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An effective phosphate adsorption treatment by one-pot synthesized graphene ceria-titania nanocomposite

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ABSTRACT

Green chemistry aims to detection and removal of pollutants from water, soil and air. Phosphate is considered as most hazardous environmental pollutants, which caused to eutrophication. Moreover, the adsorption measurements of pollutants directly related to the porous morphological structurer of the absorbents. The present study employed a direct synthesis method of ceria-titania oxide nanocomposite and employed for elimination of phosphate from aqueous solution. From the characterization data it is revealed that ceria-titania mixed oxide has an anatase phase structured and also signifying the uniform spreading of cerium in the anatase crystal lattice. Graphene ceria-titania nanocomposite further employed for phosphate adsorption with relevance to pH effect and its adsorption isotherm study.

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Key Words: Adsorption, Graphene, Ceria-titania, Phosphate adsorption.

Introduction

Every ecosystem has its peculiar necessity for the evolution and improvement of the species present in and around it. There are varieties of micronutrients which are crucial for the nourishment of organism. Phosphorous is a most necessary nutrient for aquatic ecosystem as well as terrestrial one but it’s presence in excess amount in water is responsible for eutrophication. The Phosphorous beyond of its permit limit amount is now become a serious warning for aquatic bodies [1,2]. Quality of water is gradually becoming degraded due to the high scale amount of phosphorous from anthropogenic sources, which limits the practice of water using for both human and aqua beings [3]. Rapid growth of algae with some other aquatic plants not only lessens the dissolved oxygen level as increases the biological oxygen demand level in water but also itself proven as toxic and alters the species structure of ecosystem [4,5]. Ongoing to the phosphate adsorption, the recommendation suggested by the united states of environmental protection agency (USEPA) that a discharged calculated amount of 0.05 and 0.1 mg/L of general phosphate is to be carried out in lakes as well as in flowing river [6]. Among various forms of phosphate generally organic phosphate, polyphosphate and orthophosphate forms are present in waste water. So now it become the highly essential for the detection and removal of phosphate to establish eutrophication [7, 8].

Extraction of phosphate from wastage materials can be performed by physical, chemical and biological means. The elimination of phosphate by precipitation method [9] and coagulation method [10] is an competent way but the secondary pollution produced from chemical consumption and the removal of accumulated sludge are the major drawbacks issues for chemical method [11] In addition, the use of biological method for the same propose is practicable but this process have its own draw backs i.e. very sensitive to pH and temperature of water. Here the, phosphorous stored bacteria will also disturb within the reaction method process and caused for the use of biological technique [12]. This Method has unique surface phenomenon properties with very cost effective. Many number of natural and synthetic adsorbent are available for prosperous absorbance [13-15]. Now a day’s porous materials like fly ash, zeolites, metal oxide, granular activated carbon, graphene and metal-organic framework, carbon nanotubes and functionalised grapheme are becoming the rising star in the horizon of phosphate absorption [16]. More interestingly among all methods graphene-based composites have drawn more research interest for waste water treatment application [17,18]. Graphene is a hexagonal planar arrangement of sp^2 hybridised 2D carbon atom having specific area of 2630 m2/g and also strong thermal, electrical and mechanical properties [19-20].

In many more research fields like biosensor, fuel shell, carbon quantum dots etc. graphene based Nano-composites grabed strong research attention [21]. This work aims on the phosphate adsorption by graphene nanocomposite considering the different parameters like pH, concentration of phosphate solution and weight of the catalyst etc.

Experimental

Materials and Reagents

The chemicals taken for synthesis of the sample are in analytical grade purity and during the whole synthesis of sample and its applications the milli-Q purified water were used. Ceric ammonium nitrate $(NH_4)_2Ce(NO_3)_6$ and titanium iso-propoxide Ti were used as precursor materials. Graphite powder, Iso- propanol (C_3H_7OH), sodium nitrate ($NaNO_3$), potassium permanganate powder ($KMnO_4$), sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) were purchased from sigma Aldrich. All the Borosil make brand glass flasks and beakers were used in the whole experiment process.

Preparation of Graphene-CeO_2-TiO_2 mixed oxide composite.

Here, the sol–gel method was implicated for preparation of mesoporous Cerium-Titanium oxide mixed oxides by way of 2, 5 and 10 weight % of CeO_2 with solvents of propanol and water. The method of preparation was previously carried out by our team members [22]. In a sum up discussion, aqueous solution of two precursors of titanium iso-propoxide and ceric ammonium nitrate $[(NH_4)_2[Ce(NO_3)_6]$, of 25 ml each amount mixed over 400 ml deionized water under stirred condition. After 30 minutes. 2% weight graphene oxide were added under such condition followed by addition of sodium borohydride solution as reducing agent. Then the sample allowed for another 30 minutes stirring with subsequently allowed for centrifugation, dry and keep in desiccator for rest of the study. The resulting metal oxide composites formulated as $Ce_xTi_{(1-x)}O_2$,here X is taken as 0.02, 0.05, 0.10 and represented as CTO-2, CTO-5, CTO-10 respectively. Following the same methods, CTO- 5 and CTO-10 were also synthesized with graphene oxide mixing of 2% by weight and varying the

Characterization of sample.

XRD patterns of all the synthesized samples are carried out with the configuration of Cu object and Ni filter of make name PANalytical, X'Pert PRO. For the optical absorbance experiment performed by Ultra-Visible reflectance spectra having brand name Shimadzu DRS-2450, here $BaSO_4$ is taken for the standard of reference. Field Emission Scanning Electron Microscope (FESEM) study and EDAX mapping was carried out by Quanta-250 FEI brand name instrument.

Applications and Mechanism

Phosphate Adsorption experiments

The phosphate adsorption experiment was carried out by varying the different phosphate concentration and amount of adsorbent (graphene-ceria-titania mixed oxide) in correlation to different pH value. Here the optimum pH value is signified in a distinguishing experiment. Explaining the study in a typical way, in a 100 ml conical flask (stopper cork), 50 ml of phosphate solution (concentration varies from 5-30 mg/L) and adsorbent graphene-ceria-titania mixed oxide (1.0-6.0 g/L) were taken for the experiment in different pH concentrations. Through the water shaker bath the solution was allowed to attain equilibrium after 9hrs. The as prepared solution was filtered out by Whatman 42 filter paper and employed for measurement of phosphate concentration in the filter paper through spectro-photometrically. The concentration of phosphate adsorbed was investigated from the following equation.

$$q_e = (C_i - C_e)V/m$$

where qe stands for the amount of P adsorbed on the solid.

Ci stands for the initial concentration (mg L-1)

Ce stands for the final concentration (mg L-1)

V and m stands for volume of the solution (L) and amount of adsorbent (g) respectfully.

Results and Discussion.

Analysis of Characterizations data.

The crystallinity and phase clarity of the samples were studied through the powder X-ray diffraction (PXRD) pattern Figure 1. The specific peaks are well proven with JCPDS card number 01-075-2552 for 2θ at 25.2 (111), 37.8 (004), 48.5 (200), 54.2 (105), 62.9(204), 69.5 (116) and 75.3 (215) respectively.

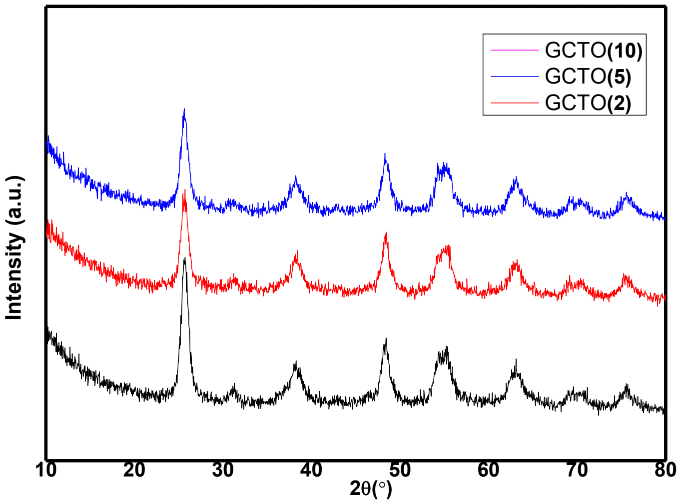

Figure.1 XRD plots for GCTO 2, GCTO 5 and GCTO 10.

This data reveals the crystalline phase of Ceria-titania with no change in crystallinity with variation of loading weightage. This also represents the plane of 200 and 215, which clarifies the titanium-anatase phase impurity only a very minute extend. The transparency for the nonappearance of any other phase is also established from the FESEM images as presented in Figure 2. From the FESEM images of GCTO-5 sample clearly exposes the perfect arranged of metal oxide over graphene sheets. Again elemental analysis by means of EDAX technique data confirms the nanocomposite. The atomic percentage of elements like C, O, Ti, and Ce as evaluated to be 4.50%, 22.30%, 69.52% and 3.51%.

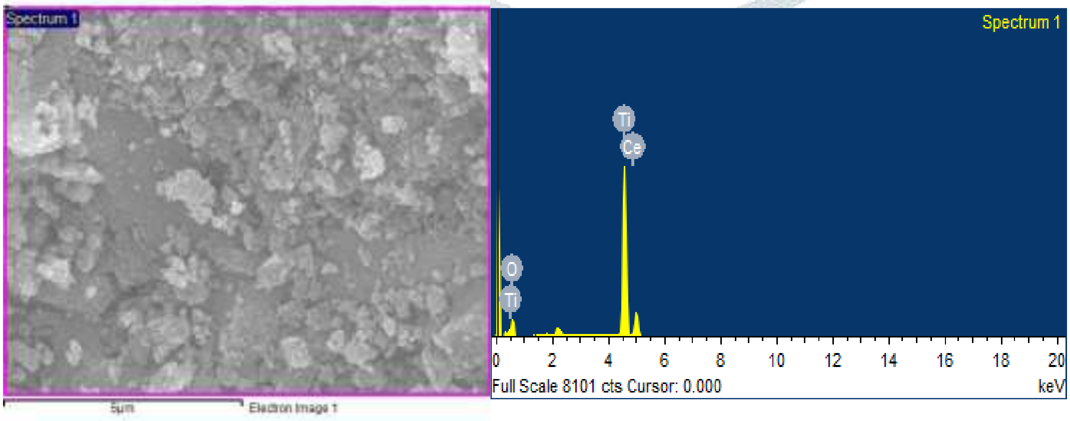

Figure.2 FESEM images of graphene-Ceria-titania Composite and EDAX data.

With this, no other atomic percentage value was noticed. This demonstrated the nonexistence of any other elements in the as prepared ceria-titania sample.

Adsorption experiment:

Preliminary observations

The adsorptive act of the synthesized nano-composite i.e GCTO-2, GCTO-5, GCTO-10 was analysed by using 20mg of adsorbent, phosphate concentration of 5mg/L and at value pH = 5.0 for time limit of 90 min. It was established that GCTO-5 sample exhibited maximum percentage of adsorption figure 3(a). Therefore, the optimum pH value of GCTO-5 sample was engaged for further adsorption study and it was find out that at pH=5 the sample shows the maximum adsorption of phosphate which is represented in Figure. 3(b). Again to study the time variance of adsorption, preliminary studies with initial phosphate amount of 5mg L^{-1} at fixed pH = 5 and adsorbent does 20mg L^{-1} using GCTO-5 sample was employed and the adsorption process is relatively slow and equilibrium is attained within 75 min which is represented in Figure.4 (a). No further change in equilibrium concentration was seen up to 90 minutes. After this time frame the adsorption is independent of initial concentration. Hence, the equilibrium time is set to 75 minutes for all further adsorption experiments Figure 4(a).

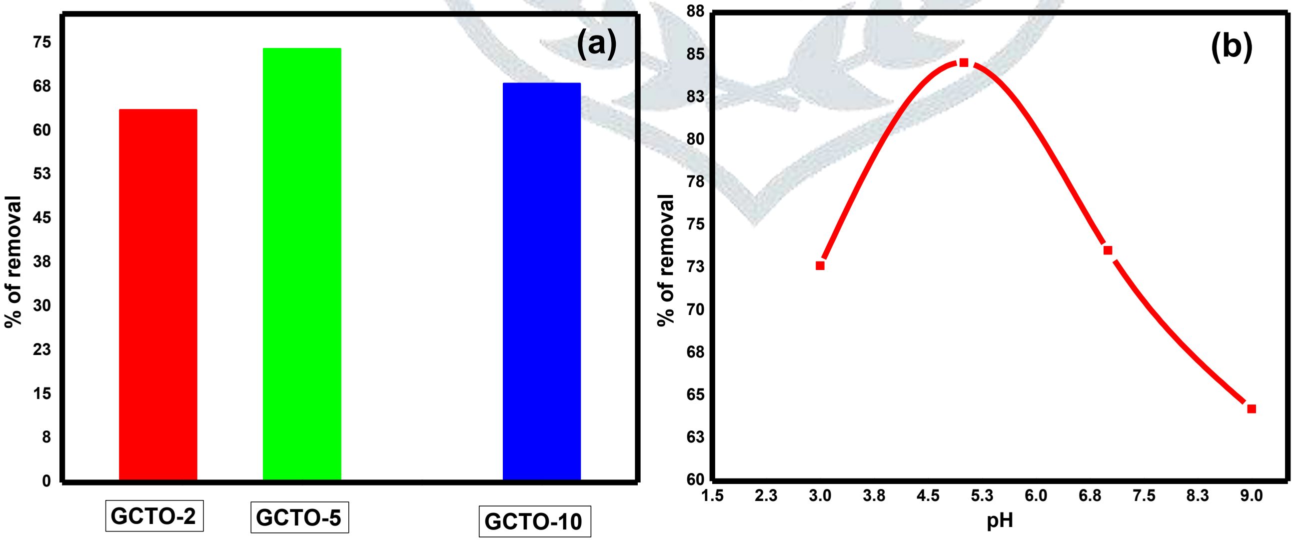

Figure.3(a) Adsorption of Phosphate by GCTO-2, GCTO-5 and GCTO-10. (b)Adsorption of Phosphate at optimum pH=5.0 value and its equilibrium.

Effect of pH on phosphate removal.

The solution pH is always plays the vital role for phosphate adsorption since its directly linked to both the surface charge of adsorbent and phosphate species. The removal of phosphate by GCTO-5 at optimized pH=5 is maximum and then declination of phosphate adsorption occurs. This debility of phosphate adsorption ability accordance the increase of pH has also been reported [23]. As discussed here, phosphate exist in different ionic form like $H_2PO_4^{-1}$, $H_2PO_4^{2-}$ and PO_4^{3-}. The richness of each species in aqueous sample is purely pH dependent. Consequently, the positively charged adsorbent could efficiently interrelate with the negatively charged $H_2PO_4^{-1}$ through electrostatic force of attraction, thus foremost to the improved phosphate removal tendency under acidic condition [24-25]. Again, when the pH value increased the percentage of divalent $H_2PO_4^{2-}$ species becomes the governing species and the surface of the adsorbent were deprotonated.

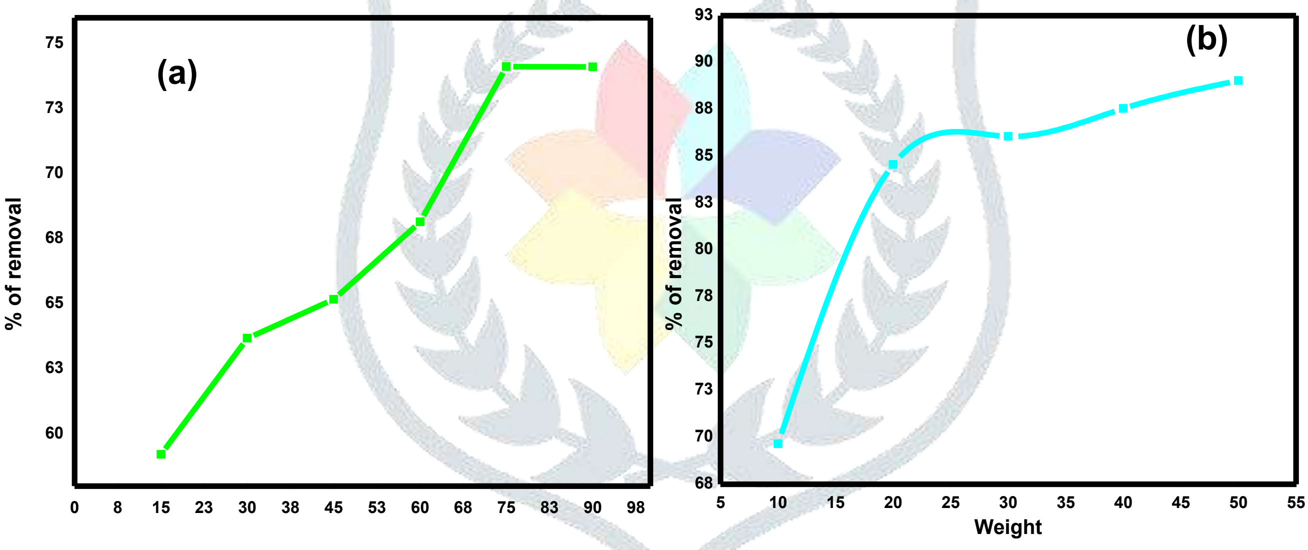

Figure.4(a) Adsorption of phosphate by GCTO-5 with time. (b) Adsorption of phosphate by varying weight of GCTO-5.

Consequently, there is electrostatic repulsion negatively charged adsorption site and the negatively charged $H_2PO_4^{2-}$. This mechanism caused for non-absorbance of phosphate after the pH=5.

Effect of adsorbent dose and initial adsorbate concentration.

The result of phosphate adsorption with variable amount of GCTO-5 (10-40 mg/L) also studied by keeping all the fixed parameters [figure.4(b)]. It is illustrated that, there is direct proportional relationship between the adsorption of phosphate with increase in adsorbent amount. And after a certain period the adsorption decreases, this first one may be due to the increase in adsorption site to a certain limit extend and then the blocking of adsorption sites with increase in adsorbent dose after the optimum period.

Phosphate adsorption isotherm study

Adsorption experiments were carried out for GCTO-5 (20 mg) with different phosphate concentrations from 5ppm to 25ppm at pH-5 with dil. HCl and NaOH [22]. The adsorption isotherm fitting curves value with maximum regression coefficient (R^2= 0.99) represents the adsorption of phosphate on optimized GCTO-5 sample follows a monolayer adsorption with uniformly distributed of the adsorbents. The maximum removal capacity calculated by Langmuir isotherm equation is 41.49mgP/g. The efficiency of adsorption process of phosphate removal and adsorbed verses time as parameter study is highly necessary [26]. It is revealed that the adsorption equilibrium attains its saturation after 1hr and gradually become sluggish due to non-availability of adsorption sites [Figure.5].

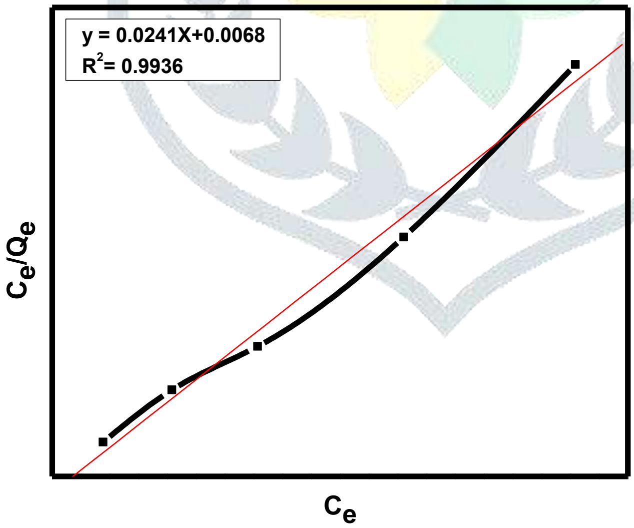

Figure. 5 Adsorption isotherm regression analysis of GCTO-5 sample.

Conclusion

The phosphate adsorption is highly necessary for eutrophication to sustain an eco-friendly environment. The adsorption activity of ceria-titania mixed oxides with graphene nanocomposite to phosphate was studied. The nanocomposite with 2 weight % ceria was established an effective an adsorbent for phosphate at pH 5.0. It was also observed that the percentage of phosphate adsorption direct proportional with increasing concentration of adsorbent and decreases with increasing initial concentration of phosphate. The nanocomposites of Ce-Ti-Rgo sample acts as a superlative degree nanocomposite materials for pollutant phosphate adsorbent and abled to extends its work for an eco-friendly green environment.

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