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Study of phosphorus compounds adsorption efficiency in sewage resources by using langmuir and freundlich equitation from ecological prospective

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Abstract

Phosphorus is the main nutrient responsible for eutrophication of aquatic ecosystems; therefore, it is important to develop new processes to remove phosphorus from aqueous solutions. In this research, performance, kinetics, and adsorbing isotherms of Bentonite and Bentonite- Alumina compound (10% Alumina (Al_2O_3), 90% Bentonite) were investigated. According to the results of this study, the Langmuir adsorption model was best to describe adsorption equilibrium data for Bentonite-Alumina mixture and Bentonite (r^2=0.999 for Bentonite-Alumina mixture and r^2=0.996 for Bentonite). The Langmuir Isotherm parameters for Bentonite and Bentonite-Alumina were Q_m=15.2, 18.1 mg/g and K=4.3, 5.5 L/mg, respectively. Moreover, the Freundlich Isotherm parameters were K=6.6, 9.12 and n=3.05, 3.7, respectively. Bentonite-Alumina mixture was found to more effective for the removal of phosphorus than Bentonite (97% in 140 min in comparison to 90% in 140 min).

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Introduction

As human interfere in the natural water cycle and in spite of excessive endeavors for hindering the destruction and pollution of various water sources, such measurements will lead to creation of irrecoverable dangers in this arena. Thus, it is necessary to pause and rethink about devising modern methods for thwarting and preventing water sources pollution. Generally speaking, sewage can be defined as the stream of waste water, which is resulted from water consume in various activities that include different physical, chemical and biological contaminants. These materials endanger human life via polluting the environment (Nadafi 2010).

Phosphorus should be considered as an important component of sewage. This component can be observed in different forms like, mineral compounds, polyphosphate and orthophosphate in sewage (Keynejad and Abrishami 2004).

In some agricultural and industrial activities like use of fertilizer, detergent, pigments and water treatment, mineral materials processing and during desalination, the phosphorus is being used as an anti-fouling (Nowak and Eston 2006).

The dose of phosphorus in the rural and urban sewage is so high, approximately between 15 to 2000 mg/lit. The removal of phosphorus from urban sewage is essential for controlling of eutrophication (Kermani *et al* 2010).

There are various available technologies for removal of phosphorus, such as physical processes (sedimentations, filtration), chemical sediments along with iron salts and aluminum, biological processes which is based on cell mass growth (Bacterial, reeky, herbal) and accumulation of phosphorus within bacterial cell. Over the past 20 years, there was a great attempt to devise new methods for removal of phosphorus from sewage (Belir *et al* 2006).

According to the researches, it is observed that about 0.5 of nitrogen and one-thirds of phosphorus is not being removed from sewage via the water treatment process and such condition leads to the problems such as reeky growth and eutrophication phenomenon (Afyoni and Erfanmanesh 2011).

If human being pays the required heed to the environment and be careful about not disturbing the ecosystem, he will tend to devise highly efficient, cheap and feasible solution for sewage treatment. Nowadays, beside the existence of chemical and biological methods of sewage treatment, extensive researches are being done on the physical methods of treatment such as the ones that are based on membranous and superficial adsorption. Biological methods are better than chemical and physical methods since of the absence of chemical materials that can lead to increase of chemical substances such as nitrate and phosphorus in urban sewage. But, this method is cheaper and leads to reduction of nitrate and phosphorus, indirectly (Gurjar 2011).

The use of various adsorbents was also evaluated over these years. During the adsorption process, a substance which is in the solution state is being accumulated on the appropriate material. To put it simple, the state is changed from liquid to solid phase.

The key point in these methods is the selection of adsorbents during the system designation. At this point, designers should consider factors such as physical and chemical properties, phosphorus retention capacity and potential of reviving phosphorus, the expense and availability of the material in the place. The use of adsorbents such as activated carbon, synthetic polymers and mineral silica adsorbents is common.

We also study eco-friendly ion exchange and adsorption methods by using natural exchanger materials like bauxite, aluminum, bonitite, fugitive ash and Leca. The task of severance of phosphorus can be done during initial, secondary or advanced treatment phases. The selection of suitable and optimized adsorbents or exchanger ions is depended on expected efficiency sewage properties and on the ilk of secondary treatment (Jonson and Gustafsson 2000).

The adsorption term in this article refers to all sorption process that causes eviction of phosphorus from solution (Miranzadeh 2010).

Generally, we can define adsorption as a process within which materials located in solution at the mutual intersection are being collected. This mutual intersection can be between liquid and Gas, liquid and solid or liquid and liquid (Metcalf and Eddy 2010).

In the past, the treatment of sewage, the adsorption process was not being used extensively as now. But, since of the requirement of high quality of output sewage from treatment system, most studies are centered on the adsorption process on the activated carbon. The sewage filtration via activated carbon is usually considered as a final severance process which is applied to the water that is exposed to biological treatment. In this case carbon is used for separating the mineral substances of remaining solution. We can also separate tiny solid particles via making a contact between water and carbon. (Esmat Saatlu *et al* 2010).

In the past, all of the urban sewage refinery system was constructed for removal of mineral pollutants such as suspended substances and microbial contaminants. With regard to the influences of nitrogen compounds and phosphorus on the aquatic environments (mostly ammonia toxicity, excessive growth of aquatic plants and the creation of eutrophication phenomenon, pollution of subsurface waters by nitrate), a series of limitation linked to the concentration of this compound was devised and applied to the input and output sewage that discharge into the receiving waters (Shamon 1999).

There are some common methods for the treatment of such sewages like chemical and biological methods, but all of them have their own advantages and limitations. Nowadays, the method of adsorption particularly via the use of activated carbon has been appealing for most of the scientists, due to the efficiency of the activated carbon in removing a minor amount of influential heavy metals. However, since of the high expenditure of the method, it is not so rampant. So, it is important to seek for other adsorbents that are so efficient, cheap and can be utilized for removal of heavy metals from sewage (Cooney 2003).

Furushani and Cherm (2005) presented a paper title Study Application Treated Sewage Sludge on the Chemical Properties and Adsorption of Heavy Substances of Soil. Their main aim was to study the influences of treated sewage sludge on the chemical properties of the soil and absorption of heavy substances existing in the soil. The study on the non-linear adsorption isotherms from aquatic solution was done. (Salarian *et al* 2011).

Babatunde *et al* (2010) studied the equilibrium and kinetic analysis of phosphorus adsorption from water solution by using sludgy garbles.

Isotherm adsorption can be defined as a mathematical relation (experimental and analytical) that refers to the equilibrium amount of chemically and physically absorbed particle on the surface of a specific solid along with gas pressure alteration in consonant temperature. In this study, the efficiency of phosphorus compound absorption is studied via the use of Bentonite and a mixture of 90 percent of Bentonite and 10 percent of Aluminum. Issues related to the kinetic and the manner of adsorption and adsorption isotherm are also analyzed and studies. Langmuir and Freundlich equitation are used for study of sorption equilibrium and the corresponding parameters in these equations are also computed.

The present study analyses the combined effects of Bentonite + Alumina as an absorbent in order to improve the amount and quality of absorption. The main purpose of the study is to investigate whether the absorption data and the related isotherms correspond to the Langmuir equation or not. Another purpose of the study is to examine whether this method is better and more cost effective in isolating phosphorus than other chemical methods or not.

Material and methods

Study of Adsorption Isotherms

During the analysis of adsorption process, an equation is required for the declaration of the equilibrium between the adsorbed amount and fluid phase concentration, this is called adsorption isotherm. Nowadays, there are different equations and isotherm for describing the adsorbent behavior, equitation and isotherms include Langmuir Isotherm, Freundlich Isotherm and Temkin Isotherm. The Langmuir Isotherm is widely used for adsorption of pollutants from an aquatic solution (Alen *et al* 2003, Englezakis 2005).

The basic assumption of this method is that, accomplished adsorptions have taken place in Homogeneous environment. Other models that are being used for describing adsorption relations are Langmuir and Freundlich models.

This equitation is utilized for quantitative determination of the adsorption in equitation (1) and (2).

In the following mathematical expressions the first method is called Freundlich and the second one is called Langmuir.

$$q_e = KC_e^{\frac{1}{n}} \quad (1)$$

$$\frac{1}{q_e} = \frac{1}{bq_0C_e} + \frac{1}{q_0} \quad (2)$$

In the mentioned equation, q_e refers to the milligram amount of adsorbed substance for every mass unit of the adsorbent in mg/g. C_e refers to the equilibrium concentration of pollutant in mg/lit. b is constant and it is provided in lit/mg. b refers to the binding energy. b and k are constants that depend on the capacity and intensity of absorption. Generally, the biological modeling is done via experimental and common chemical, physical equitation for two-component system. This modeling can express and predict system behavior. Experimental methods are generally simple mathematical equitation with a series of configurable parameters; they can prognosticate single-component and two-component system experimental data. The simplest method of illustration of two-component system is the use of predictive models; they include a set of simple mathematical formulas. These formulas use the resulted parameters from single isotherms for expressing the behavior of two-component system. Freundlich model which is generalized for two-component system can be declared as followings:

$$q_1 = \frac{n\left(\frac{K_1}{n_1}\right)^{\frac{1}{n_1}}C_1}{\left[\left(\frac{K_1}{n_1}\right)^{\frac{1}{n_1}}C_1 + \left(\frac{K_2}{n_2}\right)^{\frac{1}{n_2}}C_2\right]^{1-n}} + \Delta F_2 \quad (3)$$

ΔF_2 and n are functions linked to the remained concentration of two metals (C_1 and C_2), so configurable parameters (k_1, k_2, n_1, n_1) will be result from Freundlich isotherm for single metal system:

$$q_i = K_iC_i^{\frac{1}{ni}} \quad (4)$$

Therefore, the generalized form of Langmuir model will be as following:

$$q_i = \frac{q_i^0 b_i c_i}{1+\sum_{i=1}^{n} b_k c_k} \quad (5)$$

In equation 5, q_i is adsorption of I element in multi-component system and C_k (N is the number of available metals in the system) refers to the equilibrium concentration of every element (k=1,2,3,…,n). b_i and q_i^o are Langmuir isotherms. Temkin adsorption isotherm will be declared as linear:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (6)$$

In this relation, q_e is the adsorbed amount in mg/g. C_e is equilibrium concentration of resorbable ion in mg/lit. By using q_e curve in $\ln C_e$, we can determine isotherm constants (B_T, K_T), respectively, from slope to width, from center of the diagram.

Table 1. The equitation of the Kinetics and Isotherms Models.

Model	Nonlinear Equitation
Langmuir (Isotherm)	$q_e = \frac{abc_e}{1 + ac_e}$
Freundlich (Isotherm)	$q_e = kc_e^{\frac{1}{n}}$
Lagergren (Kinetics)	$q_t = q_e[1 - \exp(-k_1 t)$
Ho *et al* (Kinetics)	$q_t = \frac{k_2 q_e^{\,2} t}{1 + q_e k_2 t}$

q_e is the amount of adsorbed ion in an equilibrium condition in mg/g. q_t is the amount of adsorbed ion at t time in mg/lit. k_1 refers to the adsorption constant in *min*$^{-1}$.K_2 refers to the adsorption velocity in $\frac{gr}{mg.min}$. C_e is adsorbed ion in equilibrium time in mg/g. n refers to the adsorbent adsorption ability (without dimension). K is the intensity of adsorbent adsorption (without dimension). b is the maximum amount of adsorbed metal ion in mg/g. a is energy constant in lit/mg.

The Bentonite (clay) was used in dust form in this study. The chemical composition of the Bentonite was obtained thorough XRF and wet chemical analysis is presented in Table 2. The CEC for Bentonite was 100.19 meq/100gr (NH4AC method) and the percent concentration of monmorillonite in Bentonite was 75.92%.

Table 2. Chemical analysis of Bentonite.

Bentonite	SiO_2 (%)	Al_2O_3 (%)	TiO_2 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)	Na_2O_3 (%)	K_2O (%)	LOI (%)	Total
	53.72	19.2	0.85	4.93	3.29	5.28	3.46	0.44	8.75	100

Stock phosphorus solution

A stock phosphorus solution with a concentration of 40 mg/L was prepared by dissolving 175.75 mg KH_2PO_4 in 1 Lit of pure water and used to prepare solutions with lower concentrations.

Experiments

Experiments were carried out in two phases; first phase was for obtaining the phosphorus removal efficiency for two absorbents Bentonite and Bentonite–Alumina. Second phase of experiments was for obtaining the adsorption capacity of the two adsorbents. In the first phase, 1g of Bentonite as an absorbent was disposed in 14 250^{cc} beakers and then 100^{cc} of phosphorus solution with concentration of 8mg/L was added to each beaker. Beakers were mixed at 100 rpm for 1 min and then placed in ambient temperature until settled. Samples phosphorus concentrations were measured regularly by spectrophotometry method. Phosphorus removal efficiency (η) was calculated according to the equation below:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100 \qquad (7)$$

Where C_0 and C_e are initial and equilibrium phosphorus concentrations in solution (mg/Lit).

In the second phase of experiments, for determining of adsorption capacity, 1mg of selected absorbents and 10 mL of phosphorus solution with different concentrations (5, 4, 3, 2.5, 2, 1.5, 1, and 0,5 mg/L) were prepared. These solutions were then mixed at 100 rpm for 10 min and placed in ambient temperature until settled. Samples were filtered with Whitman (0.45 μm) and then the phosphorus concentrations of filtered samples were measured by spectrophotometry method. Adsorption capacity (Q) was calculated according to the equation below:

$$Q = \frac{C_0 - C_e}{m} \times V \quad (8)$$

Where C_0 and C_e are initial and equilibrium concentration (mg/L), *V* is the solution volume (mL) and *m* is the amount of absorbents (g). All the experiments were carried out according to standard method 20thedition.

Results and discussions

Fig.s (1) and (2) represent the phosphorus concentration and phosphorus removal for two absorbents (Bentonite and Bentonite-Alumina). According to the results, phosphorus removal was higher in the presence of Al_2O_3. A decrease of 97 percent in phosphorus concentration was observed for Bentonite-Alumina mixture during the maximum contact time 140 min as compared to 90% for Bentonite. Although the initially kinetics of phosphorus removal was faster for Bentonite, phosphorus concentration remaining in solution after 100 min (equilibrium time) was below 0.2 mg/L for Bentonite-Alumina in comparison to Bentonite. Replacing 10 percent Bentonite with Al_2O_3 seems to indicate that adsorption strength was improved significantly because of probably increasing the adsorption surface area and polarity of Bentonite due to alumina addition.

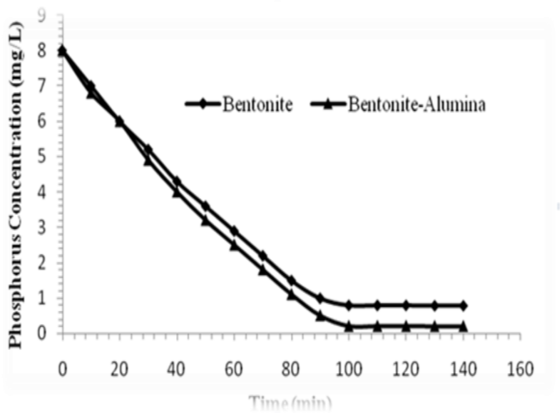

Fig. 1. Phosphorus Concentration in solution.

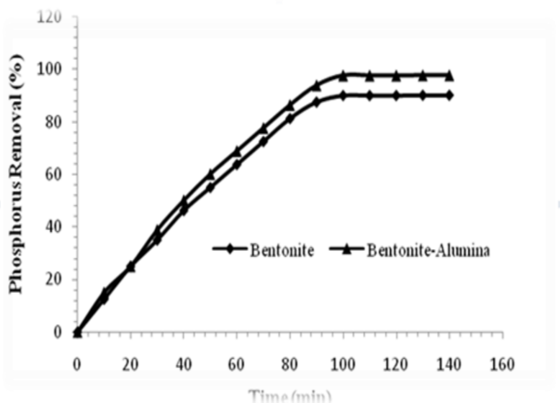

Fig. 2. Phosphorus removal efficiency.

The adsorption capacity of Bentonite was improved by replacing with 10 percent Al_2O_3. Adsorption capacity of Bentonite-Alumina was about 18mg/g in equilibrium concentration of 3.6 mg/L as compared to 14 mg/g for Bentonite. This result might be attributed to increasing the adsorption surface area and polarity of Bentonite by replacing with 10% Al_2O_3.

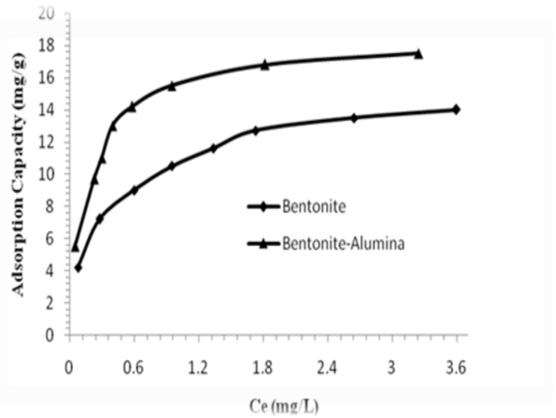

Fig. 3. Adsorption Capacity of two absorbents.

Adsorption Isotherms

Mention Fig. (3) in the text Different isotherm models such as Langmuir and Freundlich were used to describe ions distribution Explain why the other models discussed earlier – Temkin and DR – were not used. In order to find most appropriate model for the phosphorus adsorption, the data were fitted to each isotherm model. The obtained isotherm parameters and correlation coefficients (R^2) are presented in Table (4).

Fig.s (4) and (7) represent the correlation coefficients of Langmuir and Freundlich adsorption models for the two absorbents. According to the results, the Langmuir adsorption model was best to describe adsorption equilibrium data for Bentonite-Alumina mixture and Bentonite (r^2=0.999 for Bentonite-Alumina mixture and r^2=0.996 for Bentonite) as compared to Freundlich adsorption model. Correlation coefficients (r^2) of the Freundlich model for Bentonite and Bentonite-Alumina were 0.977 and 0.916, respectively.

Table3. Adsorption Isotherm constants.

Isotherm type	Isotherm constants		R^2	
	Bentonite	Bentonite-Alumina	Bentonite	Bentonite-Alumina
Langmuir	Q_m= 15.2 mg/g K= 4.3 L/mg	Q_m= 18.1 mg/g K= 5.5 L/mg	0.996	0.999
Freundlich	K= 6.6 mg/g n= 3.05 L/mg	K= 9.12 mg/g n= 3.70 L/mg	0.977	0.916

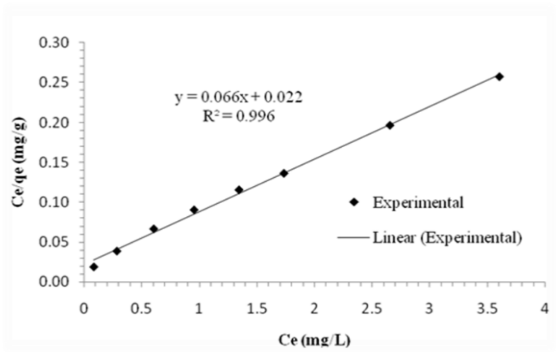

Fig. 4. Langmuir isotherm (Bentonite, Bentonite-Alumina) - (a). Bentonite.

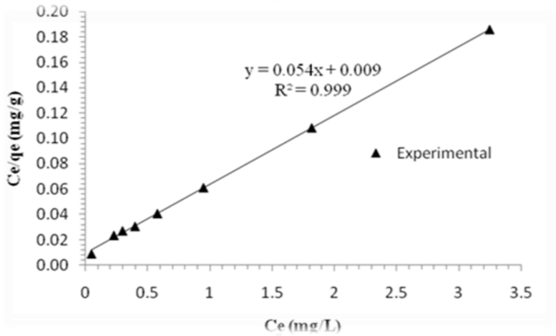

Fig. 5. Langmuir isotherm (Bentonite, Bentonite-Alumina)- (b). Bentonite- Alumina.

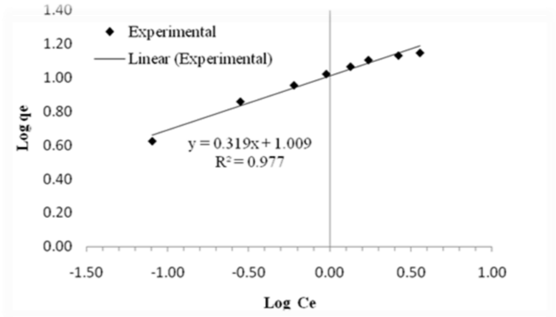

Fig. 6. Freundlich isotherm (Bentonite, Bentonite-Alumina)- (a). Bentonite.

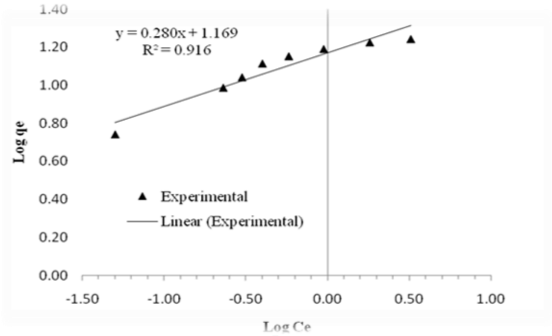

Fig. 7. Freundlich isotherm (Bentonite, Bentonite-Alumina)- (b). Bentonite-Alumina.

Conclusion

In the present study, the ability of Bentonite and Bentonite-Alumina to remove phosphorus from aqueous solutions has been investigated in maximum contact time of 140 min. Bentonite-Alumina was found to be more effective for the removal of phosphorus than Bentonite. The removal of phosphorus using Bentonite-Alumina was reached 97% at ambient temperature, equilibrium time (120 min) and mild agitation (100 rpm) as compared to 90% for Bentonite. Adsorption isotherms have been determined and data have been analyzed according to Langmuir and Freundlich models. Langmuir adsorption model was found to be best to describe adsorption equilibrium data for Bentonite (r^2=0.996) and Bentonite-Alumina (r^2=0.999). Finally, this study showed that Bentonite-Alumina could be regarded as one of the efficient adsorbent of phosphorus from aqueous solutions.

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