

ORIGINAL ARTICLE

Removal of Cyanide, Phosphate, and Nitrate from Wastewater
Using Granulated Activated Bentonite

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ABSTRACT

In this research, removal of three anionic contaminants, cyanide, nitrate, and phosphate from wastewater samples using functionalized bentonite was investigated. In order to enhance the removal efficiency, the bentonite surface was functionalized by polyvinyl alcohol after its activation by HCl. Batch adsorption experiments were performed and the adsorption processes were monitored by spectrophotometric measurements. The effect of various operating variables, i.e. initial pH of sample, amount of adsorbent and initial anion concentration has been studied and optimized. It was found that for all of the analytes, the best extraction occurs in acidic conditions. The adsorption process was relatively fast and equilibrium has been reached at 30 min contact time and the maximum removal percentage was achieved at an adsorbent loading weight of 125,135,136 mg g⁻¹ and the absorption capacity of bentonite after alteration of its surface increased 2.3, 1.8 and 1.6 times for phosphate, nitrate, and cyanide respectively. The adsorption data were represented using Freundlich and Langmuir parameters, where the sorption data were better represented by the Langmuir isotherm for phosphate, while for the nitrate and cyanide Freundlich model was better fitted. The optimized method was applied for removal of the target contaminants from wastewater of Zabol. The achieved phosphate, cyanide and nitrate removal efficiency was 96.1%, 96.3% and 96.9% by using polyvinyl alcohol functionalized bentonite respectively.

Keywords; Bentonite; Polyvinyl alcohol; Adsorption, Removal efficiency, Wase watere

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INTRODUCTION

Anionic contaminants have destructive effects on natural ecosystems. The natural hydrolysis of minerals, stones, sediments and increased entrance of industrial wastewater to natural ecosystems are among the liberating sources of these contaminants which also resulting variations in the pH of aquatic media [1]. Phosphate causes intensification of the utrification phenomenon. Cyanide in itself leads to increased corrosion of water transfer equipments and other vehicles. High concentrations of nitrate in waste disposal sites, solid waste materials, and waste burial are some ways through which this contaminant enters potable water. Increased concentration of nitrate and nitrite in potable water engenders threats to children and pregnant women. World Health Organization has announced the upper allowable limit of nitrate in potable water as 50 mg/L [2, 3].Typically, cyanide is among rare toxicities which can be found in different forms, including hydrogen cyanide (hydrocyanic acid or prolic acid), soluble salts of sodium and potassium and insoluble salts of mercury, copper, gold and silver cyanide. In addition there are a number of cyanide compounds which are known as cyanogen from them cyanide is liberated during the metabolism of medicines. Cyanide damages all tissues of the body, attacks the metalo-enzymes in the body and deactivates them. Its main toxicity might de due to deactivation of the cytochrome of cellular oxidases [4].

The usual forms of phosphorus found in aqueous solutions include orthophosphate, polyphosphate and organic phosphate. The principal phosphorus compounds in wastewater are generally orthophosphate forms together with smaller amounts of organic phosphate. Municipal wastewater may contain from 4 to

15 mg/l phosphorus as P. However, industrial wastewaters (such as detergent manufacturing and metal coating processes) may contain phosphate levels well in excess of 10 mg/l.

Application of various absorbents is another method targeted at removal of anions. Optimal and proper selection of the absorbent depends on the desired efficiency and the wastewater properties.

The important factor in these methods is selection of the type of absorbent at the stage of designing the system [5]. Absorbents widely used for this purpose are activated carbon, synthetic polymers, and mineral silicone.

In this research, natural bentonite was chosen as an adsorbent for anions because of its low cost and widespread availability in Iran. Moreover, similar researches show that it is a proper adsorbent for anionic species [1, 6]. Both natural and surface modified bentonite have been used for removal of a range of contaminants such as dyes, pesticides, nitrate, organics, pharmaceuticals and heavy metals from aqueous samples [3, 7]. The main constituent of bentonite is montmorillonite, a hydrated sodium or calcium or magnesium aluminum silica. The cations of sodium, calcium, and magnesium are easily exchangeable which give a high ion exchange capacity to montmorillonite oxide [3]. In this research, the adsorption of three contaminants, nitrate, phosphate and cyanide on bentonite which was functionalized by polyvinyl alcohol is investigated. In order to find out the adsorption mechanism and to do better optimization of the factors affecting absorption, first the adsorption of each contaminant was individually studied on the adsorbent and finally a real sample containing all anions was examined.

MATERIALS AND METHODS

Materials and equipment

All reagents were of analytical grade and obtained from Merck KGaA (Darmstadt, Germany) and used as received. Milli-Q® water (18.3 M Ω cm) was used throughout the experiment after filtering through 0.22 μm Nylon membrane. A Cecil spectrophotometer, Model CE 201 (London, UK) was used for measuring the absorbance and recording the spectra.

Synthesizing the absorbent

The method of absorbent synthesis was based on what presented by [8], with minor modification. 10 g of the Ca-bentonite was heated for 2 h at 300 °C. After then, it was poured in 100 ml distilled water and heated on a steam bath for 30 min. 10 ml of HCl 1 M was then added and this mixture was stirred for 6 h. Subsequently, it was centrifuged and the solid phase was washed with distilled water 5-6 times. Next, bentonite was dried at 105 °C in an oven and then milled. bentonite surface is now activated. In order to functionalize it, a mixture of 20 g of polyvinyl alcohol (PVA) and 250 ml distilled water was placed on a steam bath until PVA was dissolved completely. Thereafter, 90 g of activated bentonite was added and stirred well. This mixture was then dried in an oven at 65 °C. It was then milled and treated with glutaraldehyde 10%v/v. pH of glutaraldehyde was already adjusted between 3-4 using 0.1 M hydrochloric acid. Afterwards, this mixture was leaved at 50 °C for 30 min to be dried. Finally it was milled to particles either a size of 0.1-0.4 mm.

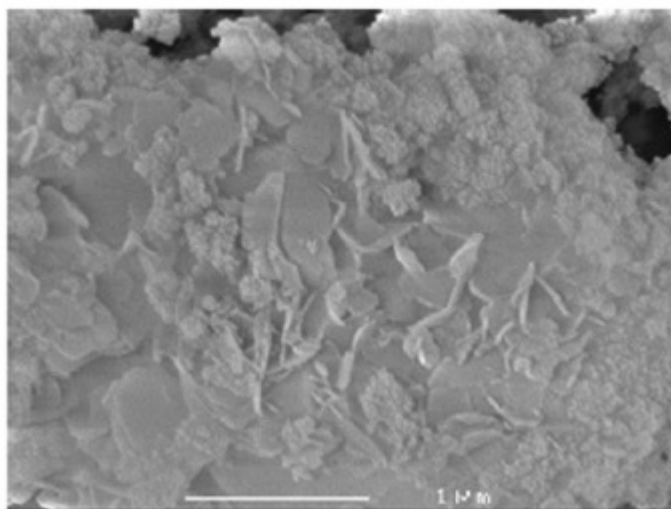
Experimental design

Batch experiments were conducted to optimize important experimental parameters which can potentially influence the efficiency of contaminants removal, such as dose of adsorbent, volume and pH of sample solution and effect of initial concentration of each contaminant. The univariate method was used to simplify the optimization procedure. The experiments were each replicated 4 times. In each replicate, the initial concentration of contaminants were selected as 100 mg/L in distilled water with an adsorbent dose of 1.0 g/L. before starting, pH of the sample was adjusted to the desired value using 0.1 M solutions of HCl or NaOH. After completion of contact time, the solutions were centrifuged and filtered. The supernatant solution was taken and spectrophotometrically examined for the phosphate, cyanide and nitrate content. Analysis method was based on what recommended by Standard Methods of Water and Wastewater book at wavelengths of 450 nm (phosphate), 650 nm (cyanide) and 500 nm (nitrate).

RESULTS AND DISCUSSION

3.1. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) images provide morphology of the bentonite at micro-scale. From Fig. 1, the contrast in surface features between the raw bentonite which is relatively smooth and flat, and the functionalizing of surface with proposed method, provides clear visual evidence for the new surface area generated by strong treatment. The treated sample shows many new cavities and coarsened exterior probably due to removal of some acid-soluble salts [9, 6].



a

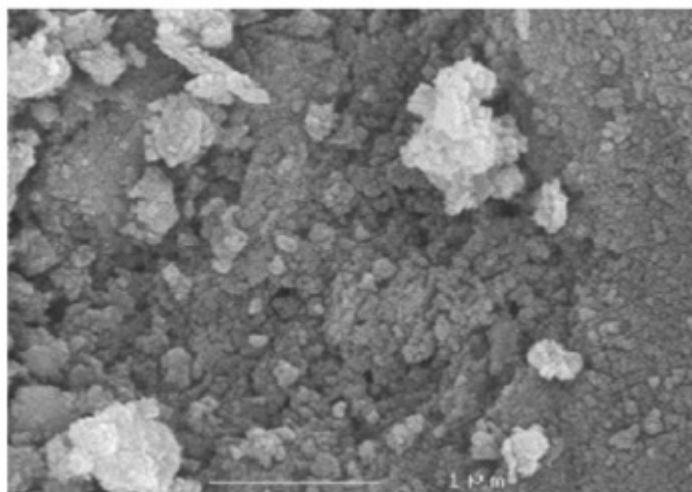


Fig.1 SEM image of a) raw bentonite and b) functionalized bentonite.

The effect of pH

An effect of solution pH on the removal of the target analytes for adsorbent is shown in Fig. 2. From this figure it seems that the best pH for all of the analytes is obtained in acidic media around the isoelectric point of the adsorbent (4.5). The effect of pH on the adsorption could be attributed to several mechanisms such as electrostatic interaction, complexation and ion exchange. It also alters the superficial charge of the adsorbent. Similarly, the ionization degree of the materials in the solution and availability of adsorbent sites bonding are also affected by pH. The superficial adsorption of different anionic and cationic genera on such adsorbents is defined based on the competition of superficial adsorption of H⁺ and OH⁻ ions with the adsorbed material. The adsorption surfaces better adsorb anions at a lower pH and in the presence of H⁺ ions. On the other hand, the surfaces are activated through elevation of pH and in the presence of OH⁻ ions [8]. Furthermore, considering the isoelectric point of the adsorbent used in this study (4.5) and the positive charge of the adsorbent surface at a point lower than the isoelectric point, a complex phenomenon is developed in determination of pH. Therefore, although the electrostatic attraction between the negative phosphates ions with an adsorbent having a positive charge increase the tendency to adsorption at a low pH, but formation of phosphoric acid is also accelerated at a low pH which reduces the efficiency of the adsorbent. As a result, the best pH was obtained around the isoelectric point. From Fig. 1 it is evident that the maximum percentage removal of phosphate, nitrate and cyanide occurs at pH 4, 5 and 5 respectively. Based on the above observations, it could be concluded that the negative surface

charges on adsorbent and repulsive forces between it and anionic pollutants decreases removal efficiency.

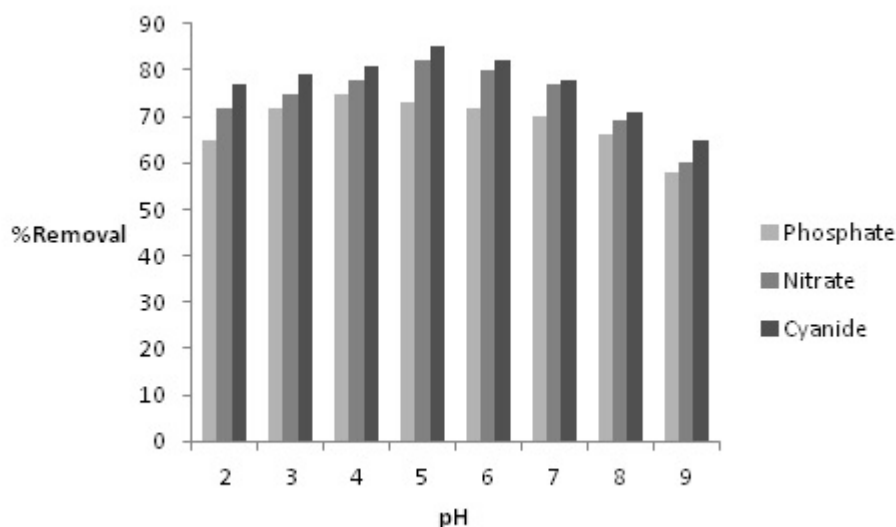


Fig. 2 Effect of pH on adsorption of anionic pollutants (adsorption time, 30min; adsorbent dosage, 1g)

The effect of amount of adsorbent

Fig. 3 demonstrates the best amount of adsorbent for all three contaminants. As can be observed, the highest efficiency of the adsorbent for cyanide is obtained at adsorbent content of 1.2 g, 0.7 g, and 0.9 g respectively for phosphate, cyanide and nitrate. The increase in percentage removal of the contaminants in the initial stage is due to the increase in adsorbent concentration and more accessibility to the absorption sites. However, with gradual occupation of the majority of adsorption sites and reaching an equilibrium balance between the adsorbent and contaminant, the absorption percentage remains almost constant with no noticeable change.

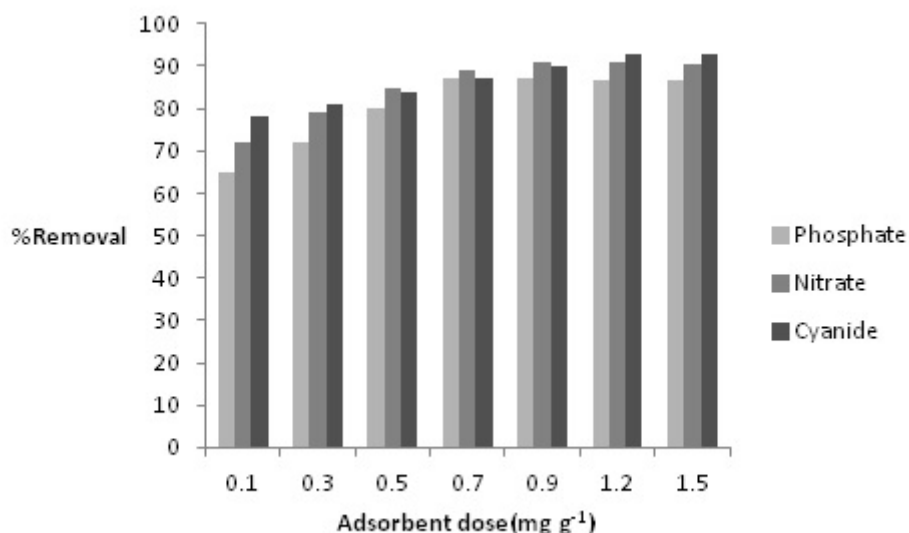


Fig.3 Effect of adsorbents dosage on removal of pollutants (adsorption time, 30min).

3.4. The effect of initial concentration of the contaminants

Varying initial concentration from 300 to 150 mg L⁻¹ of the target analytes on adsorption was investigated under the optimized conditions given in the previous sections. Fig. 4 depicts that the highest efficiency of adsorbent is obtained at initial concentrations of: 50 mg L⁻¹ for phosphate, 120 mg L⁻¹ for cyanide, and 90 mg L⁻¹ for nitrate. The reduction of contaminants removal as an efficacy of their concentrations can be explained by the restriction of available free sites for adsorption of them with

increased concentration in bulk solution for a fixed mass of adsorbent, as well as by the increase in intraparticle diffusion. In addition, in batch absorption systems, the input concentrations plays an important role as a driving force overcoming the resistance caused by mass transfer between the liquid and solid phases. Thus as the initial concentration increases, so does the absorption level, until an equilibrium attained. Since phosphate is a bulky molecule, as the amount of adsorbent increases, no rise in the adsorption efficiency observed. Therefore, initial concentration of 50 mg L⁻¹ for this species was chosen as the optimal concentration.

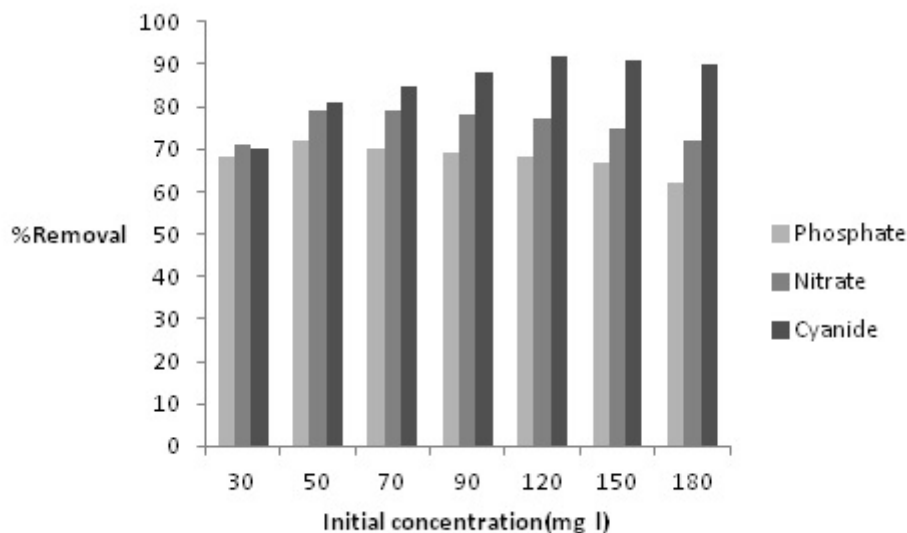


Fig.4 Effect of initial concentration of pollutants on removal efficiency (adsorption time 30 min).

Investigation of absorption isotherms

For examination of a suitable absorption isotherm for the adsorption of these anions on the studied adsorbent two isotherm models, i.e. Langmuir and Freundlich were investigated. The monolayer absorption Langmuir isotherm is valid on the adsorbent surface with limited and uniform absorption sites.

Langmuir Equation can be written as eqs. 1 and 2:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (1)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \left[\frac{1}{bq_m} \right] \left[\frac{1}{C_e} \right] \quad (2)$$

Where C_e is the concentration of the soluble material at balanced state, q_e is the absorption capacity at the balanced state, Q_m is the maximum absorption capacity, and b is the constant of Langmuir equation.

Freundlich isotherm has been based on the monolayer absorption on heterogeneous absorption sites with unequal and heterogeneous energies. In the other words, the Freundlich equation, describes absorption at a heterogeneous level in terms of absorption energy as stated in eq. 3.

$$q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

Where: K_f and n are two constants of the equation [10].

Table.1 demonstrates the absorption isotherm parameters for all of the three anionic contaminants. It is clear from the table that the absorption isotherm for phosphate follows Langmuir model, while for nitrate and cyanide it follows the Freundlich model. Also high adsorbent capacity 125.45, 135.15 and 136.64 mg g⁻¹ obtained for phosphate, nitrate and cyanide by using of granulated activated bentonite, respectively. In comparison with raw bentonite the adsorption capacity is very notable and reliable while adsorption capacity is 53, 71 and 78 mg g⁻¹ for phosphate, nitrate and cyanide by using of raw bentonite, respectively.

Table.1 Isotherm parameters for adsorption of nitrate, phosphate and cyanide

Isotherm model	Langmuir				Freundlich	
	$q_0(\text{mg/g})$	$K_L(\text{L/mg})$	R^2	$K_F(\text{mg/g})(\text{L/mg})^{1/n}$	n	R^2
Nitrate	125.45	0.05	0.9887	32.6	4.28	0.9965
Phosphate	135.15	0.043	0.9991	39.7	3.65	0.9832
Cyanide	136.64	0.073	0.9876	27.24	3.24	0.9921

Comparison of proposed technique with other methods

Table. 2 show the comparison of proposed method with other method for adsorption of phosphate, nitrate and cyanide.

Table .2. Comparison of proposed study with other studies on adsorption of cyanide , nitrate and phosphate

Target anion	Adsorption system	Adsorption capacity (mg g-1)	Isotherm model	References
cyanide	Granulated activated carbon	20	Langmuir	[11]
cyanide	Impregnated activated carbon	Ag-mpregnated:45.7 Ni-impregnated:4.3 Plain carbon:7.1	Langmuir	[12]
cyanide	Pistachio hull waste	56.2	Langmuir	[13]
nitrate	Bamboo powder harcoal	10	-	[13]
nitrate	Sepiolite Sepiolite activated by Hcl Powdered activated carbon	10 20 5	Langmuir Ferundlich Ferundlich	[14]
phosphate	Fly ash Slag Ordinary Portland cement	32 60 83	Frumkin	[15]
Phosphate Nitrate cyanide	Functionalizing bentonite with Hcl and glutaraldehyde	45 65 87	Langmuir Ferundlich Ferundlich	This study

CONCLUSION

Removals of three anionic pollutants by functionalized bentonite were investigated in this work. All of the results for removal of phosphate, nitrate and cyanide showed that this adsorbent is very effective and applicable. High adsorbent capacity obtained from Langmuir isotherm and proper adsorption time that illustrate priority of this method.

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