Adsorption of phosphate and fluoride from fertilizer industry effluent using fly ash and chitosan nano-adsorbents

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Abstract

The waste water generated from a chemical fertilizer industry contains different organic and inorganic pollutants. The adoption of low-cost, easily available materials in effluent treatment has recently attracted huge interest. The present study used fly ash and chitosan, modified with titanium dioxide, for the adsorption of phosphate and fluoride from fertilizer industry effluent. Batch adsorption experiments were conducted in the laboratory in order to evaluate the phosphate and fluoride removal efficiency of modified fly ash and chitosan. The adsorption of phosphate and fluoride onto fly ash and chitosan nano-composites as a function of initial ion concentration, adsorbent dosage, contact time and solution pH was investigated for optimization.

The adsorbents were characterized by X-ray diffraction and FTIR spectroscopy. Fly ash and chitosan nano-composites showed a removal efficiency of above 90% for phosphate from the effluent sample and the maximum adsorption was at acidic pH. Fly ash removed 60% of the fluoride, whereas chitosan removed fluoride with an efficiency of more than 80%. Effective fluoride adsorption occurs in the pH range of 4–6 and decreases with an increase in pH. The sorption data were represented using Freundlich and Langmuir isotherm models, where the data were best filled by Freundlich isotherm model.

Keywords: Fertilizer effluent, adsorption, fly ash, chitosan, nanocomposite.

Introduction

The waste water generated from a fertilizer industry contains high concentrations of pollutants like phosphates, ammonia, fluorides etc.[3,4] The high content of these pollutants and the enormous daily flow rate of effluent from fertilizer industry led to the disposal of several tons of fluorides and phosphates per year[2,14]. The untreated effluent gets accumulated in aqueous environment, causing water pollution. According to the World Health Organization, the concentration of fluoride in drinking water above 1.5 mg L^{-1} causes dental fluorosis while a concentration above 10 mg L^{-1} leads to skeletal fluorosis[9]. Moreover, the discharge of large concentrations of phosphate and nitrate into water bodies may enhance algal blooms and leads to eutrophication. In order to prevent eutrophication of surface water bodies, phosphate content in the discharged water must meet the limits for phosphate, which are 0.5 – 1.0 mg L^{-1}.

For the treatment of fertilizer industry waste water, a variety of treatment methods have been developed by considering the growing environmental and economic impact of fertilizer effluent. Lime is commonly used in fertilizer industry for precipitating phosphate and fluoride as calcium phosphate and calcium fluoride respectively[7]. Biological treatment methods are also practised for the removal of phosphorus and fluoride from fertilizer waste water[13]. Among the various effluent treatment methods, adsorption is known to be the most useful and economical method for removing pollutants[37]. Adsorption technique is comparatively more useful and economical for effluent treatment. There are different studies of adsorption using natural adsorbents like horse gram powder; shrimp shell waste, rice husk, charcoal, etc.[8,11,31] as well as using synthetic adsorbents[30]. The use of low-cost and easily available materials such as fly ash and chitosan in waste water treatment has been widely investigated in recent times[29,32].

The removal of fluoride and phosphate from fertilizer industry effluent was compared with fly ash and chitosan nano-composites. Fly ash, resulting from the combustion of coal, is one of the industrial wastes responsible for severe environmental problems and has adverse effect on human health; therefore, the development of effective techniques for its productive reuse is being highly investigated nowadays[35].

As a measure of its reuse, a number of zeolites have been synthesized from fly ash[22]. Developed countries like Germany utilize 80% of the generated fly ash whereas India consumes only 3% of the produced fly ash[28]. The Government of India focused on various methods for reuse and safe disposal of fly ash. It can be used for manufacturing cement, bricks, tiles, roofing sheets, blocks etc. Fly ash is abundantly available and inexpensive. It can also be used as an effective adsorbent in various ion separation processes[18].

Properties like large specific surface area, high carbon content and fine particle size make fly ash a good adsorbent[39]. It can be chemically modified to enhance its adsorption properties. There are numerous studies which used fly ash as a low-cost sorbent for the removal of heavy metals, organics and dyes from effluents[16,18,21,24].

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Chitosan is a biopolymeric cation[6]. It is a natural polymer obtained from the deacetylation process of chitin in alkaline medium. Chitosan, as an effective biosorbent, has drawn special attention because of its low cost and abundant source. High content of functional groups like amino and hydroxyl in chitosan is showing high adsorption potential for various water pollutants[12,20,25]. Chitosan has been extensively used as an efficient adsorbent for heavy metal cations[33] and some organic species like reactive dyes[34]. Nanomaterials have been widely used in waste water treatment process in recent times. Nanomaterials provide the best feasible way for the treatment of organic as well as inorganic contaminants[17] because of their unique properties such as high surface area and high adsorption capacity. Moreover, the interaction between nano-adsorbents and contaminants may be chemisorption or physisorption depending on the functionalization of nanomaterials[26].

The objective of this work is to study the effect of surface modified (with suitable metal oxides), low cost adsorbent materials like fly ash and chitosan for the removal of major pollutants like phosphates and fluorides from a fertilizer industry effluent. Langmuir and Freundlich isotherms have been fitted to find the best suitable equilibrium adsorption model.

Material and Methods

Effluent sample collection and analysis: The effluent sample used in the study was collected from a fertilizer manufacturing plant in Kerala, India. A 10 litre of waste water sample was collected from the plant and was used for effluent treatment as such without any pre-treatment or addition of chemicals. The sample was stored at room temperature in the laboratory. The low pH and high fluoride content of the sample prevent microbial growth at room temperature. The selected fertilizer plant produces the complex fertilizer FACTOMPHOS (ammonium phosphate sulphate) using raw materials such as ammonia, phosphoric acid and sulphuric acid. The collected sample was analysed for its initial chemical composition using standard procedures (APHA) and the characteristics of the effluent are given in table 1.

Chemical reagents required for the synthesis of nano-adsorbents were purchased from Alpha Chemicals. The pH was measured using a pH meter. The ammonia content of the effluent was analysed by Kjeldahl's method. The phosphate content and fluoride content of the sample were analysed spectrophotometrically by stannous chloride method and SPADANS method respectively.

Table 1
Initial chemical composition of the effluent

Parameter	Value
pH	6.3
Ammonia	1813 mg L^{-1}
Phosphate	1402 mg L^{-1}
Fluoride	mg L^{-1}

Fly ash-TiO_2 nanocomposite: The fly ash (FA) for this study, received from a thermal power plant, was sieved and washed with 0.1M HCl and dried and powered. Chemically treated FA was mixed with TiO_2 in an optimized ratio FA: TiO_2 = 3:1. Tween 20 (non ionic surfactant) is added to the mixture prepared in alkaline media for surface charge control and as potential templating agent. The new nano-composite material was obtained from the mixture under constant stirring at 300 rpm for 48 hr at 100^0C. The slurry was then washed many times with ultra-pure water till constant pH is obtained.

The composite obtained was filtered and dried at 105-115^0C. The composite was heated for 24 hr at 235^0C in order to remove the residual organic compounds. The novel nanocomposite material is characterized using XRD and FTIR methods.

Chitosan-TiO_2 nanocomposite: Chitosan-TiO_2 nano-adsorbent was synthesized by co-precipitation method[15]. One gram of TiO_2 was dissolved in a mixture of 100 mL of 1% acetic acid and 10 mL of 60% nitric acid. One gram of chitosan is added to this solution and stirred at 500 rpm using a magnetic stirrer for 3 hours continuously to get a clear solution. After that, sonication was performed for 15 minutes using an ultrasonicator. In order to make the solution pH 10, one molar NaOH solution was added to this in a dropwise manner. Then the precipitate formed was heated at 80^0C for 5 hours and then filtered, washed with distilled water and dried in an oven at 60 ^{0}C for 12 hours. The particle size of the prepared chitosan-TiO_2 was reduced to nano-size using a high-speed cryo ball mill. The synthesized nano adsorbent particles are characterized using Scanning electron microscopy (SEM) equipped with energy dispersive X-Ray spectroscopy.

Batch adsorption experiments: Adsorption experiments were performed in the laboratory using the batch equilibrium method. An incubated shaker was used for adsorption by varying the parameters that affect the adsorption of phosphates and fluorides on to fly ash and chitosan nanocomposites. The effect of adsorbent dosage, pH, shaking time (contact time) and initial concentration was investigated by placing 100 ml of effluent sample in sealed Erlenmeyer flasks and agitated at 140 rpm and at 30°C. The solution pH was adjusted with 0.1 M HCl and 0.1 M NaOH to obtain the desired pH value. After the predetermined time is achieved, the adsorbate solution is withdrawn and filtered to separate the adsorbent. After filtration, the concentration of phosphates and fluoride was determined using a pre-calibrated UV-VIS spectrophotometer by stannous chloride and SPADANS method respectively.

Percentage removal efficiency of phosphate and fluoride ion

$$= \frac{C0-Ct}{C0} \times 100$$

where C0 is the initial ion concentration and Ct is the concentration of ions after adsorption.

Adsorption Isotherm models: This study used both Freundlich and Langmuir isotherm equations to describe the adsorption equilibrium. The Freundlich isotherm model is represented mathematically as:

$qe = kf\ Ce^{1/n}$

where qe (mg/g) is the amount of fluoride adsorbed, Ce is the concentration of fluoride in solution (g/L), Kf and 1/n are parameters of the Freundlich isotherm, denoting a distribution coefficient (L/g) and intensity of adsorption respectively. The Langmuir equation is another widely used equilibrium adsorption model. It has the advantage of providing a maximum adsorption capacity qmax(mg/g) that can be correlated to adsorption properties.

The Langmuir model can be represented as:

$qe = qmax\ [(KLCe)/(1+KLCe)]$

where $qmax$(mg/g) and KL (L/mg) are Langmuir constants representing maximum adsorption capacity and binding energy respectively.

Results and Discussion

X-Ray diffraction analysis of fly ash TiO_2 nano-composite: The diffractogram (Figure 1) shows the X-ray diffraction pattern of the fly ash-TiO_2 nano-composite. The composite consists of titanium dioxide anatase and brookite crystalline phases. It also contains peaks of quartz (SiO_2). XRD data shows the hydrothermal process which promotes surface interactions including dissolution, re-crystallization of the fly ash components and development of new component TiO_2 etc. Thus, it can be concluded that the nano-sized TiO_2 particles were embedded in the micro-sized fly ash grains during synthesis.

FTIR Spectra of fly ash TiO_2 nano-composite: FTIR spectra of fly ash-TiO_2 nano-composite showed the major peaks stretches at wave numbers 3413.31cm^{-1} (OH-) and 1625.02cm^{-1}(Si-OH) (1086.76cm^{-1}(C=O) 756.78cm^{-1} (C-H) and 462.58cm^{-1} (Ti-O-O) as shown in figure 2. The several vibrations compared to TiO_2 spectra may be due to the incorporation of Al, Fe and Si bonds from fly ash.

Adsorption of phosphate and fluoride by fly ash and chitosan nano-composites

Effect of adsorbent dosage: Adsorbent dosage is a vital parameter affecting adsorption capacity and effluent concentration. The effect of adsorbent dosage on phosphate removal was depicted in figure 3. It was evident that the phosphate removal efficiency increased from 77 to 99% with the increase in adsorbent dosage from 0.1 to 0.5g for fly ash and from 33 to 96% increase for chitosan (Figure 3) with increment in adsorbent dose. The increased removal efficiency is due to the availability of more active sites and larger surface area at higher dosage. At a higher dosage, the equilibrium uptake of phosphate ions did not increase significantly by increasing fly ash and chitosan dosage. This result is expected because of the saturation level attained during an adsorption process. This finding agrees with the results of other authors[23,27].

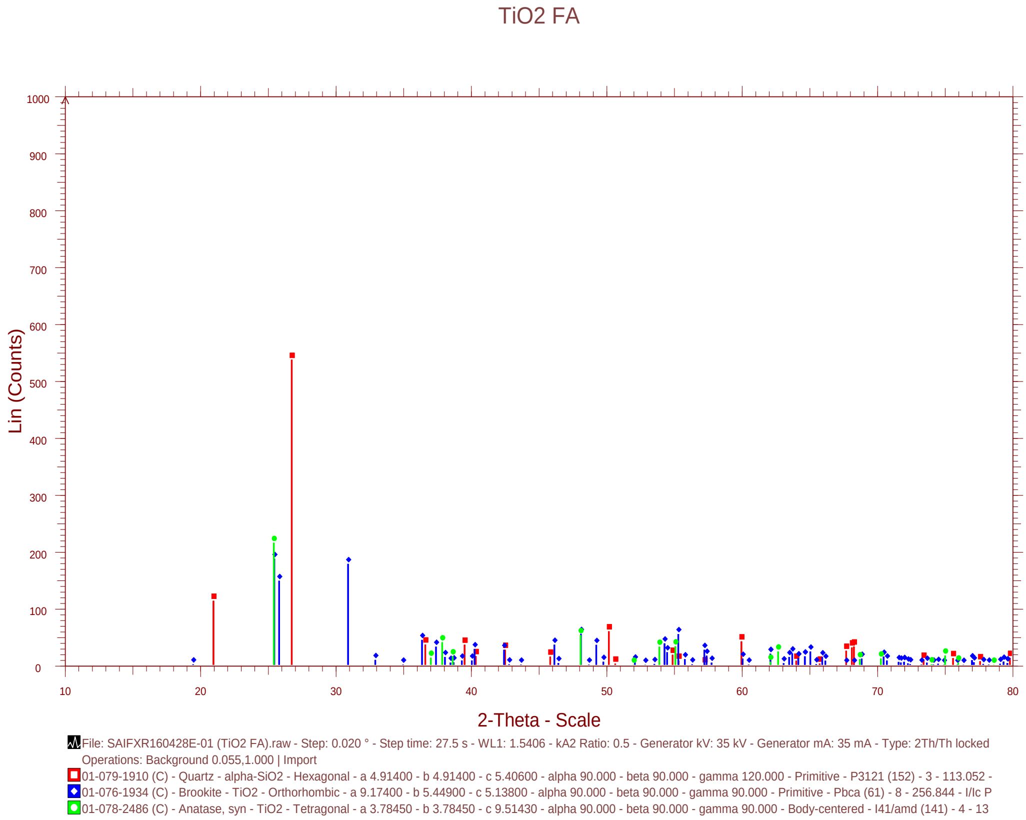

Fig. 1: X –Ray diffractogram of Fly ash –TiO_2 nanocomposite

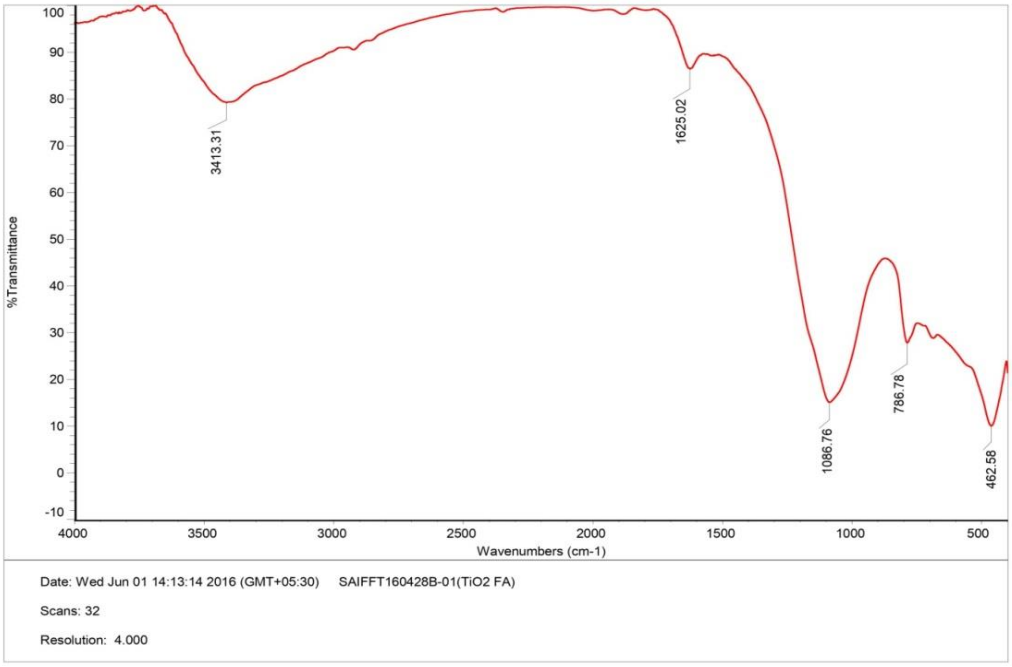

Fig. 2: FTIR spectrum of Fly ash –TiO_2 nanocomposite

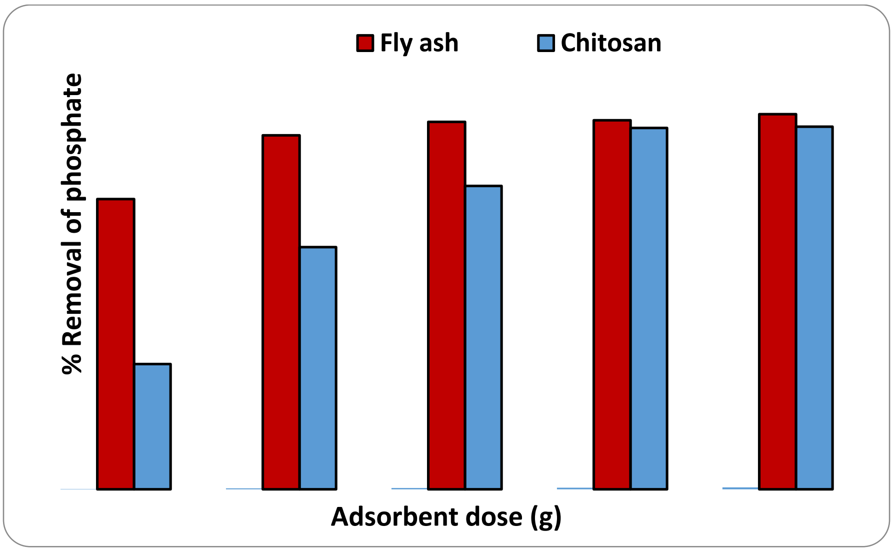

Fig. 3: Effect of fly ash and chitosan nanocomposite dosage on removal of phosphate

In the case of fluoride, the results showed that in all cases, the ability to remove fluoride ions increased with increase in weight of the adsorbent (Figure 4). The fluoride removal efficiency of fly ash increased from 20 to 60% by increasing the dose from 0.1 to 0.5g/100ml. For chitosan adsorption, the removal efficiency increased from 49 to 82% with increase in adsorbent dose. Increased removal efficiency due to increased adsorbent dosage was also observed by Zdunek et al.[38].

Effect of pH: In general, solution pH not only affects the speciation of phosphate anions, but also results in the protonation or dissociation process of the surface hydroxyl and thereby influences the adsorption behaviour of phosphate. The results of pH influence on phosphate adsorption by both fly ash and chitosan are given in figure 5. Phosphate adsorption by both fly ash and chitosan shows a similar trend that uptake of phosphate increased with increasing pH from 3 to 5, maintained stable for a certain range of pH and then declined as pH increased from 7 to 10. This observation is in agreement with other reports showing that phosphate adsorption is more efficient in acidic pH range other than alkaline pH range[10,19,36].

The removal of fluoride ions from effluent sample by fly ash and chitosan nano-adsorbents according to the variation in pH is presented in figure 6. Fluoride adsorption by fly ash under varying pH conditions showed an increase in removal efficiency with increase in pH from 3 to 6.5. Removal efficiency decreased when the pH of the solution increased from 7 to 9. Effective fluoride removal by fly ash at low pH value is also reported by other authors[38].

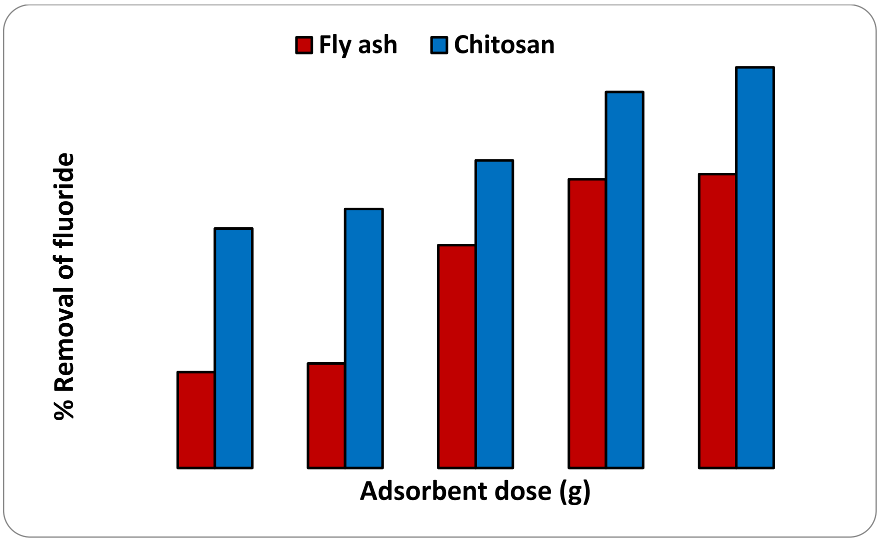

Fig. 4: Effect of fly ash and chitosan nanocomposite dosage on removal of fluoride

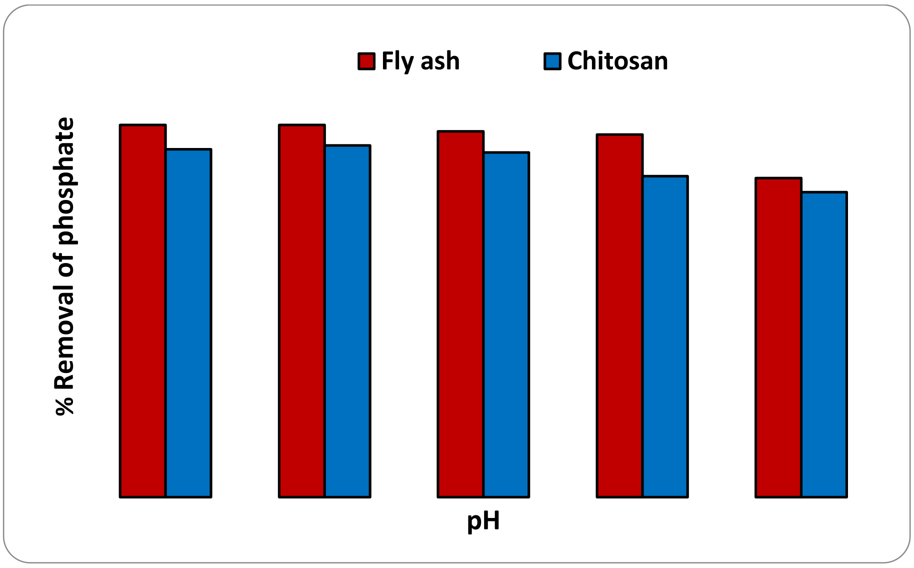

Fig. 5: Effect of sample pH on removal of phosphate

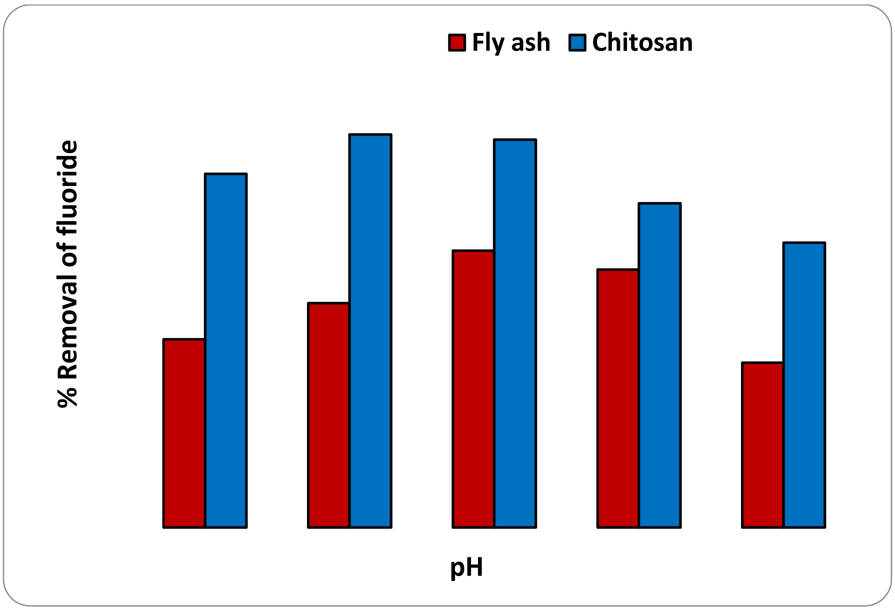

Fig. 6: Effect of sample pH on removal of fluoride

Maximum removal efficiency of 80% was observed for chitosan under pH 5. The decrease in fluoride removal efficiency appeared when initial pH exceeded 7, which may be due to the competition between hydroxide and fluoride ions for active adsorption sites and the increase in diffusion resistance of fluoride attributed by abundant hydroxide ions[1]. Therefore, pH = 5 was considered as the optimal pH for further studies.

Effect of initial ion concentration: The effect of change in adsorption efficiency with initial ion concentration is shown in the figures. Initial concentration of phosphate was changed from 3 to 30 ppm by keeping other parameters like pH, time, adsorbent dosage and temperature as constant. The removal efficiency of phosphate decreases with the initial concentration (Figure 7). The same trend was observed for both the adsorbents (fly ash and chitosan). However, in the case of fluoride, the removal efficiency of fly ash increases from 58 to 62% with increase in fluoride concentration from 1 to 2 ppm and then decreases with increase in fluoride concentration above 5 ppm as shown in figure 8. The maximum adsorption of 78% was observed for fluoride by chitosan nano-adsorbent at low initial concentration. Removal efficiency of fluoride by chitosan decreases with increase in initial ion concentration (Figure 8). This may be due to the full coverage of active surface sites at high adsorbate concentration, as such, no active surface is available at higher concentrations, which results in the reduction of fluoride removal[1].

Effect of contact time: The removal of phosphate using fly ash was very high at the first 30 to 45 minutes of solid and liquid phase contact. No further increase was observed beyond 45 minutes (Figure 9). Maximum removal efficiency of 98% was observed for a contact time of 45 minutes. Phosphate adsorption by chitosan under varying time is shown in figure 9.

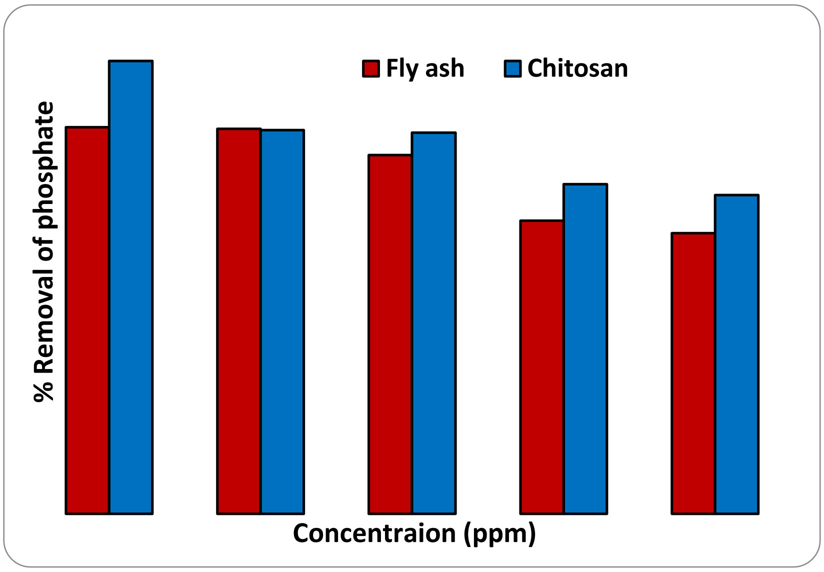

Fig. 7: Effect of initial phosphate concentration

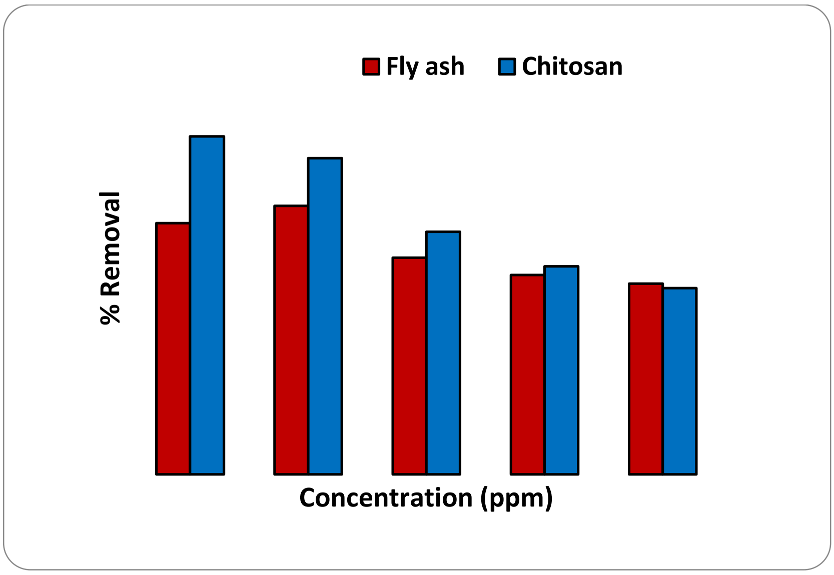

Fig. 8: Effect of initial fluoride concentration

Results showed that 92% phosphate adsorption was observed at a contact time of 75 minutes. The adsorption of fluoride by fly ash and chitosan nanocomposites under varying contact time was shown in figure 10. The removal of fluoride using fly ash was maximum (48%) at 30 minutes of solid and liquid phase contact. No further increase was observed beyond 30 minutes. Chitosan nano-adsorbent showed 75% fluoride adsorption at a contact time of 45 minutes.

Adsorption Isotherms: In order to determine the maximum adsorption capacities of fly ash and chitosan for phosphate and fluoride, the adsorption isotherms were performed with varying concentrations of phosphate and fluoride solutions. Two isotherm models namely, Langmuir model and Freundlich model were studied here to find the best described one. Langmuir isotherm, the basic adsorption isotherm, assumes that the adsorbate can form the surface of the adsorbent molecules interacting with adsorption sites and not interacting or weakly interacting with each other.

Adsorbent molecules present in the liquid phase have the impact on the surface–the likelihood of their adsorbing rises along with the available free surface. The adsorbed particles show a certain probability of desorption. Both probabilities depend on the temperature and size of the adsorption energy. The Freundlich isotherm is an experimental equation which describes the adsorption on heterogeneous (energetically heterogeneous) surfaces and on microporous adsorbents[5].

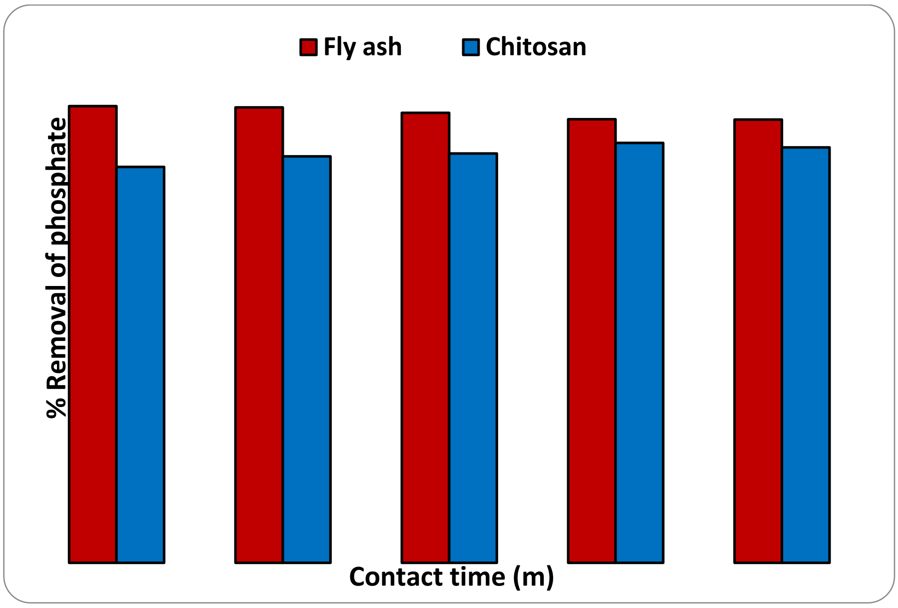

Fig. 9: Effect of contact time on removal of phosphate

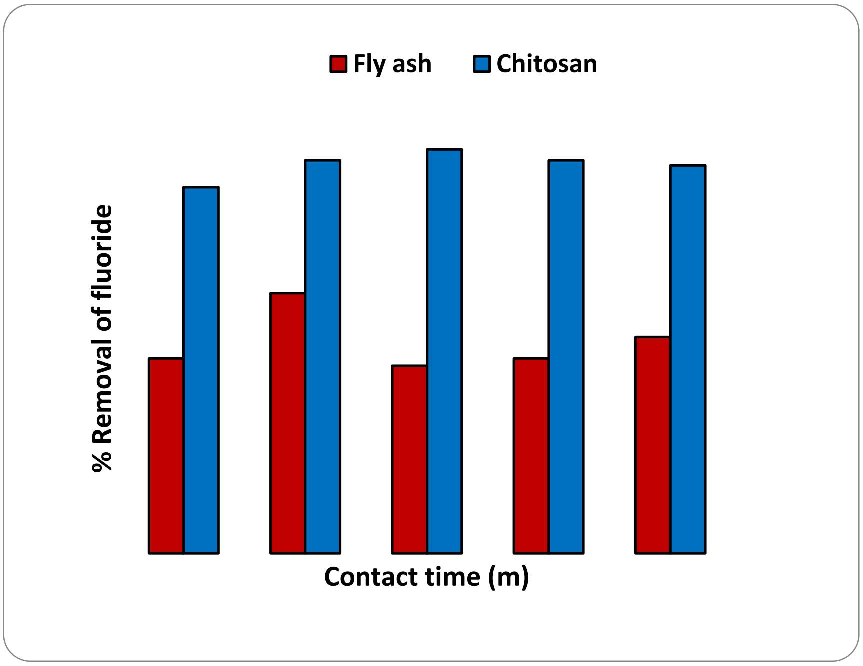

Fig. 10: Effect of contact time on removal of fluoride

In the present study the data showed that the adsorption of phosphate and fluoride using fly ash and chitosan nano-adsorbents was best described by the Freundlich model (Table 2 and figures 11 to 14).

Conclusion

The present study concluded that the prepared nanocomposites of fly ash and chitosan are effective adsorbents for removing phosphate and fluoride from fertilizer industry effluent. Compared to other costly conventional adsorbents, fly ash and chitosan are cost effective and easily available. Fly ash and chitosan nanocomposites showed a removal efficiency of above 90% for phosphate from the sample. In both cases, the phosphate adsorption is maximum at the acidic pH range below pH 6. Phosphate adsorption in both cases decreases when initial concentration of the phosphate solution increases. Maximum fluoride removal efficiency of 60% was achieved by fly ash-TiO_2.

Above 80% removal efficiency was obtained for fluoride by Chitosan-TiO_2 nanoadsorbent. Effective fluoride adsorption occurs in the pH range of 4-6 and decreased with increase in pH. Fluoride adsorption decreases when initial concentration of the fluoride solution increases. Among the two isotherm models studied, Fredunlich adsorption isotherm best described the adsorption of phosphate and fluoride.

Table 2
Adsorption isotherm models

Adsorption analysis	Langmuir model R^2 Value	Freundlich model R^2 Value
Phosphate by Fly ash	0.921	0.993
Phosphate by Chitosan	0.89	0.966
Fluoride by Fly ash	0.901	0.979
Fluoride by Chitosan	0.842	0.908

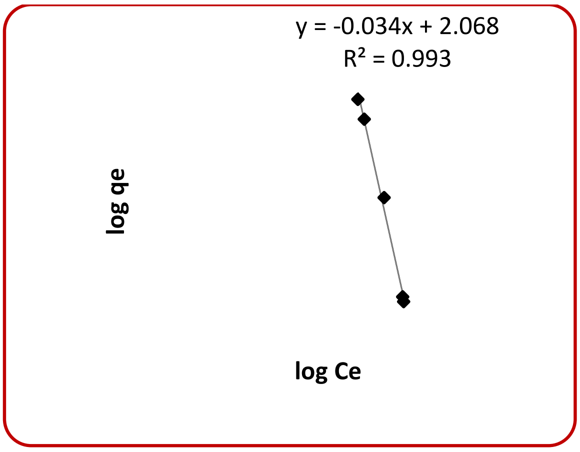

Fig. 11: Freundlich isotherm fitted for adsorption of phosphate on fly ash

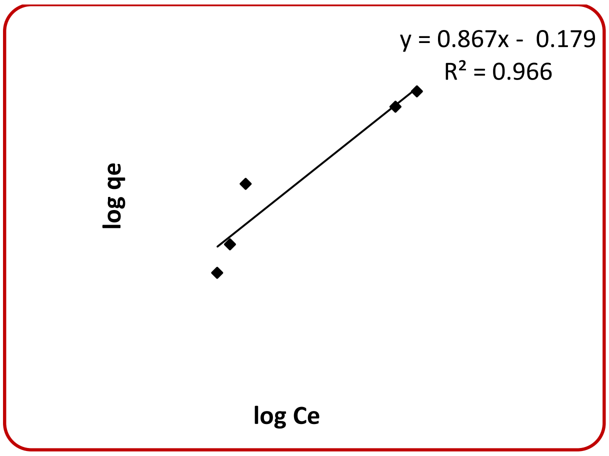

Fig. 12: Freundlich isotherm fitted for adsorption of phosphate on chitosan

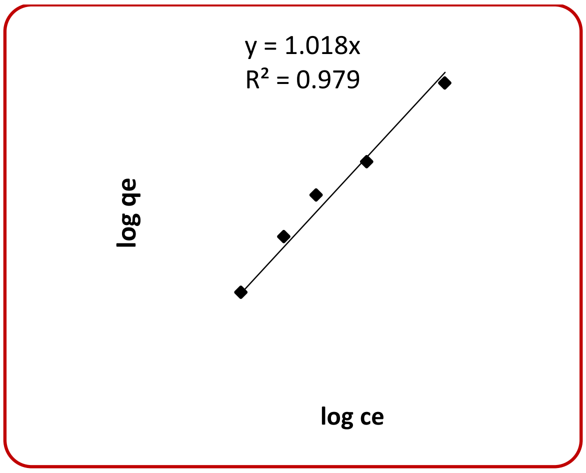

Fig. 13: Freundlich isotherm fitted for adsorption of fluoride on fly ash

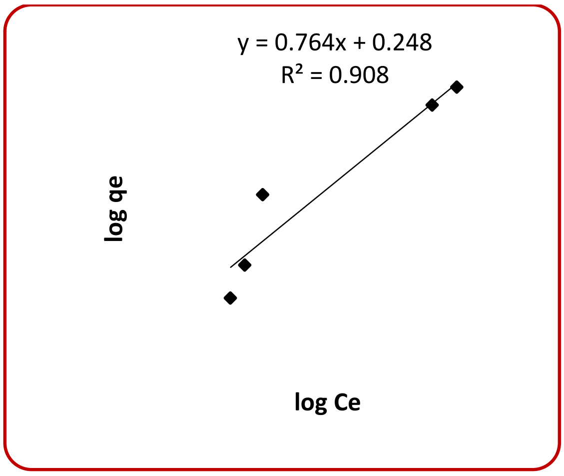

Fig. 14: Freundlich isotherm fitted for adsorption of fluoride on chitosan

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