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Phosphorus removal through adsorption on locally prepared adsorbents

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Abstract

Adsorbents were prepared from animal bones to adsorb phosphate from its aqueous solution. Samples were carbonised at 850^{o}C in the muffle furnace and activated separately with three different activating chemicals namely KOH, H_3PO_4 and $ZnSO_4$. The work compares the activating efficiencies of different chemicals, the effect of contact time and particle sizes on the equilibrium sorption.The results show that within the first five minutes of the process, the removal efficiencies of the 0.5mm particle size adsorbents that were activated with H_3PO_4, KOH and $ZnSO_4$ were 49.93%, 48.64% and 47.42% respectively while those 0.8mm particle size adsorbents of the same order of activating chemicals were 49.64%, 47.13% and 45.63% respectively.

1. Introduction

Surface waters contain certain level of phosphorous in various compounds, which is an important constituent of living Organisms. However, the excessive release of phosphorous into the receiving waters such as lakes, rivers and streams promotes the growth of algae (eutrophication) and other undesirable vegetation (Song et al.,2000). The phenomenon of eutrophication usually prevents the recreational use of water due to the resulting obnoxious odours on decaying and, in addition the waters may be toxic to aquatic, domestic and wild animals (Design Manual, 1987).The load of phosphorous discharged due to receiving waters comes from various groups of sources of which the main sources are agricultural use of fertilizers, domestic and industrial waste waters and atmospheric deposition.

Treating or purifying these waste waters involves a number of unit processes depending on the quality of the water source, affordability and existing guidelines or standards(Jenkins et al.,1971). The cost involved in achieving the desired level of treatment depends among other things,on the cost and availability of chemicals.Commonly used chemicals for the various treatment units are synthetic organic and inorganic substances such as aluminium and iron salts, limes, polyelectrolytes e.t.c(Ueda et al.,1996). In many places these are expensive and they have to be imported in hard currency. Many of the chemicals are also associated with human health and environmental problems(Jenkins et al.,1971) and a number of them have been regulated for use in water treatment systems. Natural materials can minimize or avoid the concerns and significantly reduce treatment cost if available locally. This work, therefore presents a study on the use of natural materials for adsorbing phosphate from its solution in an adsorption column.

2. Materials and Methods

2.1. Activated carbon from animal bones

Animal bones were collected from open market opposite Anambra State University, Uli campus. The bones were scrapped and washed with water to remove dirts and other impurities after which they were cut and ground before exposing it to sunlight for four weeks so as to reduce the moisture content. The sample was further dried in an oven at a temperature of 110^{o}C for two hours before it was introduced into the hot zone of the muffle furnace for charring. The furnace temperature was increased at a temperature of 10^{o}C/min from room temperature to 800^{o}C and was held at this temperature for 3hrs. The charred product was allowed to cool down to room temperature, ground to workable size and sieved(Okeola,1999;Gimba,2001;Lyman,1978) size fraction of 0.5mm and 0.8mm were used.The next step involved purification of the sample in 0.5M hydrochloric acid solution followed by rinsing with

distilled water to remove the excess acid. The sample was then dried in the oven at 110^{o}C for one hour(Okeola,1999). Activation of samples was carried out using orthophosphoric acid (H_3PO_4); Potassium hydroxide(KOH) and Zinc Sulphate($ZnSO_4$) separately as activating agents. 25.0g of each of the size fractions was put in separate beakers containing 500cm^3 of 1.0M solution of activating reagent. The content of the beaker was thoroughly stirred and left for three hours before rinsing in deionized water to remove excess acid.Finally, the rinsed samples were dried overnight in an oven at 110^{0}C, cooled at room temperature and packed in an air tight sample bag until use.

2.2. Determination of the pH of the adsorbent

5.0g of each of the samples was measured into a beaker and 100ml of distilled water was added to each of the samples. The mixture was manually well shaken and was left in the laboratory at room temperature for four days, after which the liquid was decanted and the pH of the aliquot was measured using hand pH meter.

2.3. Adsorption experiments

Adsorption experiments were carried out in a 50cm^3 capacity burette as alternative to adsorption column. The burette was blocked at the bottom with cotton wool and filter paper to disallow the passage of granules of the adsorbent with the effluent. 5.0g of the adsorbents was put into the column(burette) and was filled with distilled water. The valve was adjusted to fix the rate of flow and the water was allowed to drain out of the column. Phosphate solution was prepared from the phosphate rock, which was obtained from Federal Superphosphate Fertilizer Company, Kaduna and was added into the column. At every five minutes interval, the effluent was sampled and its concentration checked using U.V spectrophotometer model spectrumlab 752S set at wavelenght of 650mm. Constant dosage of the adsorbents was used throughout the experiment and and the effects of the contact time, particle sizes and different activating agents were studied.
The removal efficiency (E) of the adsorbent on phosphate was defined as
$E(\%)= [(C_o-C_1)/C_o] \times 100$
Where C_o and C_1 are the initial and final concentration of phosphate in the influent and effluent solution (mg/l) respectively.

3. Results and discussion

3.1. Effect of contact time

From the obtained results presented in the table of results (table1-8) and (Figures 1 and 2) it was observed that within the first five minutes of the process, close to 50% of the initial phosphate concentration (C_o=1396mg/l) was adsorbed but as time passed, the efficiency began to decrease.
This may be due to the fact that, initially the active sites of the adsorbents were fresh, so much of the solutes could be adsorbed very fast but as the sites are gradually becoming saturated with the adsorbates, the solute started escaping the surface of the adsorbent into the effluent solution thereby bringing about an increase in phosphate concentration in the effluent. In addition, high influent concentration might be another contributory factors as adsorption process is more suitable for purification of the solution with low concentration of pollutants (Metcalf and Eddy,2003).
Also, the nature of the phosphate rock which may contain trace elements and other impurities could lead to competitive adsorption (Manning and Goldberg, 1977). It was also interesting to observe that there were no significant variations between the results obtained for the effluent concentration at the set time intervals. The column capacity (50cm^{3}burette) and the fluid flow rate that could not be accurately controlled might be responsible for such effects.

3.2. Effect of particle size on sorption

Size fractions of 0.5mm and 0.8mm were used in this study. 0.5mm particle size adsorbents,(table1,3,5 and 7)and(Figures 1 and 3)owning to the large surface area of their pores, were found to be higher in efficiency than the 0.8mm particle size adsorbents(Table 2,4,6,8)and(Fig.2,3).The observation is similar in the case of all the four adsorbents used in this work.

3.3. The activating efficiency of different chemicals on the adsorbent

The adsorbents activated with orthophosphoric acid (H_3P0_4)(Table 1,2) show greater removal efficiency than those activated with $ZnSO_4$ (Table 3,4)and KOH (Table 5,6)respectively including C.A.C.(Table 7,8). The reason may be partly due to the fact that orthophosphoric acid is both a strong acid and an oxidizing agent. Thus, it may be able to open up and enlarge pores in the carbonized samples better than either $ZnSO_4$ or KOH. However, the adsorbent that was activated with KOH showed the least removal capability probably due to its high alkalinity nature.

4. Conclusion

The results obtained from this work show that adsorbents developed from common animal waste can be effectively used for adsorption of phosphate from its aqueous solution.

It was also observed that low cost adsorbents especially those activated with orthophosphoric acid have the potential to be economically viable in the treatment of waste waters with low concentration of pollutants where the discharge of such could create a problem in the receiving waters.

5. Nomenclature

C_o : Initial influent concentration of phosphate solution (mg/l)
C_1 : Final effluent concentration of phosphate solution (mg/l)
C : Concentration of the adsorbate (mg/l)
CAC : Commercial activated carbon.

6. Acknowledgement

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The results obtained in this work are as follows:

Table 1
Effect of contact time on phosphate removal
Particle size-0·5mm; Activating agent-H_3PO_4; pH of solution-7.6

S/N	t(mins)	C_1(mg/l)	C(mg/l)	E %
1	5	699	697	49·93
2	10	703	693	49·64
3	15	707	689	49·35
4	20	713	683	48·93
5	25	721	675	48·35
6	30	728	668	47·85
7	35	732	664	47·56
8	40	737	659	47·20
9	45	739	657	47·06
10	50	742	654	46·85
11	55	743	653	46·77
12	60	744	652	46·70

Table 2
Effect of contact time on phosphate removal
Particle size:0·8mm; Activating agent:H_3PO_4; pH of solution:7·6

S/N	t(mins)	C_1(mg/l)	C(mg/l)	E %
1	5	703	693	49·64
2	10	711	685	49·07
3	15	716	680	48·71
4	20	719	677	48·49
5	25	724	672	48·13
6	30	732	664	47·56
7	35	736	660	47·28
8	40	743	653	46·77
9	45	746	650	46·56
10	50	751	645	46·20
11	55	756	640	45·84
12	60	756	640	45·84

Table 3
Effect of contact time on phosphate removal
Particle size: 0·5mm; Activating agent: Z_nSO_4; Solution pH:7·6

S/N	t(mins)	C_1(mg/l)	C(mg/l)	E %
1	5	710	686	49· 14
2	10	723	673	48· 20
3	15	737	659	47· 20
4	20	739	657	47· 06
5	25	740	656	46· 99
6	30	743	653	46· 77
7	35	745	651	46· 63
8	40	749	647	46· 34
9	45	753	643	46· 06
10	50	757	639	45· 77
11	55	764	632	45· 27
12	60	762	634	45· 41

Table 4
Effect of contact time on phosphate removal
Particle size: 0·8mm; Activating agent: Z_nSO_4; Solution pH:7·6

S/N	t(mins)	C_1(mg/l)	C(mg/l)	E %
1	5	712	684	48 · 99
2	10	720	676	48 · 42
3	15	726	670	47 · 99
4	20	732	664	47 ·56
5	25	740	656	46 · 99
6	30	747	649	46 · 49
7	35	751	645	46 · 20
8	40	756	640	45 · 84
9	45	760	636	45 · 55
10	50	764	632	45 · 27
11	55	773	623	44 · 63
12	60	774	622	44 · 55

Table 5
Effect of contact time on phosphate removal
Particle size: 0·5mm; Activating agent: KOH; Solution pH:7·6

S/N	t(mins)	C_1(mg/l)	C(mg/l)	E %
1	5	717	679	48 · 64
2	10	729	667	47 · 78
3	15	730	666	47 · 70
4	20	756	640	45 · 85
5	25	763	633	45 · 34
6	30	766	630	45 · 13
7	35	772	624	44 · 69
8	40	776	620	44 · 41
9	45	779	617	44 · 19
10	50	781	615	44 · 05
11	55	782	614	43 · 98
12	60	783	613	43 · 91

Table 6:
Effect of contact time on phosphate removal
Particle size: 0·8mm; Activating agent: KOH; Solution pH:7·6

S/N	t(mins)	C_1(mg/l)	C(mg/l)	E %
1	5	738	658	47 · 13
2	10	751	645	46 · 20
3	15	752	644	46 · 13
4	20	773	623	44 · 62
5	25	779	617	44 · 19
6	30	782	614	43 · 98
7	35	788	608	43 · 55
8	40	792	604	43 · 27
9	45	794	602	43 · 12
10	50	795	601	43 · 05
11	55	796	600	42 · 98
12	60	796	600	42 · 98

Table 7
Effect of contact time on phosphate removal
Particle size: 0·5mm; Activating agent: CAC; Solution pH:7·6

S/N	t(mins)	C_1(mg/l)	C(mg/l)	E %
1	5	734	662	47 · 42
2	10	742	654	46 · 85
3	15	745	651	46 · 63
4	20	747	649	46 · 49
5	25	752	644	46 · 13
6	30	757	639	45 · 77
7	35	760	636	45 · 55
8	40	763	633	45 · 34
9	45	766	630	45 · 13
10	50	768	628	44 · 98
11	55	769	627	44 · 91
12	60	771	625	44 · 77

Table 8
Effect of contact time on phosphate removal
Particle size: 0·8mm; Activating agent: CAC; Solution pH:7·6

S/N	t(mins)	C_1(mg/l)	C(mg/l)	E %
1	5	759	637	45· 63
2	10	767	629	45· 05
3	15	770	626	44· 84
4	20	771	625	44· 77
5	25	773	623	44· 62
6	30	775	621	44· 48
7	35	778	618	44· 26
8	40	781	615	44· 05
9	45	785	611	43· 76
10	50	790	606	43· 40
11	55	791	605	43· 34
12	60	792	604	43· 26

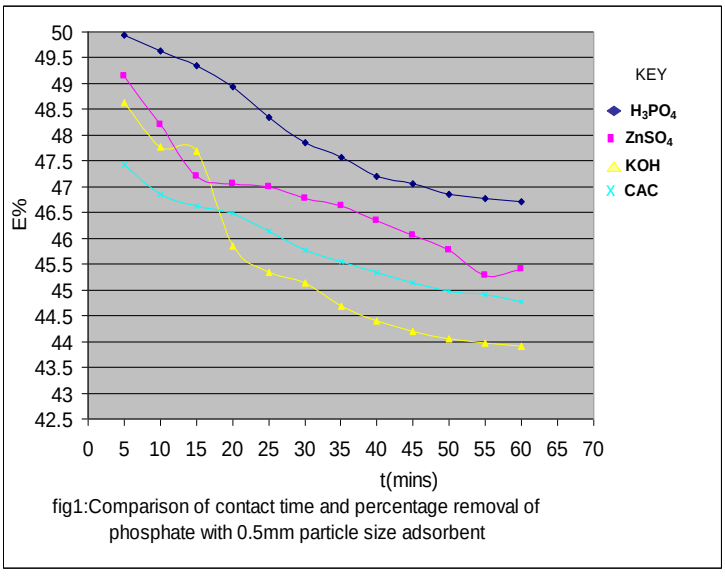


fig1:Comparison of contact time and percentage removal of phosphate with 0.5mm particle size adsorbent

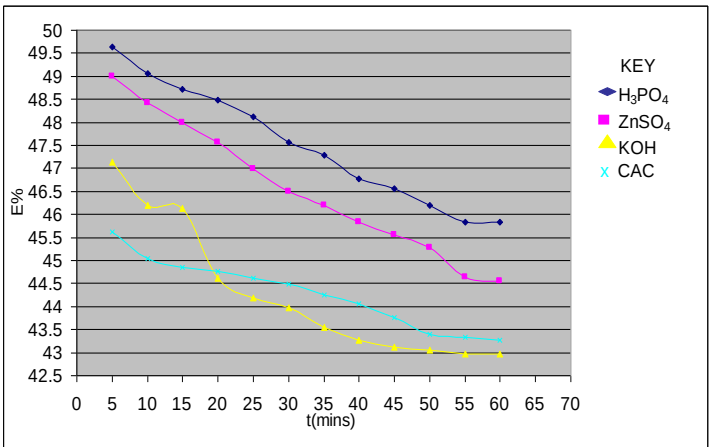


fig2:Comparison of contact time and percentage removal of phosphate with 0.8mm particle size adsorbent

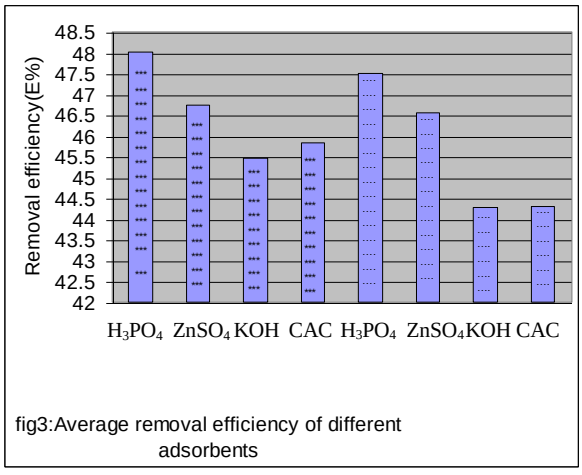


fig3:Average removal efficiency of different adsorbents