Minimization of Phosphate from Ocean Water

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Abstract Phosphates are very important basic materials in agricultural and other industrial applications. Phosphorus is often present in low concentrations in wastewater, almost solely in the form of organic and inorganic phosphates. The removal of phosphates from surface waters is generally necessary to avoid problems, such as eutrophication, particularly near urban areas. The usual methods of treatment are either biological or physicochemical by sedimentation. Among them adsorption technique has got maximum potential for the reduction of organic material. Adsorption being a physical process, in-expensive and less time consuming, is widely accepted. It is evident from last 20-25 years that many researchers have studied the feasibility of low cost adsorbents derived from natural material, industrial material, agricultural waste and bio-adsorbents and resulted in innovative approach in this area. The current research is focused on the need to develop an efficient adsorbent with cost effectiveness and high potentiality. The study was carried out for phosphorus adsorption by clay available near coastal region. The result shows that maximum 93% of phosphorus can be adsorbed with western region clay.

Keywords: adsorbents, clays, dissolved, environment, organiC

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1. Introduction

Phosphates are very important materials to many industries. Large quantities of them are used in many industrial applications, with fertilizers being the most important. Other applications include detergents, water softening, food and drinks, metallurgy etc [1]. The wide use of phosphates inevitably produces large amounts of phosphate-bearing wastes, which are usually discharged into municipal and industrial water effluent streams. Eutrophication of the water bodies is one of the most important environmental problems, which occurs in stagnant water bodies. Phosphorus has been considered as a key element causing eutrophication, which leads to abundant development of aquatic plants, growth of algae, with some kinds of them being toxic, and to balance disturbance of organisms present in water [2]. This directly affects water quality through oxygen depletion, because of high biological oxygen demands, and acidification. This, in turn, harmfully affects fish and other aquatic life, microorganism and insects' growth and natural resorts deterioration. Consequently, the removal of phosphates from surface waters is absolutely necessary to avoid any kind of problems, particularly near urban areas. Wastes containing phosphates must meet the maximum discharge limits, which is typically between 0.5 and 1.0 mg P/liter [3]. Phosphorus usually occurs in wastewater and surface water in the form of organic phosphates (e.g. detergents) and inorganic phosphates (ortho- and polyphosphates). In wastewater treatment technology, various techniques have been employed for phosphate removal.

Despite the extensive experimental work carried out, phosphorus removal and recycling technologies have not been widely adopted because of the technical and economic drawbacks. The broad categories of phosphate effluent treatment include physical, chemical, biological and crystallization methods [4]. Also, flotation has been used to remove orthophosphates from solutions. Chemical removal techniques are the most effective and a wellestablished method up to date, including phosphate precipitation with calcium, aluminum and iron salts [5]. However, the cost associated with the use of metal salts may hinder the widespread application. Besides, the product of chemical immobilization is metal phosphate sludge, which is disposed with relatively high phosphorus content, as the recovery of phosphorus from sludge is very difficult. Consequently, the removal of phosphate compounds through sorption processes onto various sorbents has been tested since a long time ago. Among the adsorbents tested the following are included: aluminum and aluminum oxides [6], iron and iron oxides [7], fly ash [8], slag, red mud, bauxite [9], silicates, active carbon and anion exchanger [10].

In ocean phosphorus are introduced through the processing, equipment cleaning of ships and industry, effluent discharge from industry, oil etc. Due to adding of this material the compositions phosphorus increase in the ocean water. The increase in the compositions affects the living and non living organism of the water body. So an attempted has been made to decrease the percentage composition of sea water by low cost treatment method. The main aim of the work is to reduced the phosphorus by using clay powder which available near by the sea only. The effect of pH, heat treated temperatures; contact time

and dose on the percentage of adsorption are examined. Scanning electron micrograph for surface and x-ray diffraction for the compositions has been also studied.

2. Material and Methods

2.1. Materials

Synethic water was produced in labotary and preserved at 20°C until used. Artificial orthophosphate solutions were used throughout the adsorption tests. Initially, a stock solution of 100 ppm in orthophosphates was prepared by dissolving a certain amount of chemically pure K_2HPO_4 ·3H₂O in distilled water. An aliquot of the stock solution was mixed with a certain volume of water so that a phosphate solution prepared at the desired experimental concentration. Distilled water was used throughout all the tests. Although distilled water was of very low hardness, fresh phosphate solutions were daily prepared to avoid possible precipitation of phosphate species. NaOH and HCl solutions 5% v/v were used as pH regulators.

Clay, picked up by hand sorting from a quarry, was used as adsorbent in the tests. Clay was collected from three different coastal region; northern region (C1), southern region (C2), and western region (C3). The physicochemical parameters of clays are mention in Table 1. The initial sample was crushed in a jaw crusher and wet ground in a porcelain mill with porcelain grinding media to avoid iron contamination. The milling product was wet sieved and the fraction 0.2 mm was used for the adsorption tests, with 45% of the particles' size being less than 0.075 mm. The particle size of clay used for zeta-potential measurements was 5 μ m.

S. No	Components	Northern region clay (C1)	Southern region clay (C2)	Western region clay (C3)
1	Silica (SiO ₂)	47.4	46.2	40.18
2	Alumina (AIO ₃)	33.2	38.2	22.63
3	Titania (TiO ₂)	0.62	0.06	0.7
4	Ferric Oxide (Fe ₂ O ₃)	2.79	0.94	20
5	Lime (CaO)	0.7	0.08	1.33
6	Magnesia (MgO)	0.3	0.15	0.8
7	Potash (K ₂ O)	1.3	0.37	0.95
8	Soda (Na ₂ O)	0.2	0.05	
9	Phosphorus penta oxide (P ₂ O ₅)	< 0.02	0.04	0.01
10	Manganic Oxide (MnO ₂)	0.1	0.03	0.2
11	Barium Oxide (BaO)	0.2	0.01	0.02
12	Strontium (Sro)	0.25	0.01	0.01
13	Loss on Ignition (LOI)	12.1	13.8	11.39

2.2. Method

A defined volume of the phosphate stock solution, with a concentration 100 ppm in $PO_4^{3^-}$, was diluted to the experimental concentration by adding distilled water of very low hardness. The pH of the solution was then adjusted to the desired value and a defined amount of adsorbent was added. The mixture was stirred at 150 RPM for a defined period, using a stirrer with a potentiometer to regulate the stirring speed. After a certain period of stirring, pH was recorded and filtering process was applied to separate solid from liquid.

2.3. Instrumentation and Analysis

A pH-conductivity meter was employed. The pH was measured with the same meter using pH glass electrode. The phosphorus determine by APHA [11].

3. Result and Discussion:

3.1. Effect of pH

The effect of pH was carried out at heat treated clay at 400°C, dose 4 gm and contact time 3 h, which is represented in Figure 1 It was found that adsorption increase with increase in pH. Maximum 78% of phosphorus adsorption shows by C3 at pH 6, C2 72% at pH 8 and C1 60% at pH 6 respectively. Several reasons may be attributed to adsorption behavior of the adsorbent relative to solution pH. The electrostatic attraction as well as the organic properties of the clays and structure of

molecules could play important roles in adsorption. At pH=2, there is high electrostatic attraction existing between the positively charged surfaces of the adsorbent and the negatively charged anionic molecules. A negatively charged site on the adsorbent does not favor the adsorption of anionic phosphorus molecules due to the electrostatic repulsion. The adsorption of these anionic charged groups onto the adsorbent surface is primarily influenced by the surface functional groups on the adsorbent, which in turn is influenced by the solution pH [12].



Figure 1. Effect of pH on percentage adsorption of phosphorus

3.2. Effect of Heat Treated Temperature

The effect of heat treated clay was carried out at optimum pH, dose 4 gm and contact time 3 h for all three clays, which graphically represent in Figure 2. It was observed that at 600°C of the heating temperature the

clays show better efficiency. Further increase in the temperature 600°C on ward shows poor performance. Maximum percentages of phosphorus adsorption show 68% C1, 77% C2 and 85% C3 respectively. It is reported that aluminium oxides are converted to γ -Al₂O₃ upon heating of clay minerals up to 600°C, and then contribute to improved adsorption characteristics. The decline in adsorption capacity above 600°C can be attributed to the gradual conversion of aluminium oxide into a-AhO₃ and iron oxides to magnetite's form of oxides that show little tendency to adsorb fluoride [13].



Figure 2. Effect of heat treated temperature on percentage adsorption of phosphorus

3.3. Effect of Contact Time

The effect of contact time was carried out at optimum pH, 600°C of heat treated clay and 4 gm of mass loading, which is shown in Figure 3. The experiment results show that percentage of adsorption was increases with increase in contact time. Maximum percentage of phosphorus adsorption 78%, 84% and 88% by clays C1, C2 and C3 shown at 5 h contact time. The experimental results clearly indicate that the optimum time to attain the equilibrium for this reaction is 5 h. The study of the distribution of the phosphorus between the adsorbent and the phosphorus solution at equilibrium is important to assess the adsorption capacity of the adsorbent for the dye stuff [14]. The results revealed that increase in contact time increases the dye uptake and remains constant after an equilibrium time for all the studied.



Figure 3. Effect of contact time on percentage adsorption of phosphorus

3.4. Effect of dose

The effect of dose was carried out at optimum pH, heat treated temperature 600°C, and contact time 5 h, which

presented in Figure 4. The experimental result shows that percentage of phosphorus increase with increase with dosing. The maximum percentage of phosphorus adsorption 87%, 90% and 93% shown by C1, C2 and C3 at 6 gm of dosing. It is apparent that by increasing the adsorbent dose the percentage of pollution reduction increases, but adsorption density, the amount adsorbed per unit mass, decreases. It is readily understood that the number of available adsorption sites increases by increasing the adsorbent dose and it therefore results in an increase in the percentage of adsorbed. The decrease in adsorption density with an increase in the adsorbent dose is mainly because of unsaturation of adsorption sites through the adsorption process. Another reason may be the inter-particle interaction, such as aggregation, resulting from high adsorbent dose. Such aggregation would lead to a decrease in the total surface area of the adsorbent and on an increase in diffusional path length [15].



Figure 4. Effect of dosing on percentage adsorption of phosphorus

3.5. Effect of Particle Size

The effect of particle size was carried out at optimum pH, heat treated temperature 600°C, contact time 5 h and dose 6 gm, which can be studied through scanning electron micrograph. The scanning electron micrograph is presented in Figure 5 (a) to (c). In Figure 4 (a) clay seen to be well arranged pattern the form of structure, which is responsible for the better efficiency. Similarly in the Figure 5 (b) and (c) the pattern are clearer and well arrange. It is important to note that larger particles with spherical surfaces, present higher external mass transfer. In this case, higher phosphorus adsorption from these particles is attributed to mass transport inside the sorbent particles [16]. At the same time as the particle size decreases the surface area for adsorption increases which in turn contribute to high adsorption at fine particle size. Optimum particle size can be obtained if precise contributions of mass transport and surface diffusion are ascertained [17].



Figure 5. Effect of particle size on percentage adsorption of phosphorus

3.6. X-ray Diffraction

The percentage composition of phosphorus was studied before and after treatment with the clay (C3) is shown in Figure 6. It was found that before treatment the percentage of phosphorus was very high which clearly saw in Figure 6 (a). Over all with respect C1 and C3, clay C3 shows high efficiency for phosphorus adsorption. After treatment with C3 clay phosphorus adsorbs up to 93%, which can clearly saw in Figure 6 (b).



Figure 6. Percentage adsorption of phosphorus (a) before treatment (b) after treatment by clay C3

4. Conclusion

Phosphorus is often present in low concentrations in wastewater, almost solely in the form of organic and inorganic phosphates. The removal of phosphates from surface waters is generally necessary to avoid problems, such as eutrophication and its concomitant effects on living organisms and environment. Clays which are naturally occurred from the coastal region land have ability to treat the phosphorus contain in the ocean water. If exact conditions are providing it can be dissolve the contaminate present in ocean water require. For the adsorption of phosphorus three clay sample was selected from different location in which C3 belong to western region show best efficiency. At pH 6, heat treated temperature 600°C, contact time 5 h and dose 4 gm will be sufficient to adsorb 93% of phosphorus. The factors which favor the selection of clays adsorbents are its low cost, widespread presence and organic composition which shows strong affinity for many compound present in water.

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