

Removal of Heavy Metals from synthetic wastewater using Peanut Husk Charcoal, Fly ash and Zeolite as adsorbents

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Abstract—Present study reveals the adsorption behavior of some low cost adsorbents of biological origin such as peanut husk charcoal, of geological origin such as natural zeolite and of derived origin such as fly ash, with respect to removal of Cu^{2+} and Zn^{2+} ions, in order to consider their application for the purification of metal finishing wastewater. The study was performed using batch method and the parameters such as effect of adsorbent dose, pH, stirring rate, contact time, and initial metal concentration were studied. Increase in adsorbent dose showed increase in removal efficiency of metals due to increase in available surface area for adsorption. At a dose of 1.8g of PHC and zeolite 78.2% and 92.3% Cu was removed whereas in case of fly ash this dose was found as 2g with removal of 55%. For zinc removal the optimum values of adsorbent dose were found as 1.8g for PHC and 2g for fly ash and natural zeolite. The influence of the pH of the metal ion solutions on the uptake levels of the metal ions by the selected adsorbents used were carried out between pH 2 and pH 10. The optimum pH for copper removal was 6 in the case of peanut husk charcoal and natural zeolite, and it was 8 in case of fly ash. In case of removal of zeolite, optimum pH found were 8 in case of peanut husk charcoal and fly ash and 6 in case of natural zeolite. The results expressed that peanut husk charcoal, fly ash and natural zeolite all possess potential to remove cationic heavy metal species from industrial wastewater in the order fly ash < peanut husk charcoal < natural zeolite.

Keywords-Adsorbents, Copper, Fly Ash, PHC, Zeolite, Zinc

I. INTRODUCTION

Water pollution due to the disposal of heavy metals continues to be of a great concern worldwide. Consequently, the treatment of polluted industrial wastewater remains a topic of global concern since wastewater collected from municipalities, communities and industries must ultimately be returned to receiving waters or onto the land [1].

Heavy metals pollution occurs in much industrial wastewater such as that produced by metal plating industries, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries. This wastewater commonly possess Cd, Pb, Cu, Zn, Ni and Cr [2]. Whenever toxic heavy metals are exposed to the natural ecosystem by any means, accumulation of metal ions in human bodies will occur through either direct intake or food chains. Therefore, heavy metals should be prevented from reaching into the natural environment [3]. In order to remove toxic heavy metals from water systems, several conventional methods have been used such as chemical precipitation, coagulation, ion exchange, solvent extraction and filtration, evaporation and membrane methods [4]. Adsorption of heavy metals on conventional adsorbents such as activated carbon have been used widely in many

applications as an effective adsorbent, and the activated carbon produced by carbonizing organic materials is the most widely used adsorbent for removal of heavy metals. However, the high cost of the activation process limits the use of activated carbon in wastewater treatment applications [5].

Agricultural waste is one of the rich sources of low-cost adsorbents apart from industrial by-products and natural materials. Due to its abundant availability agricultural waste such as peanut husk, rice husk, wheat bran and sawdust offer very little economic value and, moreover, create serious disposal problems [6]. Activated carbons derived from peanut husk and rice husk have been successfully employed for the removal of heavy metals from aqueous solutions before. [7]. The use of peanut hull carbon for the adsorption of Cu(II) from wastewater was studied by Periasamy and Namasivayam [8]; their comparative study of commercial granular activated carbon (GAC) showed that the adsorption capacity of PHC was 18 times larger than that of GAC.

Fly ash is a waste material that is produced from the combustion of coal mostly in thermoelectric power plants [9–11]; many researchers have reused fly ash for wastewater or air pollutants control and studied the removal characteristics of heavy metal ions from aqueous solutions [12,13]. The adsorption characteristics of heavy metals using various particle sizes of bottom ash were studied by Shim et al. [14]. In another study, fly ash from a coal-fired power plant was used for the removal of Zn(II) and Ni(II) from aqueous solutions; fly ash proved to be effective as activated carbon for adsorption at higher dosages [15].

Table 1 Chemical composition of PHC

Elements	C	H	O	N	Ca	Na	K	Al	Fe	Si
% w/w	55	1	15.9	0.5	1.2	2.8	2.6	1	1	19

Natural materials locally available in certain regions can be employed as low-cost adsorbents due to their metal binding capacity. Zeolites are naturally occurring hydrated aluminosilicate minerals. Most common natural zeolites are formed by the alteration of glass-rich volcanic rocks (tuff) by fresh water in playa lakes or by sea water [16]. The structures of zeolites consist of three-dimensional frameworks of SiO^{4+} and AlO^{4+} tetrahedra. The fact that zeolite exchangeable ions are relatively innocuous (sodium, calcium and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. The adsorption behavior of natural zeolite (Clinoptilolite) with respect to Co^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} was studied by Erdem et al. [17]; the results show that natural zeolite can be used effectively for the removal of metal cations from wastewater. Besides, the adsorption behavior of formulated zeolite portland cement mixture for heavy metals removal efficiency was studied as a substitute for activated carbon for wastewater treatment [4,18]. Other researchers have studied arsenic adsorption and phosphate ions adsorption from aqueous solutions on synthetic zeolites [19,20].

The adsorption behavior of peanut husk charcoal, zeolite and fly ash with respect to Cu^{2+} , Zn^{2+} was studied by Salam et.al. [29] The objective of this work is to study the adsorption behavior of some low-cost adsorbents such as peanut husk charcoal, fly ash, and natural zeolite, with respect to Cu^{2+} and Zn^{2+} ions. The batch method was employed: parameters such as adsorbent dose, pH, stirring rate, contact time, and initial metal concentration, were studied.

II. MATERIAL AND METHODS

2.1. Preparation of adsorbents

Peanut husks were collected from the local market, after collection the husks were washed thoroughly to remove dust using distilled water then dried in an oven at 100 °C for 24 h, ground using a laboratory mill, sieved to 0.3–0.6 mm, and rinsed using 0.1 N HCl. Then the pH was adjusted with 0.1 N HCl at values (6–7). Finally, PHC was dried and stored in an oven at 80 °C till it attained constant density and humidity [7].

Fly ash was taken from the Dirk India PVT.LTD, Nashik, India. Fly ash samples were dried at 110 °C for 3 h before use for tests, and sieved to the desired particle size of 0.3–0.6 mm before use. Zeolite samples were taken from Gargoti Mineral Meuseum, Nashik, India. The zeolite was crushed and ground and passed through 0.3–0.6 mm sieves and was dried in an oven at 100 ± 5 °C for 24 h.

2.2. Characterization of adsorbents

The surface area of PHC was found equal to 485 m²g⁻¹; this value is much higher in comparison with other carbons, which are having a surface area about of 10–100 m² g⁻¹. The adsorption capacity of carbon is greatly characterized by chemical structure of its surface, which are of carbon– oxygen. Carboxyl groups, phenolic hydroxyl groups, carbonyl groups (e.g. quinone type), and lactone groups are suggested most often as functional groups [7]. The chemical composition of PHC is tabulated in Table 1, and the values are expressed in w/w.

The chemical composition of fly ash in bulk was measured using XRD; the results are tabulated in Table 2. The main components found were SiO₂, Al₂O₃, and Fe₂O₃ with others found in lower concentrations. The zeolites structurally consist of three-dimensional frameworks of SiO⁴⁺ and AlO⁴⁺ tetrahedra. The structures were characterized by X-ray diffraction (XRD) and chemical analysis [19]. Al₂O₃, Fe₂O₃, CaO, and MgO were analyzed by using titrimetric methods and SiO₂ was analyzed by a gravimetric method. Na₂O and K₂O were found using flame photometry. Results of chemical analysis are presented in Table 2.

2.3. Chemical and reagents

Stock copper solution: To 200.0 mg polished electrolytic copper wire in a 250-mL conical flask, 10 mL water and 5 mL conc HNO₃. After the reaction has slowed, it was warmed gently to complete dissolution of the copper and boiled to expel oxides of nitrogen, using precautions to avoid loss of copper. Cooled, added about 50 mL water, transferred quantitatively to a 1-L volumetric flask, and diluted to the mark with water; 1 mL = 200 µg Cu. (1000 mL = 200 mg of cu).

Stock zinc solution: 1000 mg (1.000 g) zinc metal was dissolved in 10 mL 1 + 1 HNO₃. Diluted and boiled to expel oxides of nitrogen. Diluted to 1000 mL; 1.00 mL = 1.00 mg Zn. (1000 mg/L).

Stock solutions of copper and zinc were used as adsorbate in the study, and solutions of different concentrations were obtained by diluting the stock solution with distilled water. Copper and zinc concentrations were determined by UV spectrophotometer (Elico SL210). All the chemicals used were of analytical grade reagent and all experiments were carried out in 500 ml glass jars at a room temperature of 27 ± 2 °C.

2.4. Methodology

Batch adsorption study was carried out by shaking a series of jars containing various amounts of different adsorbents with different adsorbent dosage varying from 0.2mg to 2.4 mg and heavy metal ions together at optimum pH, pH of the mixture was adjusted to the desired value using 0.1 N HCl and 0.1 N NaOH until the pH was stabilized. The mixture of different concentrations of aqueous solutions of copper and zinc with varied adsorbent dosage exclusively for both metals was agitated using mechanical stirrer at 27 ± 2 °C for one hour; at the end of mixing the adsorbent particles were separated from the suspensions by filtration through Whatman filter paper no.42. The residual concentration of heavy metals were determined by the UV spectrophotometer Model Elico SL210, Hyderabad, India. Apart from the adsorption tests, a set of blank tests was conducted to evaluate the removal by metal hydroxide precipitation at various pH values.

Studies were carried out for effect on heavy metal removal using different parameters like effect of adsorbent dose, pH, stirring rate, contact time, initial metal ion concentration etc.

III. RESULTS AND DISCUSSIONS

3.1. Effect of adsorbent dose

The results showed that by using any of selected adsorbents, copper and zinc were removed efficiently even at lower values of adsorbent doses and the removal efficiency increased gradually as the adsorbent dose was increased, but after certain value of adsorbent dose in each case further increase in dose could not show much variation in removal efficiency. Copper was removed at lowest values of adsorbents dosages as 23% by PHC, 11.5% by Fly Ash and 52% by Zeolite at a dose of 0.2g. And maximum adsorption could be seen at high adsorbent dose viz. 2.4 g as 78.2% by PHC, 55% by Fly Ash and 92.3% by Zeolite (fig.1) Values of adsorbent doses for further experimentation were chosen such that after these dose value no further significant removal efficiency could be seen. So for removal of copper the best suited values of adsorbent doses are selected for further work are as 1.8g for PHC, 2g for Fly Ash and 1.8g for Zeolite.

Similarly, in case of zinc, even at smaller adsorbent dose of 0.2g, zinc could removed from solution as 27% by PHC, 11% by Fly Ash and 29% by Zeolite. And at high dose of 2.4g the values obtained are 81.3% by PHC, 69% by Fly Ash and 91.7% by Zeolite (fig.2). Here also, adsorbent doses for further experimentation are chosen such that no significant improvement in zinc removal is observed after selected adsorbent doses. Therefore adsorbent doses for further experimentation in case of zinc removal were chosen as 1.8g for PHC, 2g for Fly Ash and 2g for Zeolite.

Table 2. Chemical composition of fly ash and natural zeolite.

Chemical composition (% w/w)		
Species	Fly Ash	Natural Zeolite
SiO ₂	89.56	45.09
Al ₂ O ₃	4.74	14.43
Fe ₂ O ₃	4.24	10.59
CaO	0.01	5.76
MgO	0.13	4.49

L.O.I.	0.8	14.49
Others	0.52	5.15

3.2.Effect of pH

The pH of the test solution shows a significant influence on the uptake of heavy metals since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate[11]. The results obtained are shown in Fig. 3 and 4 and show the effect of pH on the adsorption of Cu^{2+} , and Zn^{2+} ions from the aqueous solution onto the different adsorbents in terms of the metal ions removed percent. It is clear that Cu^{2+} , and Zn^{2+} ions were effectively adsorbed in the pH range (4–8), and the maximum adsorption of Cu^{2+} , and Zn^{2+} ions using peanut husk charcoal occurred at pH 6 and 8, respectively, while the maximum adsorption of Cu^{2+} and Zn^{2+} ions using fly ash occurred at pH 8, and the maximum adsorption of Cu^{2+} and Zn^{2+} ions using natural zeolite occurred at pH 6; thus, these pH values was chosen for further experimentation. These results are equivalent to results obtained by Rodda et al. [21] for heavy metal ions sorption onto agricultural waste sorbents.

The results in Fig. 3 and 4 show that the equilibrium capacity of copper and zinc removal by the different adsorbents increased significantly as the pH of the solution was increased. If the initial pH was too high, copper and zinc ions could precipitated out and this deflected the purpose of employing the sorption process as the sorption process is kinetically faster than the precipitation [5]. The adsorptive capacities of Cu^{2+} , and Zn^{2+} ions increased rapidly as the pH value of test solution was increased; at pH values above 6 the adsorptive capacities of Cu^{2+} and Zn^{2+} ions increased, but at a slower rate because of the competitive adsorption between hydrogen ion and the heavy metal cation [22]. This is in agreement with the results obtained by Periasamy and Namasivayam [23] for adsorption of Ni (II) from aqueous solutions onto peanut hulls.

3.3.Effect of contact time

The effect of contact time on the removal efficiency of PHC, fly ash and natural zeolites for removal of copper and zinc ions was studied by varying contact time from 30 minutes to 180 minutes: the results are shown in Fig. 2(a) and (b). The rate of uptake of metal ions was quite significant at the early timings i.e.in the first 30 min, using all three adsorbent, but was significantly higher in case of zeolite. Equilibrium was reached for copper and zinc removal within 2 h using peanut husk carbon and fly ash and within three hours using natural zeolite. This is in agreement with the results obtained by Sharma et al. [24] for remediation of chromium rich waters and wastewaters by fly ash using natural zeolite. This is in agreement with the results obtained by Sharma et al. [24] for remediation of chromium rich waters and wastewaters by fly ash.

3.4.Effect of stirring rate

The effect of stirring rate on the removal efficiency of PHC, fly ash and natural zeolite was studied by varying the stirring rate from 50 to 500 rpm. Results are enclosed in fig. 5 which reveals that equilibrium was achieved at rpm 350 for PHC and fly ash and at rpm 400 for zeolite in case of copper removal. On the other side maximum removal for zinc was observed at rpm 400 using PHC, for fly ash maximum removal of zinc occurred at 350 rpm and at 300 rpm by using zeolite.

3.5.Effect of initial metal concentration

The effect of initial metal i.e. copper and zinc ion concentration on copper and zinc removal was studied by batch adsorption experiments, which were carried out at 27 ± 2 °C using

different initial metal ion concentrations (10, 20, 40, 60, 80 and 100 mg/l) at experimentally chosen optimum pH values and rpm 200. which indicate that the percentage removal decreases with the Increase in initial metal ion concentration showed decrement in removal of metal ions.(fig. 13 and 14) This is because there were no more adsorption sites on the adsorption surface of the adsorbent material. The maximum removal of Cu using natural zeolite was 92.8% at copper ion concentration 10 mg/l, and the maximum removal of zinc using natural zeolite was 93.5% at a metal concentration 10 mg/l. This is in agreement with the results obtained by Ragheb et al. [25] for heavy metals removal by low-cost adsorbents.

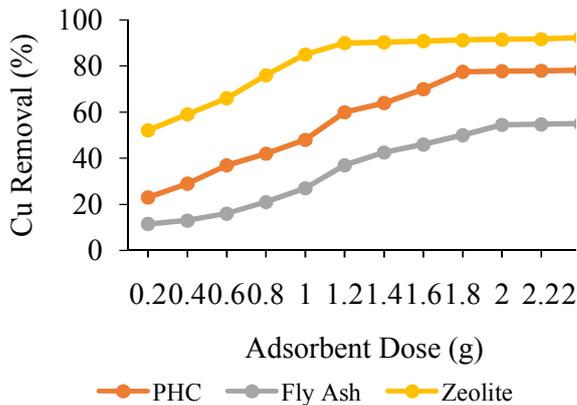


Figure 1: Comparative graph for effect of adsorbent dose (g) on Copper removal (%) (Initial concentration of Cu-10 mg/l)

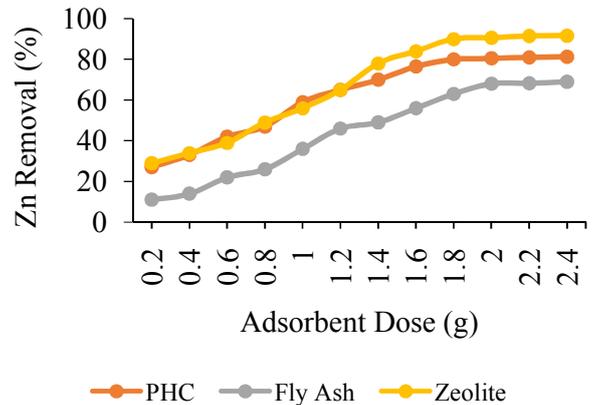


Figure 2: Comparative graph for effect of adsorbent dose (g) on Zinc removal (%) (Initial concentration of Zn-10 mg/l)

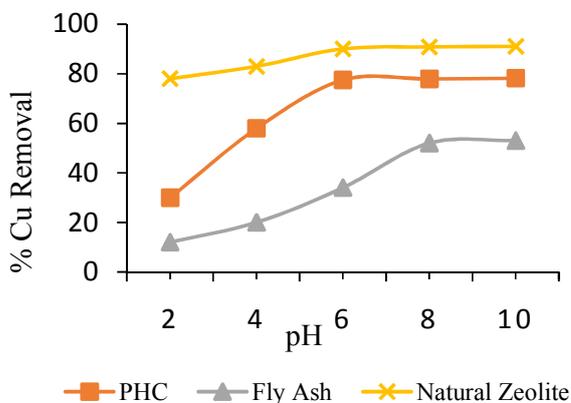


Figure 3: Comparison of effect of pH on removal of Copper using adsorbents like peanut husk charcoal (PHC), Fly Ash and Natural Zeolite.

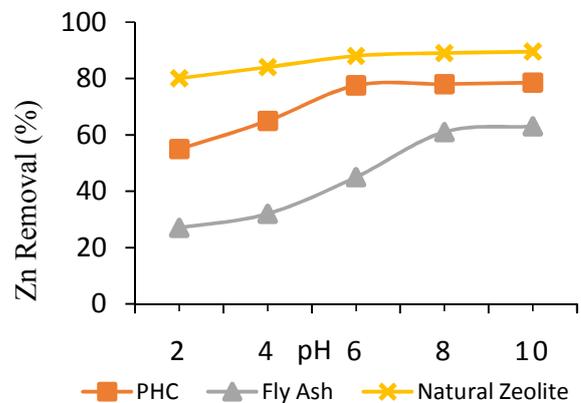


Figure 4: Comparison of effect of pH on removal of Zinc using adsorbents like peanut husk charcoal (PHC), Fly Ash and Natural Zeolite.

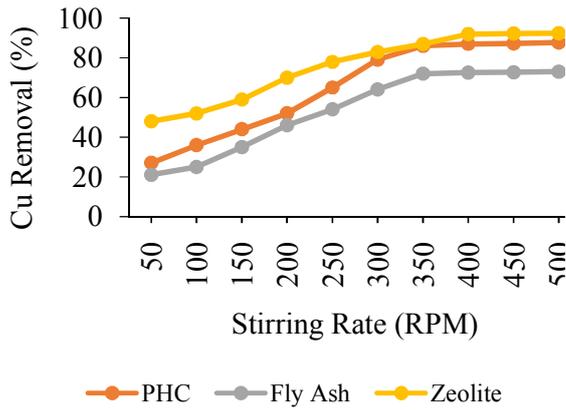


Figure 5: Comparative graph of effect of stirring rate on removal of Cu (Initial Cu Concentration -10mg/L)

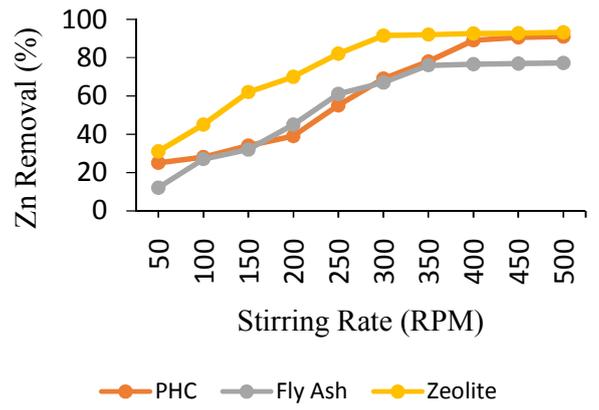


Figure 6: Comparative graph of effect of stirring rate on Zn Removal (Initial Zn Concentration - 10 mg/L)

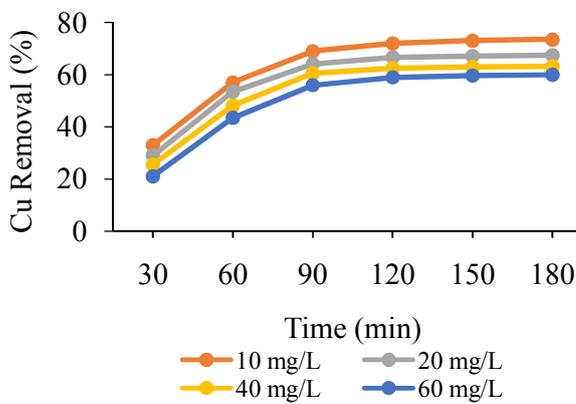


Figure 7: Effect of contact time on removal of Copper for PHC

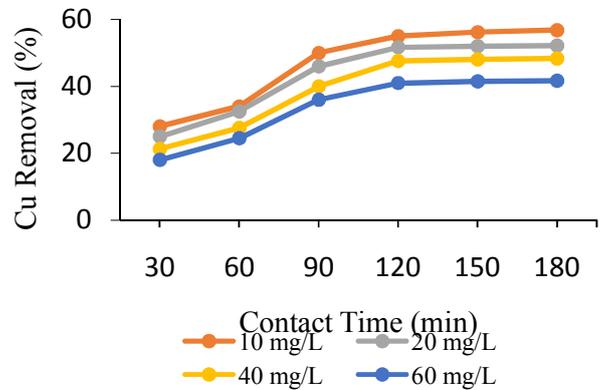


Figure 8: Effect of contact time on removal of Copper for Fly Ash

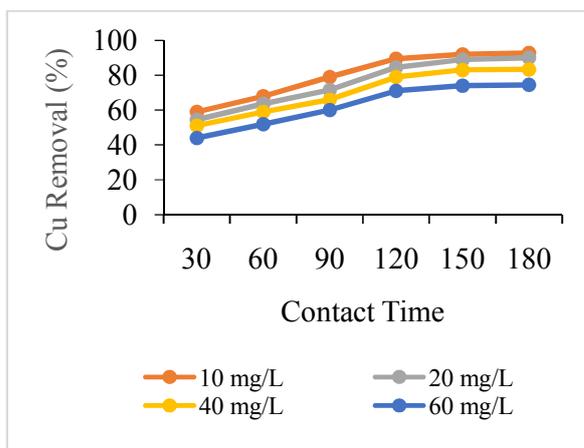


Figure 9: Effect of contact time on removal of Copper for Zeolite

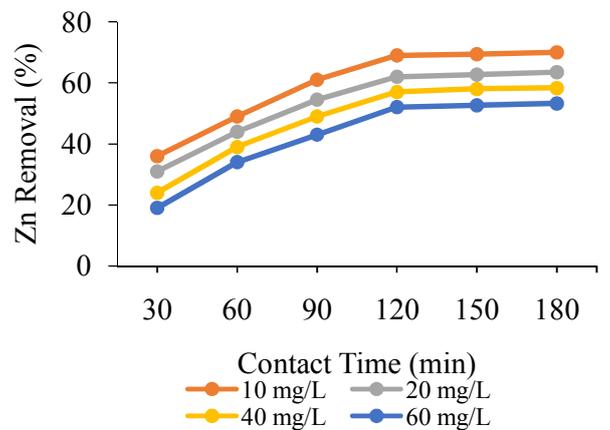


Figure 10: Effect of contact time on removal of Zinc for PHC

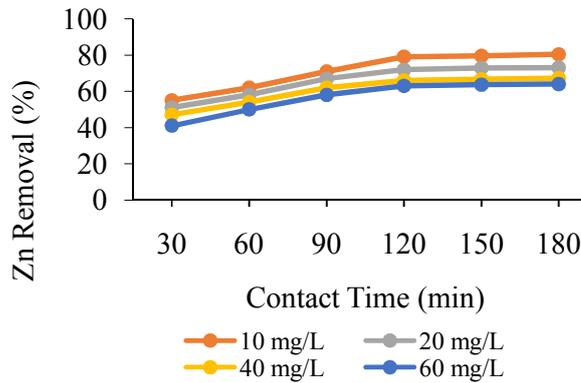


Figure 11: Effect of contact time on removal of Zinc for Fly Ash

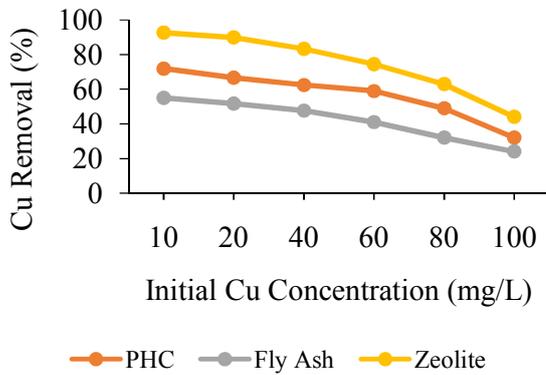


Figure 13: Comparative graph of effect of Initial Cu Concentration on Removal of Cu

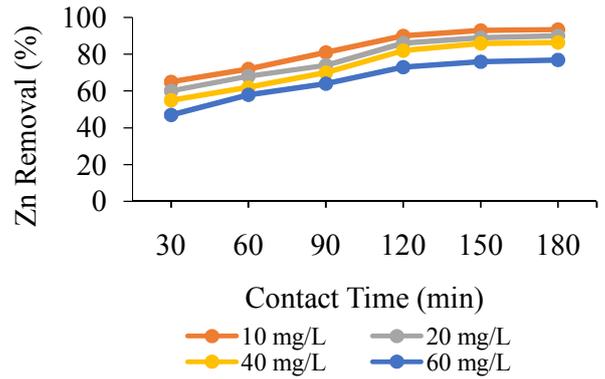


Figure 12: Effect of contact time on removal of Zinc for Zeolite

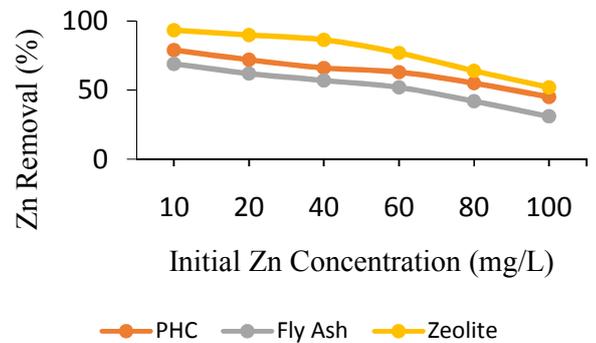


Figure 14: Comparative graph of effect of Initial Zn Concentration on Removal of Zn

IV. CONCLUSION

Low-cost adsorbents of biological, geological and derived origin like peanut husk charcoal, natural zeolite and fly ash are effective for the removal of Cu^{2+} and Zn^{2+} ions from aqueous solutions. The batch method was employed; parameters such as adsorbent dose, pH, stirring rate, contact time, and initial metal concentration were studied at an ambient temperature $27 \pm 2^\circ\text{C}$. The optimum dose for removal of Copper was found to be 1.8g in case of PHC and zeolite and 2g in case of fly ash, whereas its value was found as 1.8g in case of PHC for removal of zinc and 2g in case of fly ash and zeolite for removal of the same. The optimum pH corresponding to the maximum adsorption of copper and zinc removal was 6–8. Copper and zinc ions were adsorbed onto the adsorbents very rapidly within the first 30 min, while equilibrium was attained within 2–3 h for copper and zinc ions using all three adsorbents. Adequate stirring rate was found between 300–400 rpm for both the metals using all the three adsorbents. Hence all the three adsorbents can be fruitfully used to remove cationic heavy metal ions such as copper and zinc.

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