Removal of Phosphate from Contaminated Water Using activated carbon supported Nanoscale Zero-Valent Iron (nZVI) Particles

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In the current study activated carbon supported zero-valent iron nanoparticles were synthesised, characterized and used for phosphate adsorption study. Batch adsorption experiments were carried out to study the effect of activated carbon supported nZVI nanocomposites on the removal of phosphorus (P) from 50 mg/L P contaminated water at various pH values. When the activated carbon supported nZVI dosage increased from 2 g/L to 8 g/L the percentage P adsorbed increased from 69 % to 99.5%. The amount of P adsorbed increased with an increasing concentration of activated carbon supported nZVI dosage and decreasing pH values. Increasing adsorption of P with increasing adsorbent dosage can be due to higher adsorption site, however at higher adsorption dosages beyond 8 g/L the adsorption showed a decreasing trend due to the saturation and overlapping of adsorption sites. When the pH value of the solution increased from 3 to 11 the percentage removal of P decreased from 99.5 to 12 %. The reduction in adsorption at increasing pH values can be attributed to the repulsion between hydroxylic ions (OH^-) on the surface of iron nanoparticles and the existence of P in the form of phosphate anions ($H_2PO_4^-$, HPO_4^- and PO_4^{3-}). Langmuir and Freundlich adsorption models were fitted in the experimental data, and it was found that the Langmuir model fitted well, and the calculated maximum adsorption capacity of phosphate was 68 mg/g, suggesting significantly higher and remarkable uptake of phosphate by activated carbon supported nZVI particles. The findings of this study showed that silica coated ZVI Particles could be promising adsorbents for removal of phosphates from polluted water bodies effectively.

1. Introduction

Phosphorus is essential for life, often considered either the primary limiting or co-limiting nutrient and it is a very essential resource for industrial products. However excessive P present in natural waters is known to cause eutrophication (Loganathan et al., 2014). Eutrophication is the nutrient enrichment of waters associated with accelerated growth of algal blooms that may produce hepato- and neurotoxins severely compromising human and animal health, water quality deterioration, and other undesirable changes that interfere with water uses (Singh and Singh, 2018). Eutrophication occurs naturally over centuries as lakes age and are filled in with sediments, however, human activities have accelerated the rate and extent of eutrophication through both point-source discharges and non-point loadings of limiting nutrients, such as nitrogen and phosphorus, into aquatic ecosystems (i.e., cultural eutrophication), with dramatic consequences for drinking water sources, fisheries, and recreational water bodies (Chislock et al., 2013). Accelerated eutrophication not only affects the aquatic life but indirectly hinders the economic progress of communities that depend on aquatic food and other resources. Although both nitrogen (N) and P are considered to be the limiting nutrients for eutrophication, some algae are efficient in the fixation of atmospheric N and hence P often becomes the potentially limiting nutrient in freshwaters (Loganathan et al., 2014). Thus, the best strategy to combat eutrophication is reduction of the amount of phosphorous in water bodies to an acceptable level of 0.1 mg/l , recommended by World Health Organization (WHO) (Fadiran et al., 2008). In natural streams of water, phosphorous is present in phosphate (PO_4^{3-}) form (Loganathan et al., 2014). Many strategies have been reported for the efficient

elimination of phosphates from aqueous solutions including enzymatic biodegradation, adsorption, electrochemistry, precipitation, and floatation. Of these, the sorption process is generally considered to be an effective water treatment option because of convenience, ease of operation, simplicity of design, and economics, (Xie et al., 2017).

Recently, nanoscale zero-valent iron (nZVI) particles have received great attention in environmental clean-up studies due to their strong reducing capability, high surface area, reactivity, nontoxicity, and easy preparation process to treat various anionic pollutants including dyes and phosphates (Teng et al., 2017). Nanoscale zero-valent iron (nZVI) has been successfully applied in the removal of pollutants with various natures such as halogenated compounds (e.g., chlorinated organic solvents, organochlorine pesticides, polychlorinated biphenyl, etc.,), nitrate, phosphate, polycyclic aromatic hydrocarbons, and heavy metals. In the presence of dissolved oxygen, reactions like adsorption, reduction, precipitation, and oxidation of nZVI have been exploited for a wide range of contaminants removal, including halogenated organic compounds, nitroaromatic compounds, organic dyes, phenols, heavy metals, inorganic anions such as phosphates and nitrates, metalloids, and radioactive elements (Kang et al., 2018). However, due to high surface energy and strong interparticle, magnetic, and van der Waals interaction nZVI has a strong tendency to coalesce and form large aggregates. This in turn blocks the surface-active sites, decreases its reactivity, and leads to fast inactivation and low efficiency of phosphate removal (Teng et al., 2017). Therefore, devising mechanisms to avoid aggregation and oxidation is critical for developing effective applications of nZVI. It is well known that well-developed pores of activated carbon (AC) could efficiently disperse and stabilize nanoparticles (Singh and Singh, 2018). Thus, immobilization of nZVI on porous material is hypothesized to prevent aggregation of ZVI particles, protect ZVI against oxidation, and potentially enhance the removal performance of contaminants. In the current study activated carbon supported nanoscale zero-valent iron (nZVI) particles were synthesised and their potential application for phosphate remediation from polluted water is investigated.

2. Experimental

2.1 Activated carbon supported nZVI Synthesis and Characterization

Activated carbon supported nZVI was synthesized via reduction of dissolved Fe(III) chloride by using sodium borohydride ($NaBH_4$), following a modified method proposed by Singh and Singh (2018). Briefly, 5g of finely ground commercial activated carbon was dissolved in 100 mL of Millipore water in a two-neck round-bottom flasks fitted with septum around its necks and 0.05 M $FeCl_3$ solution was added to it. It was then deaerated by passing N_2 gas for 1 h. In another flask, 50 mL of 0.3 M of $NaBH_4$ solution was prepared and it was purged with nitrogen gas for 15 min. Then, this deaerated $NaBH_4$ solution was added dropwise to the above ferric chloride and activated carbon solution in an inert atmospheric condition under vigorous stirring for 2h. After some time, the colour of the solution turns grayish black because of the formation of the nZVIs. The activated carbon supported nZVIs were collected by centrifugation washed three times with ethanol, and dried under nitrogen environment and used for phosphate adsorption study. The morphology and sizes of the nZVI particles were analysed using a JEOL JEM-2010 Transmission Electron Microscopy (TEM).

2.2 Batch adsorption experiment

Batch adsorption experiments were conducted to study the phosphate removal efficiency of activated carbon supported nZVIs under various experimental conditions. In all experiments, a known concentration of phosphate and specified amount of activated carbon supported nZVIs were mixed in 100 mL distilled water in 250-mL Erlenmeyer flasks. The adsorbent was equilibrated by shaking with 0.01 M $CaCl_2.2H_2O$ for 12 hours before the actual experiment to maintain a constant ionic strength and minimize cation exchange (Barrow and Shaw,1982). The pH of phosphate solution and pumice mixture was set intended values using 0.1 M HCl and 2M NaOH solutions.

Batch experiments were conducted to evaluate the effects of pH, initial phosphate concentration, contact time, and adsorbent dosage on the adsorption capacity of Activated carbon supported nZVIs for phosphate removal. Briefly, desired amounts of activated carbon supported nZVIs were added into the 250 mL Erlenmeyer flasks containing 100 mL of KH_2PO_4 solution.

The effect of solution pH on phosphate removal was studied with a phosphate solution of 50 mg/L and activated carbon supported nZVIs dose of 8 g/L solution. Equilibrium adsorption studies were carried out by mixing by mixing 8 g/L dosage of activated carbon supported nZVIs with 100 mL phosphate solution at pH 5 with concentrations ranging from 10 to 350 mg/L for a period of 24 hours until equilibrium is reached.

The flasks were then shaken at 120 rpm at room temperature and periodically 50 mL of the solution was sampled, centrifuged (Centrifuge 5804, Eppendorf AG, Hamburg, Germany) at 7500 r/min for 10 minutes and

the supernatant was analysed for phosphate concentration using a spectrophotometer at wavelength of 860 nm (Pradhan and Pokhrel, 2013).

The removal percentage and adsorption capacity of the adsorbent at any time t were determined using Equations (1) and (2), respectively

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (1)$$

$$q_t = \frac{(C_O - C_t)V}{M} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (2)$$

where q_t is the amount of phosphate adsorbed per unit mass of the adsorbent (mg/g), C_o is the initial concentration of phosphate in the aqueous phase (mg/L), C_t is the concentration of phosphate as phosphorus in the aqueous phase at time t (minutes) in mg/L, M is the dry mass of the adsorbent (g), V is the initial volume of the aqueous phase in contact with the adsorbents during the adsorption test in litre (L), and R (%) is the percentage of phosphate adsorbed at time t.

3. Results and Discussion

3.1 Characterization of activated carbon supported nZVIs

TEM analysis was performed to examine the morphology, dispersion and nanostructure of Activated carbon supported nZVIs. From TEM images of activated carbon supported nZVIs nanocomposite Fig. 1 shows nZVIs embedded on the surface of the activated carbon effectively preventing aggregation and subsequent loss of active surface area.
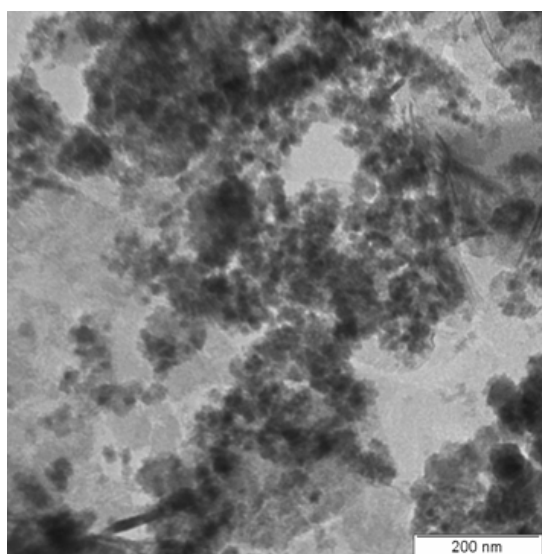

Figure 1: TEM images of activated carbon supported nanoscale zero-valent iron (nZVI) particles.

The rough and porous surface morphology of the activated carbon as displayed provided the suitable sites to support nZVI (Figure 1). The nZVI particles that were immobilized on the activated carbon were well dispersed and firmly attached to the activated carbon through the phenolic, lactonic and carboxylic functional groups via electrostatic and Vander Waals forces (Taha et al., 2020).

3.2 Effect of adsorbent dosage on adsorption of phosphates

The effect of activated carbon supported nZVIs on phosphate removal was evaluated with an increasing adsorbent dosage (0, 2, 4, 8 g/L). As displayed on the graph (Figure 2a), the phosphate removal efficiency rose from 69% to 99.5% as the activated carbon supported nZVIs dosage increased from 2 g/L to 8 g/L. The increase in phosphate removal extent with an increasing adsorbent dosage implies that the accessibility of a larger amount of available active sites for a higher adsorbent dosage enabled activated carbon supported nZVIs adsorb an increasing amount of phosphate ions. However, a slow upward trend was observed as the

activated carbon supported nZVIs amount increased continuously, which may be due to an overlapping of adsorption sites as a result of over-crowding of adsorbent particles (Patil Mansing and Raut, 2013).
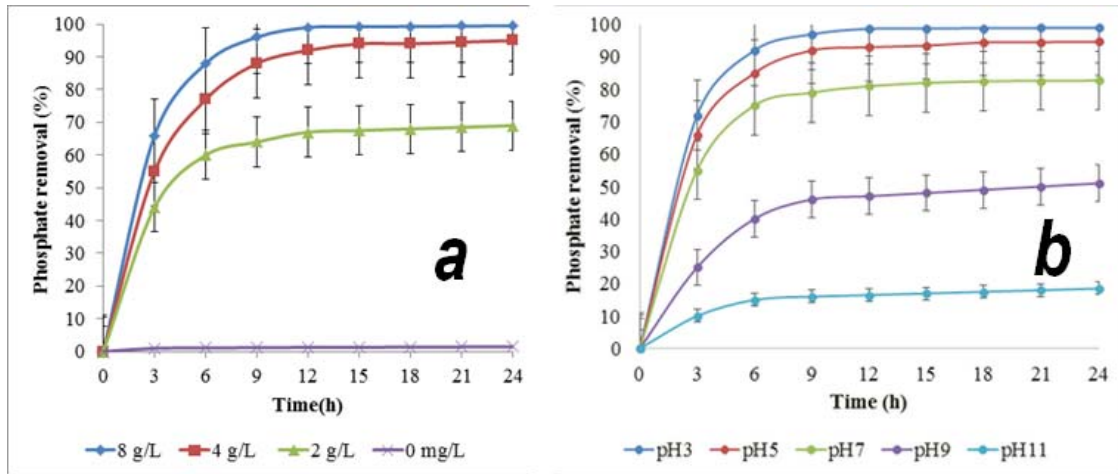

Figure 2: Removal percentage of phosphate ions by the activated carbon supported nZVI with increasing adsorbent dosages (a) and with different initial solution pH values (b).

3.3 Effect of pH on the phosphate adsorption

The effect of solution pH on the removal of phosphate using the activated carbon supported nZVI nanocomposites has been investigated. Solution pH plays an important role in controlling the surface charge of the adsorbent, the degree of ionization of the adsorbate in the solution as well as dissociation of various functional groups on the active sites of the adsorbent (Banerjee and Chattopadhyaya, 2017). Figure 2b, reveals the effect of the solution pH on phosphate adsorption by activated carbon supported nZVIs nanocomposite with the initial pH values ranging from 3.0 to 11.0. It can be seen that adsorption of phosphate on the activated carbon supported nZVIs nanocomposite was highly pH dependent and the adsorption capacity of the adsorbent decreased with increasing solution pH from 3.0 to 11.0. The hydrogen ion and hydroxyl ions are adsorbed quite strongly on the adsorbent and therefore the adsorption of the phosphate anions is affected by the pH of the solution. Thus reduction in adsorption at increasing pH values can be attributed to the repulsion between hydroxylic ions (OH⁻) on the surface of iron nanoparticles and the existence of P in the form of phosphate anions ($H_2PO_4^-$, HPO_4^- and PO_4^{3-}). At the lower pH values adsorption increases at the adsorption sites because of increasing protonation and subsequent electrostatic attraction between the phosphate anions and adsorbent surface. At high pH values, the competition between the phosphate anions (-PO_4^{3-}) and the hydroxyl ions increases, and phosphate adsorption decreases (Antelo et al., 2005).

3.4 Adsorption isotherms study

An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent, q_e, to the concentration of the solute in the liquid, C_e, with which it is in contact at constant temperature (Kuang et al., 2020). Adsorption isotherm models are usually used to describe the interaction between the adsorbent and the adsorbate when the adsorption process reaches equilibrium, offering the most important parameter for designing a desired adsorption system. In this study, we evaluated the fitness of equilibrium data with non-linear forms of the Langmuir, and Freundlich isotherm models (Equations 4 and 5 respectively). These isotherms relate phosphate anion uptake per unit mass of adsorbent, q_e, to the equilibrium adsorbate concentration in the bulk fluid phase, C_e.

The amount of chromium adsorbed per unit mass of the adsorbent (mg g⁻¹) was determined by the following expression:

$$q_e = \frac{(c_i - c_e).V}{W}$$

………………….…………(3)

Here, q_e is the amount of phosphate adsorbed per unit mass of the adsorbent (mg/g) C_i and C_e (both in mg/L) are the initial and the equilibrium concentrations of the adsorbate (phosphate) respectively. W is the weight of adsorbent (g), and V is the volume of solution (L).

$$q_e = \frac{q_m k_L c_e}{1 + c_e k_L} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$q_e = k_f . c_e^{\frac{1}{n}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \ldots(5)$$

Where q_e = adsorbed amount at equilibrium, q_m = maximum adsorption capacity, k_L = Langmuir constant (mg/L), k_f is Freundlich isotherm constant (mg/g) n = adsorption intensity applying nonlinear regression directly to (2) and (3) is the preferred strategy. Isotherm parameters were determined by minimising the error distribution between the experimental data and the predicted isotherm using the solver add-in with Microsoft's spreadsheet, Excel. The nonlinear plots of the isotherms are presented in Figure 3.
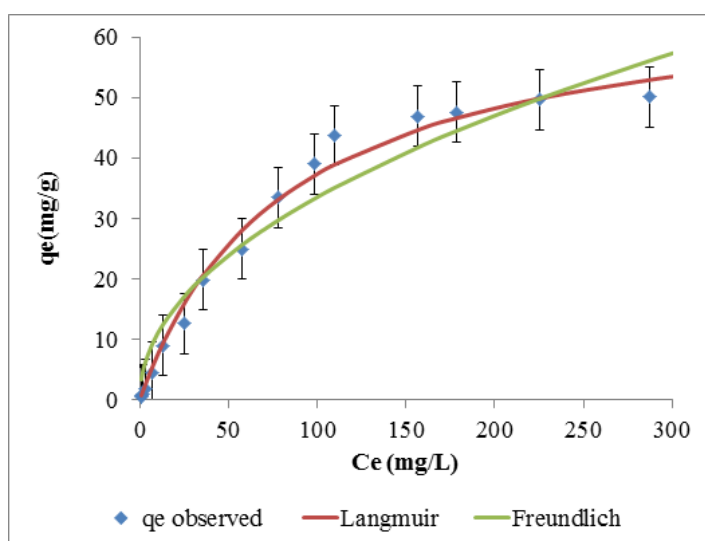

Figure 3: Non-linear curve fits of the Freundlich and Langmuir isotherm models for the phosphate adsorption onto activated carbon supported nanoscale zero valent iron (nZVI) nanocomposites.

Figure 3 shows the adsorption isotherms of phosphate adsorption onto Activated carbon supported nZVIs. The equilibrium adsorption data fitted well to the two models, but gave a better fit to the Langmuir isotherm model (R^2 value of 0.98 compared to 0.95 of Freundlich model) with a maximum adsorption capacity, q_m of 68 mg/g of adsorbent. The Langmuir isotherm parameter q_m which measures the monolayer capacity of the adsorbent and the Freundlich isotherm parameter k_f which indicates the extent of adsorption follow the same trend and were good measures of the adsorption capacity of the nanocomposite (Kuang et al., 2020). Our observation suggests that adsorption is limited to a monolayer: only a single layer of molecules on the adsorbent surface are absorbed, adsorbent surface is homogeneous and adsorption energy is uniform for all sites and there is no transmigration of adsorbate in the plane of the surface. Once a pollutant occupies a site, no further adsorption can take place in that site; the intermolecular attractive forces rapidly decrease as distance rises (Choy et al., 2000). It can be seen that the adsorption capacity of Activated carbon supported nZVIs increased with the increasing equilibrium concentration of the adsorbate. This could be due to the increasing driving force of the concentration gradient with the increase in the initial phosphate concentration.

4. Conclusion

In recent years, nano zero-valent iron (nZVI) has been shown to be a highly effective sorbent for various inorganic and organic contaminants in aqueous solutions, due to their large surface area to volume ratio, high surface energy, reactivity and adsorptive capacity compared to their bulk materials. However, despite its advantages nZVI nanoparticles tend to agglomerate and grow to micron scale, thereby rapidly losing their mobility and chemical reactivity. In the current study activated carbon supported zerovalent iron nanoparticles were synthesised characterized and used for P adsorption study. The activated carbon supported nZVIs nanocomposites demonstrated efficient adsorbent dosage and pH dependent removal of phosphate ions, the adsorption capacity of the adsorbent decreased with increasing solution pH from 3.0 to 11.0. The

Langmuir model revealed a satisfactory fit to the equilibrium data with a maximum adsorption capacity of 68 mg/g, suggesting a remarkably high uptake of phosphate by activated carbon supported nZVI particles. The current study revealed that activated carbon materials can not only effectively decrease nZVI aggregation, but also facilitate the mass transfer between nZVI particles and phosphate anion pollutant. The findings of this study showed that activated carbon supported ZVI Particles could be promising adsorbents for removal of phosphates from polluted water bodies effectively.

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