Adsorption of phosphate from aqueous solution by marble dust

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Abstract— A simple and economic experimental sorption procedure is developed for efficiency removal of phosphates from aqueous solution using experiments batch system. Many experiments were conducted to use marble in powder form which collected from the workshop was used to adsorption phosphate PO_4^{3-} from aqueous solution. Equilibrium concentration has been measured using distribution coefficient to evaluate the removal efficiency. The PO_4^{3-} adsorption experiments were carried out to analyze the influence of governing factors such as pH of the solution, mass of marble dust MD, initial PO_4^{3-} concentration, temperature and contact time, on the adsorption efficiency of PO_4^{3-}. The equilibrium test showed that, the sorption efficiency depended on the pH of the solution. The adsorbed of PO_4^{3-} increased with range (pH 5.0 - 6.5). It was found that the maximum adsorption capacity of MD for removing of PO_4^{3-} reached to 13.68 mg g^{-1} and 13.57 mg g^{-1} at pH 6.0 and 6.5 respectively.

Keywords— marble, phosphate, adsorption, removal, water, pH value, batch system

introduction

Phosphorus is the most abundant element on the surface of the earth, and its common compounds are abundant in phosphates, which exist in water system naturally by dissolving out of igneous rock, anthropogenic activities and the environmental practices of industries and agricultural practices through the use of large quantities in fertilizers [1], detergents [2] and some other industries [3]. PO_4^{3-} plays an important role in biochemical processes as well as enriching surface water [4]. The excess of phosphate into the water bodies causes a significant low of oxygen and excessive growth of algae [5] which causes of environmental system for plants that need oxygen. Some studies confirmed that the exposure to high concentration of PO_4^{3-} cause chronic kidney disease and cardiovascular [6-8].Various technologies are employed for removing PO_4^{3-} from polluted waters such as HFeO [9] Mg-laden biochar synthesized at different temperature [10], lanthanum-modified zeolites [11]. Many previous studies used low-cost material which requires little processing, ,abundant in nature, or a by-product or waste material from another industry such as shale, sandstone, and laterite [12]. Electrochemical removal is one of the most procedural for removing PO_4^{3-} by using Electrocoagulation as a green technology [13, 14].

Various Mesoporous sorbent materials, including metal-coordinated amino-functionalized silicas, ammonium-functionalized silicas [15] and ,6-amine–functionalized copper ferrite [16] have a strong affinity for removing phosphate. Oxide as Fe_3O_4, nanocomposite of titanium oxides and magnetite core/zirconia is expensive, available and chemically stable over a wide pH range. Many previous studies [17-20] confirmed that the oxides have high sorption affinity toward phosphate. The use of natural sorbent material of the removal contaminated substance such as activated carbon, clay. Zeolite, vegetal cords, carp scales, [21-24] which give promises results with low cost technologies. The use of the those natural or recycled materials in the removal of PO_4^{3-} such as seashell, biochar, proteins, cotton stalk, steel byproduct [25-28] provide high adsorption capacity without additional cost. One of the sorbent materials which give high capacity in the removal of PO_4^{3-} from aqueous is marble dust MD as a natural material, which produced from crashing and cutting of the founded marble block, where the main component is calcium which has good affinity for bonding with PO_4^{3-}ions as conception to form of amorphous calcium phosphate $Ca_2(PO_4)_2$, dibasic calcium phosphate $CaHPO_4 .2H_2O$

, and $Ca_5(PO_4)_3OH$ [29]. A simplified scheme of the MD process (chemical sorption) based on the activity of Ca^{2+} is presented in fig.1

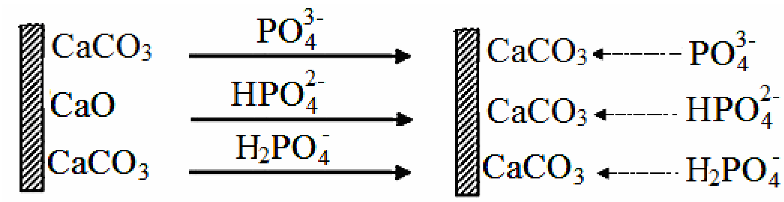

Fig.1. Scheme of the sorption of PO_4^{3-} on the surface of MD

This research reports the use of marble dust as natural sorbent materials, inexpensive and easy to find to remove $PO_4^{3-}$from aqueous solution by forming insoluble metal phosphate.

EXPERIMENTAL PROCEDURES

Materials

In this experimental work, the following chemicals were used: sodium dihydrogen phosphate KH_2PO_4 p.a Aldrich (Munich, Germany); HNO_3 p.a sigma; NaOH p.a Merck; Ammonium molybdate , ascorbic acid ; Stannous chloride $SnCl_2$ p.a Merck.

Phosphate

A stock solution of PO_4^{3-} (1000 mgL^{-1}) was prepared by dissolving 1.43g of sodium dihydrogen phosphate KH_2PO_4 in 1L: volumetric flask with deionized water.

Method for the determination

The concentration of PO_4^{3-} before and after adsorption was analyzed with ammonium molybdate method by using a CO7500 Colorimeter (WPA UK)

Physical and chemical properties of MD.

The marble powder used in this study was collected from marble workshop considered as refused material. The chemical and physical properties are listed in Table 1.

Table 1. Physical and Chemical Properties of Marble Powder

Chemical Composition		Physical Properties	
Test	**Mass %**	**Test**	**Unit**
Loss on ignition	39.05	Moisture 0.036	%
Calcium Carbonate	98.61	Particle Size <300	micron
Magnesium Carbonate	0.59	Density 1.42	g/cm^3
Calcium Oxide	55.16		
Silicon Oxide	1.09		
Aluminum Oxide	0.69		

The MD was used in this experimental work without any further preparation.

Method of sorption process

The phosphate sorption process was investigated in the batch system, a vessel used was 500mL glass beaker holding of the PO_4^{3-} solution, with a range (0.5 mgL^{-1} – 15 mgL^{-1}) concentration of 100 ml of solution, a shaker speed used to distribute the MD into solution at 25 C°,30 C°, and 40 C° was 120 rpm, the pH of solutions were conducted within range (pH 3.0 to pH 8.0), the mass of MD was varied from (0.5g to 5.0g) and the contact time was constant (90min).

The following equation was used to evaluate the sorption capacity:

$$q = \frac{C_i - C_f}{m} V$$

Where:

q : sorption capacity, mg/g.

C_i : initial PO_4^{3-} concentration, mgL^{-1}

C_f : final PO_4^{3-} concentration, mgL^{-1}

m : mass of MD, g.

V : volume of solution, L.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH value of aqueous solution contaminated with PO_4^{3-} on the adsorption capacity was studied. The conditions of the procedure were: pH value was varied pH 3.0 to pH 8.0, mass of MD (m=1.0 g), concentration of PO_4^{3-} (15 mgL^{-1}), temperature (room temperature), volume of solution (V= 100 mL), shaker speed (120 rpm), and contact time (90 min) was constant.. The efficiency of phosphate adsorbed on MD is calculated for each pH value. The mass of PO_4^{3-} removed from aqueous solution is presented in fig.2.

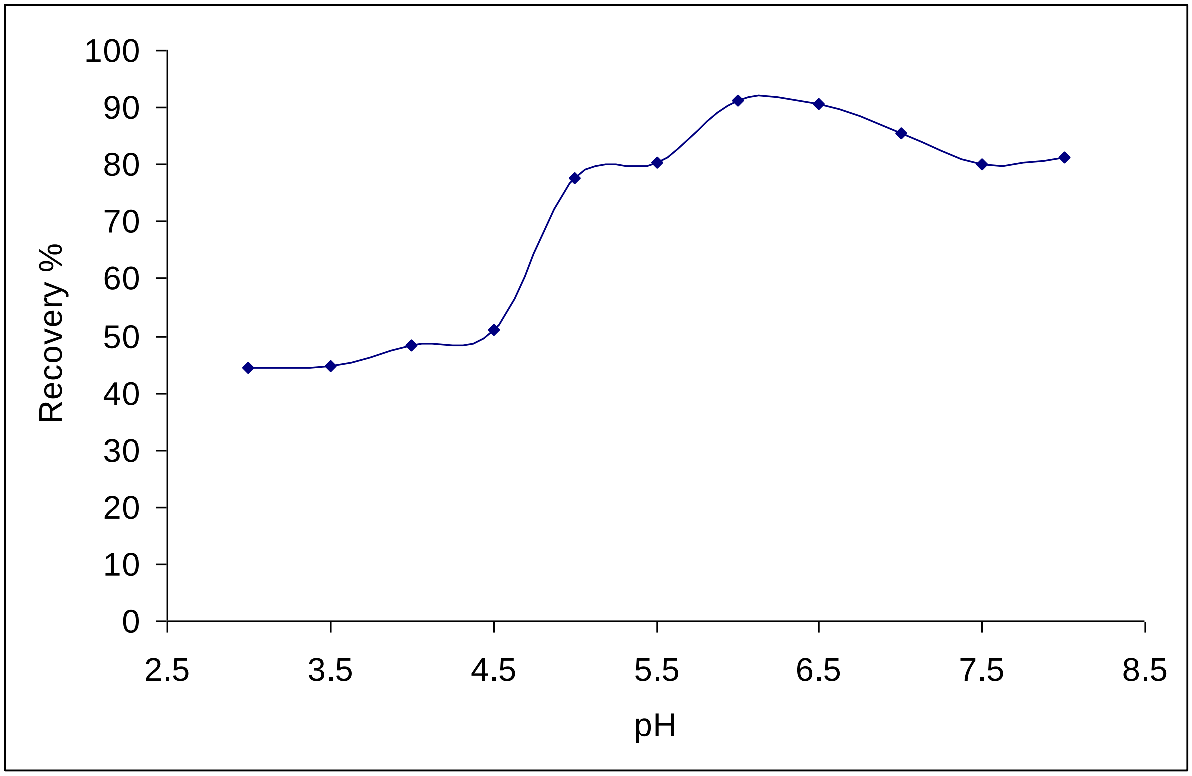

Fig.2 The effect of pH on removing PO_4^{3-} by using MD

The fig.2 showed that the adsorption of PO_4^{3-} by using MD is affected by pH value, the PO_4^{3-} is highly sensitive to the change in pH. At low pH value 3.0 to 5.0 (acidic media) the removal capacity up to 50% , while at pH 4.5-6.0 up to 80% .The optimal pH for MD is 5.5 and 6.5, at this pH value the MD has excellent efficient reached to 91.0% . At higher pH value the Ca-MD is consumed in the form of hydroxides $Ca(OH)_2$

Effect of MD mass

Elucidate the effect of the mass of MD on adsorption capacity was studied and presented in fig.3, the procedures were carried out following the standard experimental, pH of the solution was constant 6.0, concentration of PO_4^{3-} (0.5, 1.0, 5.0, 10, 15 mgL^{-1}), volume of solution (V=100 mL), temperature (room temperature), time of contact (90 min), shaker speed(120 rpm) and mass of MD was varied between (0.5g and 5.0 g). For each mass of MD the capacity of PO_4^{3-} adsorbed (in %) and bonded to the MD is calculated and presented.

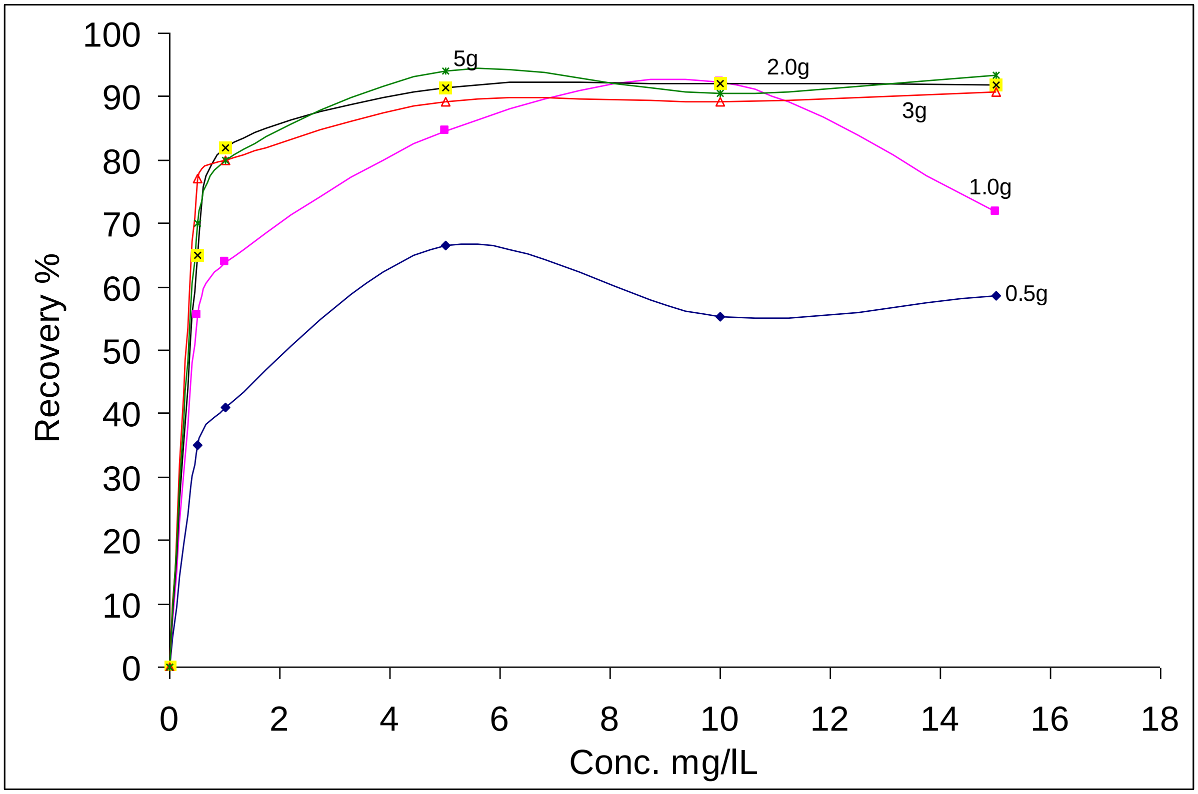

Fig. 3 Adsorption capacity of MD for PO_4^{3-} at various masses

Fig.3 shows the results of influence of MD mass on adsorption of PO_4^{3-}. The PO_4^{3-} adsorption efficiency increased with the mass of MD increase , 58% at 0.5g of MD , 93.5% at 5.0 g, while the adsorbed capacity was approximately the same it were, 91.5%, 89% and 94% at 2.0g, 3.0g, 5.0g respectively. In this case the concentration of PO_4^{3-} was 10 mg L^{-1}.

Effect of temperature

The influence of temperature on the adsorption of PO_4^{3-} was studied at temperature rang (20 °C to 35 °C) . The results are shown in fig.4. Removal of PO_4^{-3} was conducted using the following condition: the concentration of PO_4^{3-} (10 mgL^{-1}), mass of MD (m= 2.0g), pH of the solution (pH 6.0), volume of solution (V=100 mL), shaker speed (120 rpm) and contact time (90 min).

The result shows that the adsorption capacity of MD with respect to PO_4^{-3} was good recoveries at 25°C and 30 °C , while the adsorption capacity shows acceptable affinity at 35 °C due to dissolving of calcium carbonate and calcium phosphate with increase of temperature, where the solubility of PO_4^{3-} is dependent of pH of solution.

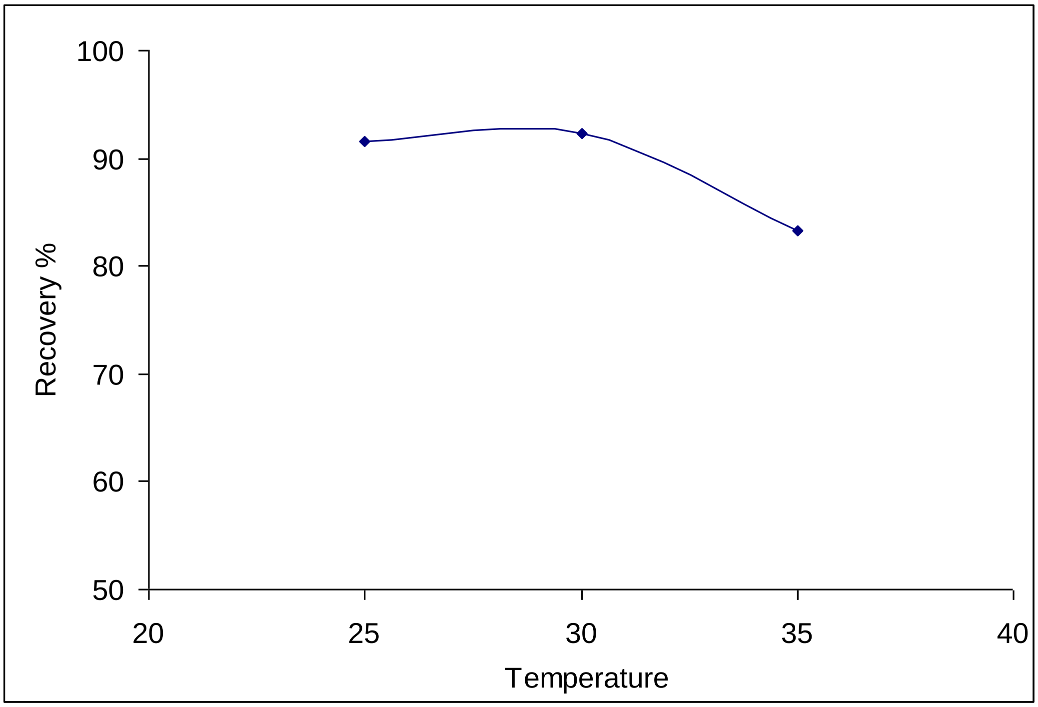

Fig.4. Effect of temperature on removal of PO_4^{3-}

Interference: effect of Carbonate

The carbonates as the common ions present in water, and MD as sorbent material are strongly affected by pH value. The results of MD tests for efficiency adsorbed PO_4^{3-} and carrying carbonate concentration (at pH=6 converted to bicarbonate) in the solution was studied and presented in fig.5.

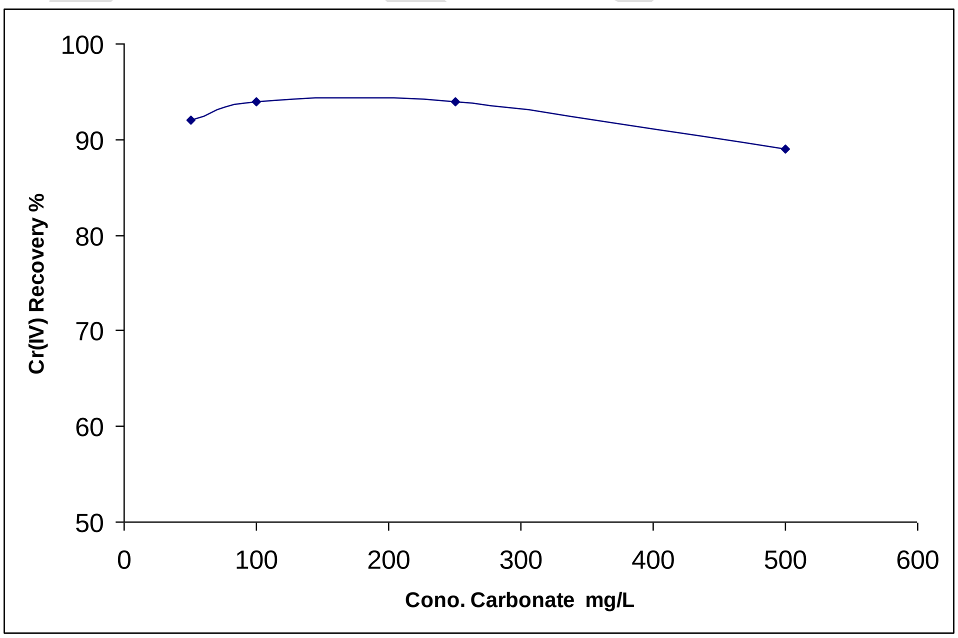

Fig5. The effect of Carbonate on adsorption process.

The conditions procedures were: mass of MD (m=2.0 g), volume of solution (V=100 mL), concentration of PO_4^{3-} (10 mgL^{-1}), pH value (pH= 6.0), contact time (90 min), shaker speed (120 rpm), temperature (room temperature), and concentration of carbonate was varied (50 mgL^{-1}, 100 mgL^{-1}, 250 mgL^{-1} and 500 mgL^{-1}). The efficiency of MD to remove PO_4^{3-} from aqueous solution was measured and the result showed that the 50 mgL^{-1} , 100 mg L^{-1} and 300 mg L^{-1} of carbonate not have any effect on capacity of adsorbed PO_4^{3-} , where the 500 mgL^{-1} of carbonate will have slightly effected on adsorption capacity.

Applications simple method to standard solution and real water samples

Standard samples

Four standard samples of deionized water were spiked with addition of different concentration of PO_4^{3-} , the experiment was based through the optimum procedure, mass of MD (m=2.0 g), volume of samples (V=100 mL), pH of water (pH = 6.0), contact time (90 min), and shaker speed (120 rpm).The spiked range of deionized water was 0.5 mg L^{-1}, 1.0 mgL^{-1}, 5.0 mgL^{-1} and 10.0 mgL^{-1}). The results of samples analysis were spiked with different concentration of $PO_4^{3-}$are presented in Table 2.

Table 2. Results of Adsorption recovery by MD in spiked standard solution.

Standard solution	PO_4^{3-} content , standard addition mg L^{-1}	Removed mg L^{-1}	Recovery %
1	0.5	0. 45±0.004	91.45
2	1.0	0.967±0.03	96.7
3	5.0	4.56±0.052	91.2
4	10	9.31±013	93.1

The results in table 2 showed that, the good recoveries of 91.5%, 96.7% , 91.2% and 93.1 % were obtained and the relative standard deviation (RSD) was 0.8, 2.98 , 1.14, and 1.4 for 0.5, 1.0, 5.0 and 10 mgL^{-1} respectively.

Real water samples

The Results of two real water samples were spiked with different concentration of PO_4^{3-} presented in the table 3. The concentration of carbonate and bicarbonate of two samples were analyzed before adsorption procedures (nil CO_3^{2-} , 34.1 mgL^{-1} HCO_3^{2-} , nil CO_3^{2-} , 170 HCO_3^{-}) for sample 1 and 2 respectively. The procedure of adsorption of PO_4^{3-} based through the optimum procedure, mass of MD (m=2.0 g), volume of water samples (V=100 mL), pH of water (pH = 6.0), contact time (90 min), and shaker speed (120 rpm).

Table 3. Results of adsorption of PO_4^{3-} using MD in real water samples spiked with addition different concentration of PO_4^{3-}.

Sample No.	PO_4^{3-} content , standard addition mg L^{-1}	Removed mg L^{-1}	Recovery %
1	5.0	4.72±0.05	94.4
1	10	9.20±0.12	92.0
2	1.0	0.93±0.017	93.1
2	10	9.66±0.23	96.6

The results presented in table 3, showed that good recoveries were found in the two samples (94.4%, 92.0%) and (93.1%, 96.6%) while RSD were (1.1% ,1.31%) and (1.8% , 3.2%) respectively.

CONCLUSION

Adsorption of PO_4^{3} on natural material was studied using marble dust as sorbent material. The pH of solution had a significant effect on the adsorption of PO_4^{3-}. When the mass of MD was 2.0 g , 96% removal efficiency was achieved. The reaction occurred in mass of MD scale and the reaction efficiency increased significantly from 0.5 g to 1.0 g, while the reaction between MD and PO_4^{3-} approximately had constant removal efficiency with increasing of mass of MD from 1.0 g to 5.0 g at pH value 6.0, the adsorption of PO_4^{3-} was favorable, where the effect of the presence of carbonate ions in the sample had no effect on the adsorption of PO_4^{3-}. This study indicated that the MD can be used as natural material which has good capacity in bonding of PO_4^{3-} in water samples.

REFERENCES:

1. Wandruszka, R. V., Phosphor retention in calcareous soil and the effect of organic matter on its mobility, *Geochem. Trans*. 6(7), (2006) 1-8
2. Shyla, B., Mahadevaiah, and Nagendrappa,G., A simple spectrophotometric method for the determination of phosphate in soil, detergents, water, bone and food samples through the formation of phosphomolybdate complex followed by its reduction with thiourea, *Spectrochim. Acta A* 78(1), (2011) 497-502.
3. Oladegi, S., Adelowa, F., and Odelade, K., Evaluation of level in water samples (Ogbomoso Rivers) using UV-Visible spectrophotometric method, *J. Scien. Rese. Envion. Sc*i. 4(4), (2016) 102-108.
4. Sawyer,C. N., Perry,M. L., and Gene, P. F., Chemistry for Environmental Engineering and Science.5th Ed, McGraw- Hill Publishing Company Ltd: 677 (2002).
5. Abowei, J. F. N., Davies,O. A., and Eli, A., Physicochemistry, morphology and abundance of fin fish of Nkoro River, Niger Delta, Nigeria. *Int. J. Pharm. Biosci*., 6(2), (2010) 1-11.
6. Ritz, E., Hahn, K., Ketteler, M., Kuhlmann, M. K., and Mann, J., Phosphate additives in food – a health risk, *Dtsch. Arz. Inter.*109, (2012) 49-55.
7. Foley, RN., Collins, AJ., Herzog, CA., Ishani, A., and Kalra, PA. Serum phosphorus levels associate with coronary atherosclerosis in young adults, *J. Am Soc Nephrol*, 20 (2), (2009) 397-404.
8. Tonelli, M., Sacks, F., Pfeffer, M., Gao, Z., and G. Curhan, Relation between serum phosphate level and cardiovascular event rate in people with coronary disease, *Circulation*, 112, (2005) 2627–2633
9. Ramirez, A., Giraldo, S., Garcia- Nunez, J., Florez, E., and Acelas, N., phosphate removal from water using a hybrid material in fixed-bed column, *J. Watert. Proc. Eng.* 26, (2018) 131-137.
10. Jiang, D., Chu, B., Amano, Y., and Machida, Mremoval and recovery of phosphate from water by Mg-laden biochar: Batch andcolumn studies, *Colloids Surf., A*, 5584, (2018) 29-437.
11. J. Goscianska, M. Ptaszkowask, M. Frankowski, M. Franus, R. Panek, and W. Franus, Removal of phosphate from water by lanthanum-modified zeolites obtained from fly ash, *J. Colloid Interface Sci.*, 513, (2018) 72-81.
12. Mallet, M., Coulibaly, L., Abdelmoula, M., and Ruby, C., Phosphate removal from water by natural occurring shale, sandstone, and laterite: The role of iron oxides and of soluble species, *C.R. Geosci.*, 351(1), (2019) 37-47
13. Hashim, K. S., AlKaddar, R.. Jasim, N., Shaw, A., Phipps, D., Kot, P., O. Pedrola, M., Alattabi, A., Abdulredha,M.,and Alawsh, R., Electrocoagulation as green technology for phosphate removal from river water, *Sep. Purif. Technol.*210, (2019) 135-144.

14. Hashima,K. S. Idowu,I., Jasim,N., Al Khaddar, R., Shaw, A., Phipps, D., Kot, P., Pedrolaa, M., Alattabi, A., Abdulredha ,M., Alwash, R., Teng, K.H., Joshi, K.H., and Aljefery M. H., Removal of phosphate from River water using a new baffle plates electrochemical reactor, *Methods X*, 5, (2018) 1413-1418.
15. Zhang, J., Shen, Z., Mei, Z., Li, S., and Wang, W., Removal of phosphate by Fe-coordinated amino-functionalized 3D Mesoporous silicates hybride materials, J. Environ. Sci., 23(2) (2011) 199-205.
16. Gu, W., Xing, M., Fang, W., and Wu, D., Removal of phosphate from water by amine-functionalized copper ferrite chelated with La(III) *Sci. Total Environ*. 619-620 (1), (2018). 42-48.
17. Jiang, D., Amano, Y., and Machida, M., Removal and recovery of phosphate from water by a magnetic Fe_3O_4@ASC adsorbent, *J. Environ. Chem. Eng.*5 (5), (2017). 4229-4238.
18. Nie, G., Wu L., Du, Y., Wang, H., Yanhua ,X., Ding, Z., and Liu, Z.,). Efficient removal of phosphate by a millimeter-sized nanocomposite of titanium oxides encapsulated in positively charged polymer, *Chem. Eng. J*. 360, (2019) 1128-1136.
19. Wang, Z., Xing, M. Fang, and Wu, W. D., One-step synthesis of magnetite core/zirconia shell nanocomposite for high efficiency removal of phosphate from water *Appl. Surf. Sci*, 366, (2016) 67-77.
20. Gan, L., Lu, Z., Cao, D., and Chen, Z., Effect of cetyltrimethylammonium bromide on the morohojogy of green synthesized Fe_3O_4 nanparticles used to remove phosphate, *Mater. Sci. Eng., C.* 82, (2018) 41-45.
21. Pavonia, B., Drusiana, D., Giacomettia, A., and Zanetteb, M., Assessment of organic chlorinated compound removal from aqueous matrices by adsorption on activated carbon, *water Res*. 40, (2006) 3571-3579.
22. Buchanan, W., Roddick, F., and Porter, N., Removal of VUV pre-treated natural organic matter by biologically activated carbon columns, *Water Res.*42, (2008) 3335-3342.
23. Cherifi, H., Hanini, S., and Bentahar, F., Adsorption of phenol from wastewater using vegetal cords as new adsorbent, *Desalination*, 244, (2009) 177-187.
24. Bajic, Z., Djokic, V., Velickvic, Z., Vuruna, M., Ristic, M., Benissa, N., and Marinkovich, A., Equilibrium kinetic and thermodynamic studies on removal of Cd(II), Pb(II) and As(V) from wastewater using carb (Cyprinus Carpio) scales, *Dig. J. Nanomter. Bios*.8, (2013) 1581-1590.
25. Christoph, J., Lina, P., Krenz, M.,and Pleissner, D., Is seashell powder suitable for phosphate recovery from fermentation broth, *New Biotechnology*, 49, (2018) 43-47
26. Jiang, D., Chu, B., Amano,Y., and Machida, M., Removal and recvery of phosphate from water by Mg-Laden biochar: Batch and column studies, *Colloids Surf.,A*, (2018) 558, 429-437.
27. Kiteshwarna, K. Pokhrel, N., Hussein, F., Antony, E., and Mayer, B., Phosphate removal and recovery using immobilized phosphate binding proteins, *water Res. X*, 1, (2018)1-9.
28. Sellner, B. M., Hua, G., and Ahiablame, L. M., Fixed bed column evaluation of phosphate adsorption and recovery from aqueous solution using recycled stell byproducts, *J. Environ. Manage.* 233, (2019) 595-602.
29. Wandruszka, R. V., Phosphorus retention in calcareous soils and the effect of organic matter on its mobility, *Geochemical transaction*, 7 (6), (2006) 1-8.