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Development of multivalent metal ions imprinted chitosan biocomposites for phosphate sorption

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ABSTRACT

In this present work, to overcome the problem of eutrophication due to phosphate an attempt was made to develop eco-friendly composite materials using chitosan and bentonite. To improve the properties of bentonite (bent) and chitosan (CS), chitosan supported bentonite (CSBent) composites were prepared and utilized for phosphate removal. To enhance the uptake capacity of CSBent, various multivalent metal ions like Zr^{4+} , Fe^{3+} and Ca^{2+} were imprinted on CSBent composites namely $Zr@CSBent$, $Fe@CSBent$ and $Ca@CSBent$ biocomposites respectively. The synthesized $Zr@CSBent$, $Fe@CSBent$ and $Ca@CSBent$ biocomposites possess the efficient phosphate sorption capacities (SCs) of 40.86, 22.15 and 13.44 mg/g than the individual CSBent composite. The systematic study for various adsorption influenced parameters such as agitation time, presence of co-existent anions, solution pH, temperature and initial phosphate concentration has been verified in batch mode. The prepared biocomposites was exemplified by FTIR, TEM, SEM and EDAX analysis. The experimental data was fitted to various isotherms and thermodynamic parameters. The mechanism of phosphate removal by $M@CSBent$ composites was governed by ion-exchange, electrostatic attraction and inner sphere complexation. This study reveals a feasibility of biocomposites for phosphate uptake from polluted water sample at field situation.

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1. Introduction

Phosphate is deemed as macronutrients for aquatic plant growth and their metabolism [1]. Conversely, major concentration of phosphate in water bodies was observed from agricultural fertilizers, detergents, soaps, demographic and industrial expansions which have leads to eutrophication of reservoirs, rivers and lakes [2]. Eutrophication causes explosive growth of algae, depletion of the photic zone, esthetic problems and reduction of dissolved oxygen in water which terminates the abundance of aquatic plants and animals [3]. The tolerance limit of phosphate content in water is < 0.5 mg/L [4]. Subsequently, there is a necessary in the development of reliable, economical and easiest technique for phosphate sorption.

Various phosphate removal technologies have been utilized noticeably like membrane process [5], microbial remediation [6], adsorption [7], ion exchange [8], biological treatment [9] and chemical precipitation [10]. Among all the technologies, adsorption process reveals as an eminent challenger due to effective, ease operation, low expensive and selectivity towards aquatic pollutants [11,12]. In recent the numerous adsorbents have been utilized for

phosphate removal [13,14]. Bentonite (Bent) is a smectite type of clay having isomorphous substitution of Si^{4+} with Al^{3+} in the tetrahedral sites and Al^{3+} with Fe^{3+} and Mg^{2+} in the octahedral sites which makes net electrical charge on their surface [15]. Some drawbacks of bentonite like high swelling property, pressure drops during the filtration and stable colloid forms of bentonite create aversion to separation and as well as sorption nature [16].

To succeed the various troubles, make use of biopolymer for ions removal in water treatment has developed [17]. Chitosan (CS) is nitrogenous biopolymer which is main ingredient of naturally occurring crustacean shells. Chitosan and its derivatives has distinctive features due to readily abundant in nature, biodegradability, reactivity, biocompatibility, anti-bacterial activity, non-toxicity and hydrophilic which improve very good adsorbent character of chitosan towards toxic ions removal in water [18,19]. However chitosan is moderately weak base ($pK_a \sim 6.2$) which leads to increase the solubility nature of chitosan at acidic pH < 5.0 [20]. To enhance the phosphate sorption capacity (SC) in acidic medium, the available active amine ($-NH_2$) sites in chitosan favors chemical modifications like functionalization [21], grafting [22], cross-linking [23] and biocomposite forms [24]. The significance in use of biocomposites is rapidly escalated in terms of fundamental research, owing to its immense benefits such as eco-friendly nature, economical, renewable and biodegradable [25].

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A metal have the tendency to become positively charged species by losing their electrons present in the outermost orbit. When positive charge character on the metal increases it behaves as Lewis acid means that it will ready to combine with negatively charged species like phosphate which is considered as strong Lewis base. Only few reports are available with metal ions anchored composites for phosphate removal. Therefore, the various metal ions like Zr^{4+} , Fe^{3+} and Ca^{2+} was loaded onto CSBent biocomposite to enhance stability and SC towards phosphate removal in aqueous solution.

The specific objectives of the present work are the imprinting of tetra (Zr^{4+}), tri (Fe^{3+}) and di (Ca^{2+}) valence metal ions on CSBent biocomposite towards phosphate removal. The synthesized composites will be characterized using FTIR, SEM, TEM and EDAX analysis. The influences of solution pH, agitation time, co-existing anions and temperature on phosphate sorption will be carried out. The adsorption isotherms and thermodynamic parameters of the synthesized biocomposites will be determined by using experimental data. The suitability of biocomposites at field conditions will be checked by collecting field water samples from nearby industrial area.

2. Experimental section

2.1. Materials

Chitosan (85 % degree of deacetylated) with average molecular weight of 25 kDa was obtained from Pelican Biotech and Chemicals Labs, Kerala (India). Bentonite clay, $ZrOCl_2 \cdot 8H_2O$ (98.0 %), $FeCl_3 \cdot 6H_2O$ (99.9 %), $CaCl_2 \cdot 2H_2O$ (≥ 97.0 %), glacial CH_3COOH (99–100 %) and all other chemicals are used in AR grade. The standard phosphate stock solution was prepared by anhydrous potassium dihydrogen ortho phosphate (≥ 98.0 %) using double distilled water.

2.2. Synthesis of metal ions imprinted CSBent (M@CSBent) biocomposites

About 2 g of chitosan (CS) is dissolved in 2 % solution of acetic acid at 40 °C and incessantly stirred upto 2 h separately. At the same time 6 g of Bentonite (Bent) clay was dispersed in 50 mL of double distilled water over 2 h. Thereafter, Bent dispersion was added slowly to the prepared chitosan polymeric solution over 24 h with vigorous magnetic stirring at 60 °C. After the formation of CSBent biocomposite colloid solution, the metal ions was loaded by adding 3 % $ZrOCl_2 \cdot 8H_2O$ solution (w/v). Then the acquired slurry of Zr@CSBent biocomposite was kept to 24 h for aging purpose followed by filtered using double distilled water. Likewise, the synthesis of Fe@CSBent and Ca@CSBent were obtained by using 3 % of $FeCl_3 \cdot 6H_2O$ and $CaCl_2 \cdot 2H_2O$ to CSBent solution individually. The metal ions loaded CSBent biocomposites was dried in hot air oven at 70–75 °C and ball mill (IKA, Germany) is used to crush the composites to fine powder then must be sieved in order to get the consistent size and utilized for studies of phosphate recovery.

2.3. Batch adsorption experiments for phosphate removal

The significant of batch sorption studies were accomplished to observe the various factors which are affecting the sorption process such as the effect of agitation time, solution pH, aggressive anions and sorption isotherms for phosphate removal. The studies have been carried out in stopper iodine flask holding 50 mL of 100 mg/L initial phosphate concentration and 0.1 g of adsorbent at neutral pH. Then the reaction mixture was stirred up in thermostat shaker with a rotating speed of 200 rpm at 303 K for varying time intervals followed by filtration. The left out concentration in the

supernatant solution after sorption process was analyzed spectrophotometrically. The influence of solution pH was identified by adjusting the pH to a definite value by using 0.1 M of HCl/NaOH solution. The isotherm studies were carried by varying the initial phosphate concentration as 80, 100, 120 and 140 mg/L at 303, 313 and 323 K. The SC can be calculated by the Eq. (1) as given below

$$\text{Sorption capacity (SC)} = \frac{C_i - C_e}{m} V \text{ mg/g} \quad (1)$$

where C_i and C_e is the initial and final concentration of phosphate in aqueous medium at equilibrium time (mg/L), m is the adsorbent dosage (g) and V is the solution volume (L).

2.4. Analytical methods

The phosphate concentration was analyzed by ultraviolet spectrophotometer kit (Model: Spectroquant Pharo 300, Merck) in which the absorbance was measured at wavelength of 400 nm. The pH measurement was investigated by using Thermo Orion Benchtop multiparameter kit (Model: VERSA STAR92) using pH electrode. The pH drift method is used to determine zero point charge (pH_{zpc}) of the synthesized adsorbents [26]. The standard methods were used to investigate the other water quality parameters [27].

2.5. Instrumentation studies

The functional groups analysis of metal ions anchored CSBent biocomposites was found by using FTIR with JASCO-460 plus model. The surface morphology of biocomposites was predicted by SEM with Vega3 Tescan model. Elemental spectra of the biocomposites were acquired using an EDAX with Bruker Nano GMBH model and TEM CM 200 (Philips) model was utilized to accumulate the TEM images of synthesized metal ions loaded CSBent biocomposite.

2.6. Statistical tools

Microcal Origin (Version 8.0) software was utilized to compute all the experimental data. The regression correlation coefficient (r), standard deviation (sd) and chi-square analysis (χ^2) were used to find the goodness of the fit and best model.

3. Results and discussion

3.1. Effect of agitation time

The phosphate sorption onto the synthesized biocomposites was examined as a function of agitation time by varying in the range of 0–60 min. The outcome of agitation time for various adsorbents used in this study such as Bent, CSBent, Zr@CSBent, Fe@CSBent and Ca@CSBent was shown in Fig. 1a. The observed results provides that as increase in time, there is a gradual increase in phosphate SC due to the presence of active vacant sites on the adsorbents surface. Further rise in time after 40 min showed no significant change in phosphate SC because of lack of available vacant sites of the adsorbents and they reaches equilibrium stage. Consequently the agitation time is fixed as 40 min for throughout the study. The phosphate SCs of Bent, CSBent, Ca@CSBent, Fe@CSBent and Zr@CSBent composites was found to be 7.75, 10.35, 13.44, 22.15 and 40.86 mg/g respectively. Among them metal ions anchored Zr@CSBent, Fe@CSBent and Ca@CSBent biocomposites holding efficient phosphate SC when compare to other adsorbents. Hence further studies were limited to these three metal ions loaded synthesized biocomposites.

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