wastewater. This study focused on the production of chemically modified activated carbon using various concentrations of phosphoric acid for removal of lead and zinc metals from aqueous solution. Activated carbon was produced from waste banana peel through thermal pretreatment at temperature of 450°C preceding chemical modification with different concentrations of phosphoric acid of 0.5 M, 1.0 M and 1.5 M. The three different concentrations of the phosphoric acids represent sample X, Y and Z respectively. To study the adsorption efficiency of chemically modified activated carbon using different concentrations of phosphoric acid, batch experiments were conducted on chemically modified samples to assess the adsorption of lead (II) and zinc metals from aqueous solution. The three adsorbents were interacted with varying parameters such as effect of initial concentration of lead and zinc metal of concentration of 10 mg/L and 2 mg/L respectively. Based on batch experiments conducted, results indicated that adsorbent dose, pH, initial concentration as well as contact time are important factors influencing lead (II) and

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Zinc metals adsorption from aqueous solutions. Percentage adsorption of lead (II) and zinc metals was above 80 % for all three chemically modified adsorbents investigated. The adsorption capacities of the adsorbents under study showed high adsorption capacity for both zinc and lead metals. This implies that sample X, Y and Z are good adsorbents for adsorption of both zinc and lead metals in an aqueous solution.

Keywords: Activated Carbon, Banana peel, Heavy metal ions (Pb^{2+} and Zn^{2+}), Adsorption, Phosphoric acid

INTRODUCTION

One of the biggest problems confronting man globally is centered on management of waste generated from daily activities of both domestic and industries. Solid agricultural raw materials are harnessed, processed, utilized, and eventually result as waste, which leads to environmental contamination and pollution (Wang *et al*., 2019). One method normally applied is incineration of solid agricultural waste. Combustion of solid agricultural waste is not a holistic approach, because it leads to air pollution. The noncombustible solid agricultural waste remain as dumps and constitute as nuisance in the environment (Negroiu *et al*., 2021a).

The conventional approaches applied in managing agricultural solid waste materials include: heat decomposition and by chemical process that leads to formation of greenhouse gases such as carbon monoxide, carbon dioxide, methane, steam and ammonia etc. Solids such as organic matter and carbon ash are formed, but the problem of environmental pollution is not resolved holistically, this amounting to greater release of greenhouse gases and the quantity of solid waste upsetting the ecosystem (Vilardi *et al*., 2018; Esparza *et al*., 2020).

The major and critical necessity of living organism is the ability to live in a friendly environment, uncontaminated air and water. Agricultural activities, increases in nativity, industrial revolution, urbanization, and use of hazardous chemicals are major factors contributing to contamination and pollution of both surface and ground water in any ecosystem (Vakili *et al*., 2014).

In this study, batch experiments have been carried out for optimization of various process parameters like initial pH, contact time, adsorbent dose and initial metal ion concentration. The study therefore aimed at developing a relatively cheaper adsorbent using banana peel modified with different concentrations of phosphoric acid that is capable of removing lead and zinc heavy metals from aqueous solution.

Previously reported investigations are those that produced activated carbon from banana peels for the removal of As (III) from water (Maharjan and Jha, 2022), Cd^{2+} and Cr^{6+} from brewery wastewater (Wyasu, 2018), $Co^{2+}$and Ni^{2+} from aqueous solution (Abbasi *et al*., 2013) as well as Pb^{2+} from aqueous solution (Nurain *et al*., 2021). Given the above, there has not been any study in Nigeria, to the best of our knowledge that has scientifically reported the production of activated carbon from banana peel for expunging both Pb^{2+} and Zn^{2+} from aqueous solution. Therefore, this investigation evaluated, for the first time in Nigeria, the efficiency of chemically modified activated carbon derived from banana peel for removal of Pb^{2+} and Zn^{2+} from aqueous solution.

MATERIALS AND METHODS

Plant collection

The bunch of banana fruits were obtained from Auta Balefi and Masaka market, Nasarawa State, Nigeria. After removing the fruits, the back peels were collected and dried. The collected banana peels were properly dried and kept for further preparation. The collections and purchase of the banana fruits was done in the month of February, 2022. 5 kg banana peels were collected from Auta Balefi and Masaka town, Nasarawa State, Nigeria.

Reagent preparation

Concentration of 1000 ppm or 1000 mg/L was prepared by weighing 1.60 g of dried $Pb(NO_3)_2$ salt and dissolved in 1000 mL of deionized water. Serial dilutions of the stock solution were carried out to prepare the required concentrations. Similarly, dried $ZnSO_4$ salt was used to prepare the stock solution of zinc metal by weighing 2.48g of dried $ZnSO_4$ salt and dissolved in 1000 mL deionized water to give 1000 ppm or 1000 mg/L solution of zinc metal (Gupta *et al.*, 2001).

Adsorbent preparation

The collected dried banana peels were soaked in deionized water for 30 minutes and washed to remove any adhered dirts. The peels were further dried in an oven at temperature 105 ℃ for ten hours until a constant weight was obtained. The oven dried peels were powdered using a pestle and mortar and blended into small particles with the aid of blender and sieved with sieve of diameter of 250 µm. The sieved peel particles was calcinated using muffle furnace at temperature of 450 ℃ for two hours (Zein *et al.*, 2010).

Chemical modification

Mortar and pestle were used to ground the calcinated charcoal and treated with different concentrations of phosphoric acid H_3PO_4 for chemical modification purpose. The calcinated charcoal of weight 120 g each was agitated in a 250 mL beaker with 100 mL of 0.5, 1.0 and 1.5 M standard H_3PO_4 solution respectively, and stirred manually using a glass stirrer, after which the slurries was left for some time for activation to take place at room temperature. After activation, the samples were washed several times with deionized water to remove the excess H_3PO_4 acid. The washed samples were dried to a constant weight at 110 ℃ for 4 hours to obtain the final product. These chemically modified banana peels using different concentrations of H_3PO_4, 0.5, 1.0 and 1.5M was labelled sample X, Y and Z respectively (Pagnanelli *et al.*, 2003).

RESULTS AND DISCUSSION

Batch Experiment Results and Adsorption performance analysis

The plotted graphs of the interactions between the chemically modified samples X, Y and Z with parameters such as effect of initial concentration, effect of pH, effect of contact time and effect of adsorbent dose are presented in Figures 1 - 8.

Effect of Initial Concentration on Adsorption of Pb (II) Ions

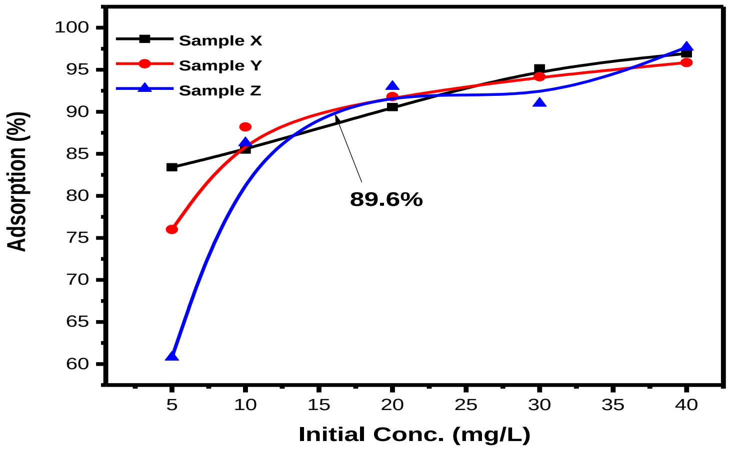

Figure 1: Effect of initial concentrations on adsorption of Pb (II) ions by chemically modified sample X, Y and Z at room temperature and pH 4

From the result on the adsorption of Pb (II) ions on samples X, Y and Z studied with variation of initial concentration of Pb (II) ions in the range 5 – 40 mg/L is presented in Figure 1. The three adsorbents showed increasing adsorption of Pb (II) as the initial concentration increases, until it got to the maximum adsorption of 89.6 % for sample Z and 95.0 % for sample Y, while sample X showed a linear increase in adsorption capacity from 83.0 to 96.0 % with increase in initial concentration. The adsorption of Pb (II) ions continue to increase until the adsorbate is saturated on the adsorbent site. The three adsorbents sample X, Y and Z show a very high adsorption capacity ranging from 83.0 to 96.0 % for sample X, sample Y from 75.0 to 95.0 %, while sample Z is from 60.0 to 89.6 %. The adsorption capacity obtained in this study were found to be similar to those reported by Negroiu *et al*. (2021) where adsorption capacity obtained was over 97.0 % for Cd, Cu, Cr, Fe, Mn, Pb and Zn heavy metals.

Effect of Initial Concentration on Adsorption of Zn Ions

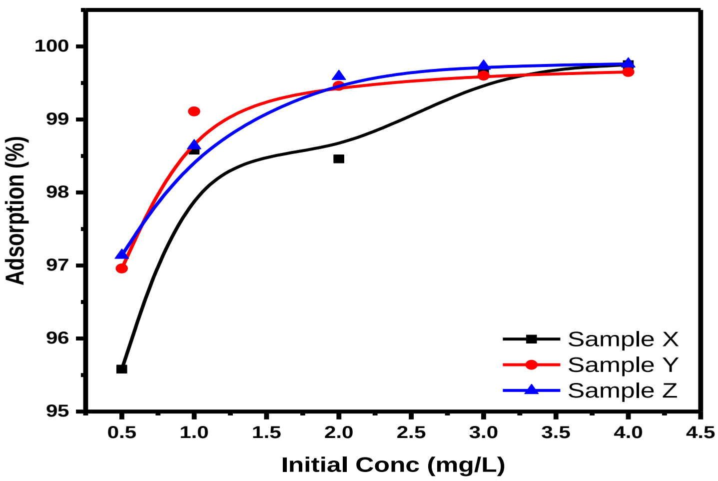

Figure 2: Effect of initial concentration on adsorption of Zn ions by chemically modified sample X, Y and Z at room temperature and pH 4

The result of the effect of variation of initial concentration of zinc ions adsorption ranging from 0.5 – 4 mg/L by sample X, Y and Z adsorbents carried out and presented in Figure 2. Shows that the three adsorbents have brilliant adsorption capacity performances. The adsorption capacities of the three adsorbents increased from initial concentration of 0.5 mg/L with adsorption rate of 95.5 % to a maximum adsorption of 99.5 % at initial concentration of 3.5 mg/L. The adsorption process increases, as the initial concentration increases, until it got to maximum adsorption of 99.5 %. This implies that adsorbent adsorptive capacity increase until the surface is saturated. The optimum initial concentration stands at 3.5 mg/L.

The obtained result in this study is similar to the report by Ali (2017) where adsorption capacity of banana peel used as an adsorbent was 95.0 %. On the other hand, the corresponding increase in initial concentration with adsorption capacity may also be attributed to concentration driving force, since it is responsible for overcoming the mass transfer resistance associated with the adsorption of metals from solution by the adsorbent (Budhalakoti, 2019; Abou-Zeid *et al*., 2021; Al-Sahlany *et al*., 2022). Therefore, as the initial concentration increases, the driving force also increases, resulting in improved efficiency of the heavy metal removal process (Hospital *et al*., 2018; Ibiyinka *et al*., 2021). Then, after the system reaches saturation point, the initial solution concentration does not show any significant change in the amount adsorbed due to a decrease in the number of active sites (Kosseva, 2017; Khayyyn and Mseer, 2019).

Effect of Contact Time on Adsorption of Pb (II) Ions

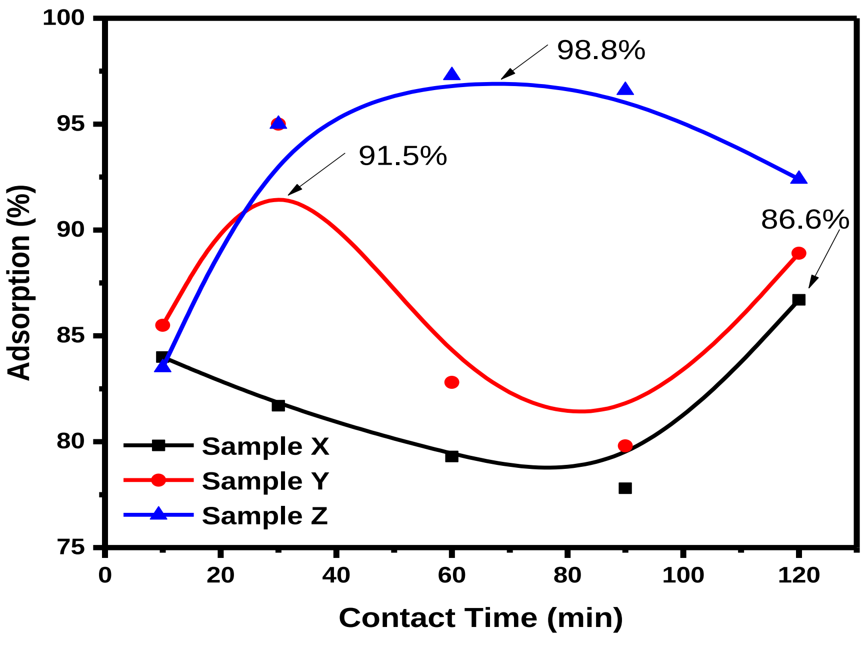

Figure 3: Effect of contact time on adsorption of Pb (II) ions by chemically modified sample X, Y and Z with initial concentration 10 mg/L, at room temperature and pH 4

The effect of contact time on the adsorption of Pb (II) ions was evaluated for initial lead concentration of 10 mg/L at different contact time interval of between 10 – 120 minutes, the result is presented in Figure 3. The result showed that maximum adsorption of Pb (II) ions by sample X occurred at the first 10 minutes contact time, and then decreased to contact time of 80 minutes; and then got to maximum adsorption capacity of 86.6 % at contact time of 120 minutes; while the sample Y got to maximum adsorption of 91.5 % at contact time of 30 minutes. Sample Z shows very excellent adsorption capacity, it increases until it got to maximum adsorption of 98.8 % at contact time of 60 minutes. The optimum contact time for sample X was 120 minutes, while for sample Y and Z it was at 30 and 60 minutes respectively. The increase in Pb (II) ions removal with increase in contact time is due to the higher interaction between the adsorbent surface and metal ions, and after the equilibrium has been established there is no significant increase in metal ion removal. The result obtained agree with the report by Arifiyana and Devianti (2021) in which maximum adsorption capacity of banana peel adsorbent on Co (II) and Ni (II) are 36 and 25 % respectively.

Effect of Contact Time on Adsorption of Zn Ions

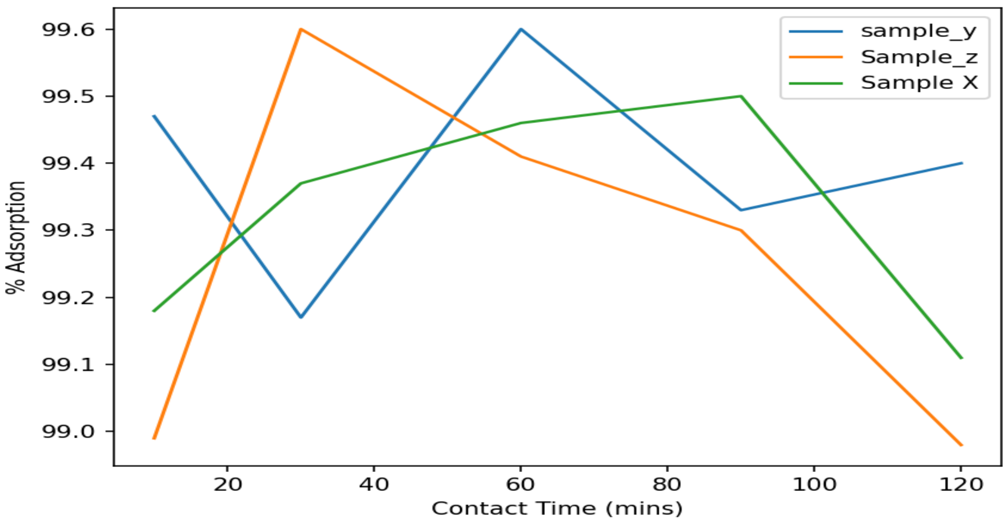

Figure 4: Effect of contact time on adsorption of Zn ions by chemically modified sample X, Y and Z with initial concentration 2 mg/L, at room temperature and pH 4

The effect of contact time on the adsorption of Zn ions was equally evaluated for initial zinc ions concentration of 2 mg/L at different contact time interval of between 10 – 120 minutes. The outcome of the plotted graph for this interaction were presented in Figure 4. The results obtained show that adsorption capacities of the three adsorbents increase as the contact time increases until equilibrium is established. The adsorption capacity of sample Z is 99.6 % at contact time of 30 minutes, while the adsorption capacity of sample Y is also 99.6 % but at a longer contact time of 60 minutes. Sample X has adsorption capacity of 99.5% at contact time of 80 minutes. The adsorption of the adsorbates on the active sites of the adsorbents continued until the active sites are saturated and at this point any further increase in the contact time will lead to decrease in adsorption capacities of the adsorbent (Li *et al*., 2016; Masindi and Muedi, 2018; Matei *et al*., 2019). The maximum adsorption of nano adsorbent for adsorption of Pb (II) and Zn metals reached 99.27 and 99.07 % at a contact time of 120 minutes as reported by Khairiah *et al*. (2021).

Effect of pH on Adsorption of Pb (II) Ions

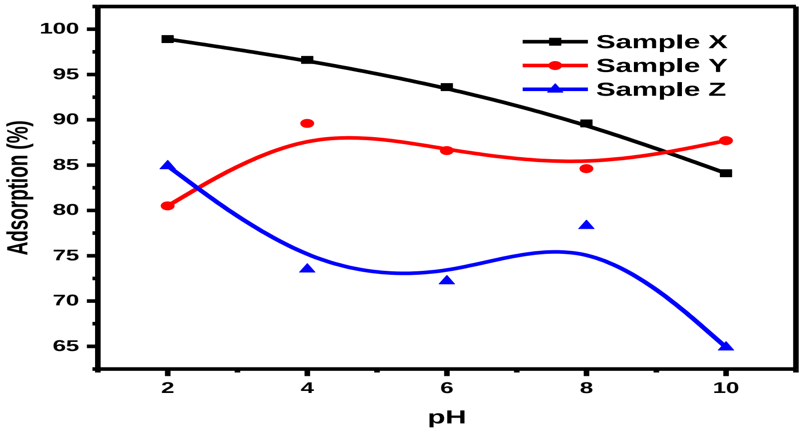

Figure 5: Effect of pH on adsorption of Pb (II) ions by chemically modified sample X, Y and Z with initial concentration 10 mg/L at room temperature and pH 4

The effect of pH on Pb (II) ions adsorption was evaluated with pH ranging from 2 to 10 at initial concentration of 10 mg/L, and the result of the adsorption process is displayed in Figure 5. From the result it was observed that pH of adsorbent can greatly affect adsorption process. Steady decrease in the adsorption of lead ions by sample X was observed with increase in pH of the solution. Maximum adsorption of lead ions by sample X was observed at lowest pH of 2, with adsorption removal rate of 99 %. The adsorption trend of sample Y was quite different as compared to other adsorbents, its increased from pH 2 to 4 and got to maximum adsorption of 88 % and then decreased slightly. Sample Z has its maximum adsorption as 85 % at the lowest pH 2. The optimum pH for sample Y and Z stands at pH 2, while sample X is at pH 4. This implies that low pH favours the electrostatic forces which regulate rate of the adsorption of heavy metal on adsorbent sites. In the same vein, the decrease observed after pH 2 and 4 is due to lowering of the attraction between the positively charged lead metal ions and the negatively charged adsorbent (Negara *et al*., 2019; Na *et al*., 2020; Mohd Dom *et al*., 2021). The result obtained tallies with those reported by Khairiah et al. (2021) in which optimum pH is 2.

Effect of pH on Adsorption of Zn Ions

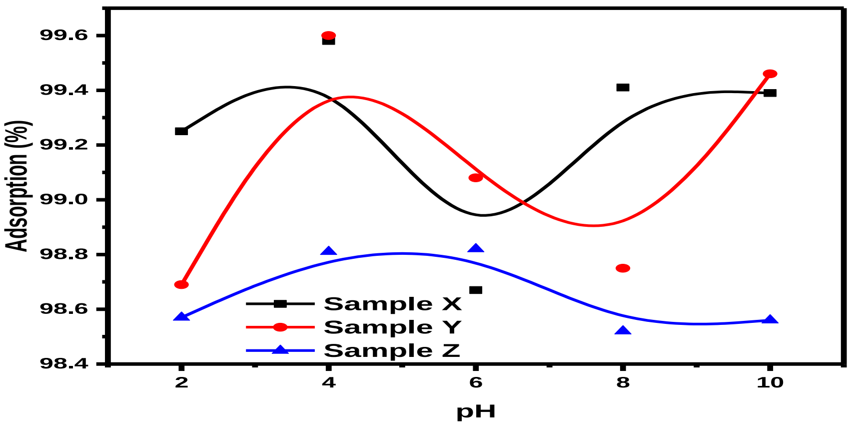

Figure 6: Effect of pH on adsorption of Zn ions by chemically modified sample X, Y and Z with initial concentration 2 mg/L at room temperature and pH 4

The adsorption process of zinc ions by sample X, Y and Z with initial concentration of zinc ions 2 mg/L presented in Figure 6, reveals that adsorption of Zn by sample X increase sharply from pH 2 to 4 and got to maximum adsorption of 99.4 %, while sample Y also has adsorption increase from pH 2 to 4 and maximum adsorption stands at 99.3 %. The adsorption trend of sample Z was relatively different compared to those of samples X and Y. Sample Z has maximum adsorption of 98.7% at pH 5. The three adsorbents show good adsorption efficiency. The optimum pH was 4 for sample X and Y while for sample Z it was 5. The variations observed in the adsorption efficiency of zinc and lead metals on the adsorbents is attributed to electrostatic forces that exist between the metallic ions and adsorbents (Prastuti *et al.*, 2019; Queiroz *et al.*, 2020). This conform with the result reported by Cecilia (2015) in which the maximum adsorption of banana peel adsorbent was 73.3 % at optimum pH 4.

Effect of Adsorbent Dose on Adsorption of Pb (II) Ions

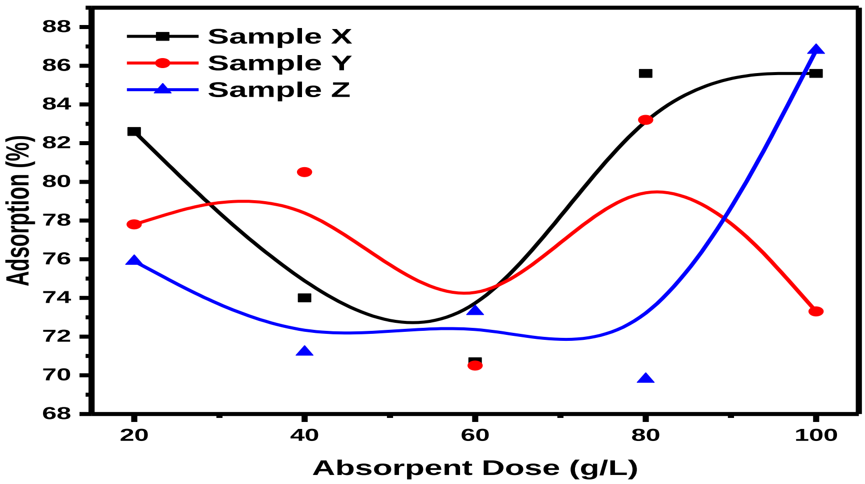

Figure 7: Effect of adsorbent dose on adsorption of Pb (II) ions by chemically modified samples X, Y, Z with initial concentration 10 mg/L at room temperature and pH 4

The effect of adsorbent dose on Pb (II) ions adsorption was carried out at initial concentration of 10 mg/L with adsorbent dose ranging 20 – 100 g/L. The obtained result is represented in Figure 7. From the result it was observed that the adsorption of Pb (II) ions by sample X decreases initially for adsorbent dose of 20 g/L and adsorption efficiency of 83 % and increased rapidly for adsorbent dose 50 g/L and then increase sharply until it got to maximum adsorption 85 % for the use of adsorbent dose of 90 g/L. For Sample Y, maximum adsorption was attained at 79 %, while sample Z was 87 % at adsorbent dose of 80 g/L and 100g/L respectively. The results obtained clearly show that when the adsorbent mass was increased, this resulted in an increase in the adsorption of the lead metal ions. The main reason for this is that as the adsorbent mass increases more adsorption sites are available per mass of adsorbent surface and thus the total amount of lead metal ions that is removed increases (Raza *et al.*, 2018; Rapa *et al.*, 2019). This result indicates that the adsorbent mass in the solution can affect the adsorption capacity for the removal of lead metals as it determines the availability of adsorption sites (Viena *et al.*, 2018). The result obtained in this study agreed with those reported by Negroiu et al. (2021b) in which the optimum dose banana peel was 80 g/L.

Effect of Adsorbent Dose on Adsorption Zn Ions

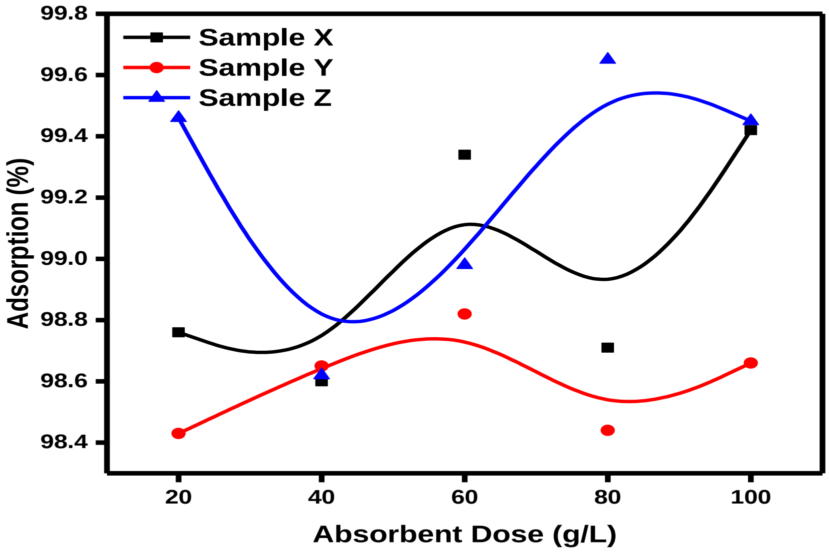

Figure 8: Effect of adsorbent dose on adsorption of Zn ions by chemically modified sample X, Y and Z with initial concentration 2 mg/L at room temperature and pH 4

The effect of adsorbent dose on zinc ions studied by varying adsorbent dose from 20 – 100 g/L with initial zinc ions concentration of 2 mg/L is presented in Figure 8. The result reveals that by the adsorbents have maximum adsorption efficiency of above 98%. Sample X has its maximum adsorption as 99.4% at adsorbent dose of 100 g/L while sample Y and Z has their maximum adsorption as 98.7 and 99.5 % at adsorbent dose of 60 g/L and 100 g/L respectively. The optimum adsorbent dose for zinc ion is 100 g/l for sample X and While sample Y has its optimum adsorbent dose of 60 g/L. This result is in agreement with those reported by Singh *et al*. (2020) in which recorded results show that the removal efficiency increases as the amount of absorbent dose increases.

CONCLUSION

The prepared standard zinc and lead metals concentrations of 2 mg/L and 10 mg/L of the two heavy metals were found to be considerably adsorbed by the three adsorbents. The adsorbents possess a very promising adsorption efficiency which can compete favourably with commercial adsorbents. The entire process was found to be cheaper than convectional approach resulting to low operating cost and mild condition of zinc and lead heavy metals adsorption. The adsorbents were found to be a good substitute for zinc and lead adsorption and the results obtained was very encouraging.

SUGGESTION FOR FURTHER STUDIES

There is need for further quantitative assessment of phosphoric acid modification of adsorbents using scientific models. Also, investigate other active chemical modification substance that can enhance better adsorption performance. Moreso, the best concentration of the modification agent, in order to obtain good and efficient adsorbent for optimal adsorption properties should be determined. More insight into the use of artificial intelligence (AI) in model development, prediction and optimization should be done.

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CONFLICT OF INTERESTS
The authors have stated that there are no conflict of interests in connection with this article.

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