The effect of nano composite on phosphate adsorption in rich black soil

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Abstract. Industrial waste disposal is one of the major causes for the contamination of water bodies and soil. This leads to increase in the amount of elements like phosphorous in the water bodies. As a possible solution to this problem, we investigate the effect of introducing a nano sized coating of graphene on coastal sand in the adsorption of phosphate. In the present study we employ batch adsorption techniques to perform Phosphate adsorption (p-Adsorption) on rich black coastal sand and nano composite. This will help us in understanding the physical properties of clay soils, the effect of nanoscale coating on the adsorption of phosphate in soil and its dependence on contact time, concentration and ph values.

1. Introduction

One of the major environmental problem in todays world is the pollution of water bodies and water soil. Some of the main causes for this pollution are disposal of waste from industries, dumping of municipal and domestic waste near the coastal areas, increasing application of pesticides, chemical fertilizers etc. Most of these pollutants contain nutrients like phosphates and nitrates, which cannot be effectively retained in the soil, and they get drained easily into water bodies during heavy rains. If their level exceed a particular limit, they lead to an increase in the growth of aquatic plants and algae. Due to the excessive growth of aquatic plants and algae, the water ways get blocked, and the dissolved oxygen is used up for their decomposition and hence, the biological oxygen demand of the water body increases, and also leads to the blockage of light to the deeper waters. This affects the respiratory ability of fish and other animals that reside in water. This leads to eutrophication of lakes, rivers, and other water bodies, which gradually causes thier filling with sediments, and organic matter [1, 2, 3]. As mentioned above, when the oxygen levels drop below 3-5 ppm, many types of fish and other aquatic animals cannot survive causing a very large disruption in the food chain. Hence, some special must be given to reduce the use of fertilisers which contain phosphates and nitrates. Steps should also be taken to increase the retention of phosphorous in the soil. In a recent study, Ambili et al. had evaluated the phosphate adsorption behavior of soils of the tsunami affected coastal area (Alappad coast, Kerala, India) as a function of pH, concentration, isotherm behavior, and monolayer uptake and computation of Langmuir constants through batch process under laboratory condition [4]. They had observed that the phosphorus retention in the soil has
increased. In the present work, we propose to impart a nano scale graphene oxide (GO) coating for the black sand to improve its phosphorous retention capacity.

Adsorption of impurities by carbon have been conventionally used to remove various pollutants from aqueous solutions. With the advent of nanotechnology, various new allotropes of carbon have been discovered and the use of these in water filtration is largely investigated. Among them graphene and its composites offers a great advantage over other allotropes of carbon because of its features like large surface area, possibility of functionalisation etc. But one of the roadblocks in developing graphene or its composites for water filtration is to anchor these nanoscale adsorbents onto an inexpensive and reliable substrate so that they can remain stationary in a flowing water stream. Sreeprasad et al. had developed a strategy to immobilize graphene over river sand and their experiments showed that these composites could effectively remove metal ions like mercury from drinking water at low cost [5]. Later Gupta et al. had developed a green methodology for the synthesis of graphenic material from cane sugar and introduced suitable methodology to immobilize this material on sand without the need for any binder [6]. Parvathi et al. had biosynthesized graphenic material from common sugar and successfully anchored it on sand particles [7]. Though works have been carried out in the preparation of graphene sand composites there has not been a systematic analysis on the preparation of GO sand composites from coastal sand. In the present work, we investigate the effect of graphenic coating on coastal sand on the adsorption of phosphate. We have done the experiments using the rich black soil and GO coated soil and compared both the results. This paper deals with the preparation of GO coated soils and measuring the Phosphorus retention capacities of those samples at various pH values, contact times and various phosphorus concentrations.

2. Methodology

Samples of rich black sand was collected from Alappad coastal area, Kerala, India. Using these samples the GO coated composite was prepared by the following method proposed by Sreeprasad et al. [5]. The method is as follows:

- Coastal sand was washed with water followed by washing it with Conc. Nitric acid and finally three washings with distilled water.
- The washed sand was dried in a hot air oven for 30min to completely dry it out.
- 10g of this sand was weighed and mixed with 50ml of saturated sucrose solution.
- This mixture was dried at around 95°C for 6 hours in a magnetic stirrer with constant stirring at regular intervals so as to obtain a uniform mixture.
- This dried mixture obtained was heated in a furnace with the temperature programmed as follows:
  - From room temperature to 100°C in 30 minutes
  - 100°C – 200°C in 30 minutes
  - Held at 200°C for 1 hour (to melt sugar to form a uniform coating)
  - Ramped to 750°C in 1 hour
  - Held for 3 hours at 750°C (to ensure complete graphitization)
- After the above process the material was cooled to room temperature.
- For activation, 5g of the GO coated sand was treated with 10ml of Conc. Sulphuric acid and kept at room temperature for around 30 minutes. Washing with conc. Sulphuric acid will enhance the number of adsorption sites.
- This was later filtered and dried at a temperature of 120°C

Adsorption studies were performed on black soil and GO coated sand by conducting batch experiments for varied contact time, different concentration, and initial pH. A volume of 50ml of
phosphate solution was taken in a 100ml Erlenmeyer flasks containing 5g soil samples and varied conditions for initial P concentrations, different contact time, and different pH were maintained in separate batches. Each batch of the samples were stopped and kept in shaking incubator for the required period of time. After completion of the shaking period, 1ml of solution is pipetted out and 24ml distilled water is added. This is filtered using Whatman No: 1 filter paper. To the filtrate 25ml of distilled water is added to make the total volume 50mL. This is followed by the addition of 8ml combined reagent and adsorption of phosphate is estimated using spectrophotometric method. All forms of phosphate should be converted to orthophosphate which in acid medium reacts with ammonium molybdate and potassium antimonyl tartrate to form phosphomolybdic acid that is reduced to molybdenum blue by reduction with ascorbic acid. The absorption of molybdenum blue at 880nm is a measure of the phosphate concentration in solution.

To optimize the contact time required for maximum adsorption efficiency, 50ml of 50 mg/l of phosphate solution was added to 5g of black sand and equilibrated for varied range of contact time, viz: 10min, 20min, 30min, 1hr, 2hr, 4hr, 6hr, 8hr, 12hr, 18hr, 24hr. Different initial concentration viz: 5, 25, 50, 75, 100, 250, 500, 750, 1000, 1500 mg/l were subjected to black sand and soil was equilibrated for a fixed contact time of 8h, in-order to study the suitable concentration to be used for optimum adsorption. Different pH covering the range from 1 to 9 were adjusted and subjected to fixed amount of black sand and contact time of 8 hour, in-order to select the optimum pH for phosphate removal.

3. Results and Discussion
The adsorption studies on black sand showed that a contact time of 8 hours is optimal. This was in accordance with the results obtained by Ambili et al. [4]. The effect of pH on the adsorption behavior was also found to be similar to their results. Hence, we conducted the subsequent studies at a contact time of 8 hours. Figure 1 shows the comparison of the contact time graphs
Figure 2. Effect of contact time on the phosphorous adsorption by GO coated sand. (a) 4 hr (· · · · · ·); (b) 6 hr (- - - -); (c) 8 hr (——); (d) 20 hr (— - -); (e) 24 hr (— · · —)

Figure 3. Effect of contact time on the maximum amount of phosphorous adsorbed by GO coated sand.
for black sand and GO coated sand for 8 hours. The results show that the adsorption behavior is largely enhanced by with the help of nanoscale GO coating. This can be attributed to the large surface area available in the case of GO coated sand.

Figure 2 shows the effect of contact time on the phosphorus adsorption by GO coated sand. Figure 3 shows the effect of contact time on the maximum amount of phosphorus adsorbed by GO coated sand. The results clearly show that, in the case of GO coated sand also, the optimum contact time is 8 hours. Hence, the results indicate that preparation of GO coated sand is a low cost and easily performable method for reducing the pollution of water bodies due to leaching of phosphorous from the soil.

4. Conclusion
Industrial waste disposal is one of the major causes for the contamination of water bodies and soil. This leads to increase in the amount of elements like phosphorous in the water bodies. As a possible solution to this problem, we have investigated the effect of introducing a nano sized coating of graphene on coastal sand in the adsorption of phosphate. The research was carried out on Phosphate (p-Adsorption) on rich black coastal sand and nano composite sand through batch adsorption techniques. It was found that the nano coated sand was having a better adsorption rate than the normal black soil.

Acknowledgments
The authors would like to thank Amrita Vishwa Vidyapeetham, Amritapuri, India, for providing us with the financial support for conducting this project under the Faculty Seed Grant.

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