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Phosphate Removal From Wastewaters Using Fly-Ash Adsorption

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ABSTRACT

In this research, removal of phosphorus in aqueous stream was investigated by using fly-ash obtained from Afsin-Elbistan thermal power plant station. The parameters such as initial phosphate concentration, adsorbent (fly ash) concentration, stirring speed and initial pH, temperature and electrolyte concentration were investigated. It was seen that phosphorus removal rate increased, increasing fly-ash concentration and stirring speed additionally it was observed that increasing the stirring speed shortened equilibrium time of adsorption process. An increase in the pH didn't affect the adsorption yield. Finally, it was found that fly-ash could be used as a suitable adsorbent for the removal of phosphate from aqueous streams.   © 2006 Trade Science Inc. - INDIA

INTRODUCTION

Phosphorus is one of the nutrition elements and available in the structure of ATP molecules which conduct transportation of energy additionally of teeth and bones. Phosphorus appears exclusively as phosphate (PO_4^{-3}) in aquatic environments. There are several forms of phosphate including ortho-phosphate, condensed-phosphates (pyro, meta and polyphosphates) and organically bounded phosphates. These may be insoluble or particulate form or may be constituents of plan tor animal tissue. Phosphate ia a constituent of soils and used extensively in fertilizer to replace and/or supplement natural quantities on agricultural lands. Phosphate is also a constituent of animal waste and may become incorporated into the soil in grazing and feeding areas. Runoff from agricultural areas is a major contribu-

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tor to phosphate in surface water[1].

These phosphorus compounds, dissolved in ground or surface waters, are responsible for the eutrophication(excess nutrients and associated effects such as rapid growth of blue-green algae and hyacinth-like plants) which leads to-short and-long term environmental and aesthetic problems in closed water systems, especially in lakes and enclosed bays where the water is almost stagnant[2-5].

When wastewater containing high concentrations of phosphate and nitrogen discharged to a water body nitrogen and phosphates, which are essential nutrients for algae, are delivered to aquatic environment, so algae and some kind of microorganisms excessively grow and water quality deteriorates, so taste, odor and turbidity increases[6].

Adsorption can be defined as the accumulation of substances at the interface between two phases. The material removed from the liquid phase is called "adsorbate", and the material providing the solid surfaces is called the "adsorbent"[1].Adsorption, in general, is the process of collecting soluble substances that are in solution on a suitable interface. The interface can be between the liquid and a gas, a solid or another liquid. In the past, the adsorption process has not been used extensively in wastewater treatment, but demands for a better quality of treated wastewater effluent have led to an intensive examination and use of the process[6].

Molecules of solutes (adsorbate) are removed from solution and taken up by the adsorbent during the adsorption process of adsorption. The majority of molecules are adsorbed onto the large surface area within the pores of an adsorbent and relatively few are adsorbed on the outside surface of the particle. The transfer of adsorbate from solution to adsorbent continues until the concentration of adsorbate remaining in solution is in equilibrium with the concentration of adsorbate adsorbed on the adsorbent. When equilibrium is reached, the transfer of adsorbate stops. The equilibrium distribution of adsorbate between the liquid and solid phases is an important property of adsorption systems and helps define the capacity of the system.

Three distinct steps must take place for adsorption to occur:

The adsorbate molecule must be transferred from the bulk phase of the solution to the surface of the adsorbent. In so doing, it must pass through a film of solvent that surround the adsorbent particle. This process is referred to as film diffusion.

The adsorbate molecule must be transferred to an adsorption site on the inside of the pore. This process is referred to as pore diffusion.

The adsorbate must become attached to the surface of the adsorbent[6].

Many factors influence the rate and the extent of adsorption. These factors can be summarized as stirring speed, characteristics of adsorbent, solubility of adsorbate, pH, temperature and size of adsorbate molecule[7,8].

Fly ash is a waste product of power stations burning pulverized coal. Most of the inorganic matter in coal ends up as fly-ash, with composition essentially the same as the bulk composition of the ash in the coal from which it is derived. The physical and chemical properties of any fly-ash depend, among the other factors, on the coal type from which it is produced. In turn, the particular coal type used in power generation depends to a large extend on the geographical location of the plant. The annual production of lignite exceed 44 million tons in 1993, which gives an emission of 10 million tons of particle matter – namely fly ash- to the environment[9].

Aim of this investigation is to determine the effects of, parameters such as stirring speed, fly-ash concentration and initial pH, on phosphate removal from wastewaters by using fly-ash adsorption.

MATERIAL AND METHOD

Fly ash used in the experiments was obtained from the power plant of Afsin-Elbistan, Turkey and used without further treatment. The chemical composition of used fly ash which was determined previously by Bayat (as oxides in wt %) was 15,14 SiO_2; 7.54 Al_2O_2; 3.30 Fe_2O_2; 23.66 CaO; 4.50 MgO; 0.28 K_2O; 0.57 Na_2O; 1.03 TiO_2; 13.22 SO_3. Specific surface area, bulk density, specifik gravity and LOI of the fly ash have been determined as 0.342 m^2/g, 1.05 g/cm^2, 2.7 g/cm^2 and 2.31 wt %, respectively. The particle size distribution on the fly ash was found

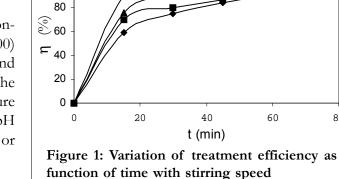## Current Research Paper

between 2 and 300 μm by Bayat[9].

The determination of phosphate was done using the yellow vanadomolybdophosphoric acid method described in AWWA[10].

Batch mode adsorption experiments were conducted in a rotary shaker (Thermolyne Rosi 1000) using the desired concentrations of phosphate and fly-ash in 250 ml screw-cap conical flasks. All of the experiments were carried out in room temperature and in a period of 2 h. contact time. The initial pH was adjusted to a desired value using 1 N NaOH or HNO₃.

Figure 1: Variation of treatment efficiency as function of time with stirring speed

RESULT AND DISCUSSION

The Langmuir or Freundlich isotherms have been commonly used to describe P sorption data the experimental data for the fly-ash fitted the isotherm equations well with correlation coefficients ranging from 0.98 to 0.99. The estimated values of the isotherm parameters are shown in TABLE 1.

concentration increased. While phosphate removal efficiency equals to 25% at a fly-ash concentration of 0,5 g/L, removal efficiency rises over the 80% at a fly-ash concentration of 2 g/L.

Investigating the effect of contact time on the treatment efficiency, experiments were performed at fly-ash concentration of 2 g/L, stirring speed of 200
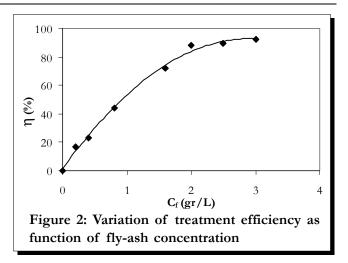
TABLE 1: Estimated Freundlich and Langmuir isotherm coefficients for fly-ash

Langmuir isotherm coefficients			Isotherm equation	Freundlich isotherm coefficients			Isotherm equation
a	b	R^2	$\dfrac{1}{x/m} = \dfrac{1}{b} + \dfrac{1}{axbxC}$	K	1/n	R^2	$\dfrac{x}{m} = KxC_e^{1/n}$
259.42	0.1014	0.98	$\dfrac{1}{(x/m)} = 0{,}1014 + 0{,}038x\dfrac{1}{C}$	2.85	3.49	0.99	$\dfrac{x}{m} = 2{,}85xC_e^{1/3,49}$

The experiments, carried out investigating the effect of stirring speed, were conducted within the range of 50-200 rpm and at fly-ash concentration of 2g/L, initial phosphate concentration of 100 mg/L.

As seen in figure 1, phosphate removal efficiencies almost keep constant, but removal rates rise with increasing stirring speed. While stirring speed equals to 200 rpm, adsorption reaches the equilibrium within 20 min, however at 50 rpm equilibrium period rises up to 75 min.

Investigating the effect of fly-ash concentration on the treatment efficiency, experiments were performed at fly-ash concentration varied between the range of 0,2-3 g/L, and stirring speed of 200 rpm . Obtained results were shown in figure 2. As seen in figure 2, as expected in any adsorption process, phosphate removal efficiency has been risen as fly-ash
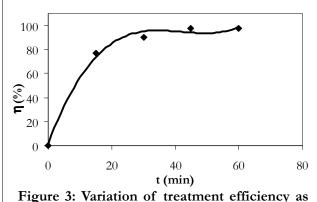

Figure 2: Variation of treatment efficiency as function of fly-ash concentration

rpm and initial phosphate concentration of 100 mg/L. Obtained results were shown in figure 3. As seen in figure 3, at an initial phosphate concentration of 100 mg/L, system reaches the equilibrium within 45
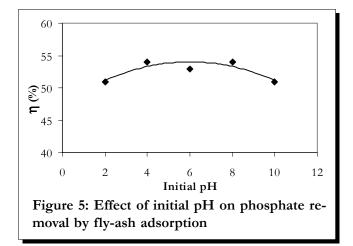
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Figure 3: Variation of treatment efficiency as function of time

Figure 4: Relation between initial and equilibrium pH

Figure 5: Effect of initial pH on phosphate removal by fly-ash adsorption

Figure 6: Effects of temperatures on phosphate removal by fly-ash adsorption (C_p=200 mg/L and n=200 rpm)
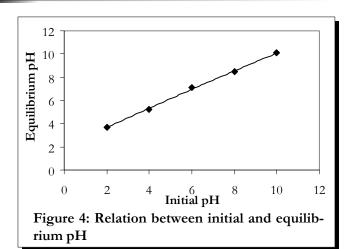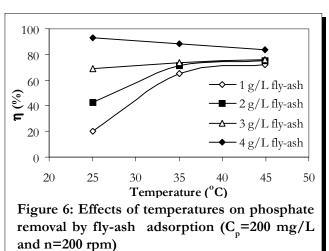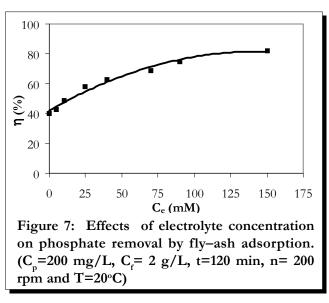
min.

Investigating the effect of initial pH on the treatment efficiency, experiments were carried out at fly-ash concentration of 2 g/L, stirring speed of 200 rpm and initial phosphate concentration of 200 mg/L. Obtained results were shown in figure 4 and 5. It can be seen that equilibrium pH is a function of the initial pH and equilibrium pH of the solution rises, as initial pH increases.(see figure 4) This tendency is in accordance with literature(Yildiz, 2004).

When examined the figure 5, initial pH of the solution-within the investigated range- is not highly effective. It was concluded that while initial pH 2,6 and 10, removal rates were found as 51%, 53% and 51% respectively.

Investigating the effect of temperature, experiments were carried out in different temperatures. Obtained results have been shown in figure 6. As seen figure 6, efficiencies of phosphate removal have risen while temperatures are rise. These increases are

Figure 7: Effects of electrolyte concentration on phosphate removal by fly–ash adsorption. (C_p=200 mg/L, C_f= 2 g/L, t=120 min, n= 200 rpm and T=20°C)

more evident in low fly-ash concentrations.

However. Electrolyte concentrations have been investigated on the effects of phosphate removal efficiencies. For this aim experiments for carried out in

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different NaCI concentrations. Obtained results in these experiments have been figure 7.

As seen figure 7, electrolyte usage have affected on phosphate removal by adsorption with fly ash. While efficiency of phosphate removal has been 42% without electrolyte, efficiencies of removal have been 58% for 25 mM NaCI, 68% for 75 mM NaCI and 80% 150 mM NaCI.

CONCLUSION

Fly ash usage as adsorbent by adsorption on phosphate removal is an effective process. Fly ash that is waste from thermal power-plant has been evaluated. In this study of phosphate removal using fly ash has increased when stirring speed has increased. Efficiency of phosphate removal has increased to increase adsorbent concentration. But efficiency of removal have not been influenced on initial pH of solution. Removal rate and efficiency of removal have increased to increase temperature. Thus, It can be said that reaction is endothermic. Besides, efficiency of adsorption have increased to use electrolyte.

NOMENCLATURE

η	Phosphate removal efficiency	(%)
C_f	Fly-ash concentration	(g/L)
C_p	Initial phosphate concentration	(mg/L)
t	Time	(min.)
n	Stirred speed	(rpm)
T	Temperature	(ºC)
C_e	Electrolyte Concentration	(mM)

REFERENCES

[1] H.S.Peavy, D.R.Rowe, G.Tchobanoglous; 'Environmental Enginering', 195, Mc Graw Hill International edition Civil Engineering Series, Singapore **(1985)**.

[2] S.H.Lee, S.Vigneswaran, H.Moon; Separation and purification technology, **12**, 109-118 **(1997)**.

[3] D.Zhao, A.K.Sengupta; Water Research, **32(5)**, 1613-1625 **(1998)**.

[4] E.Yildiz; Seperation and Purification Technology, **35**, 241-252 **(2004)**.

[5] Y.S.Yildiz, S.Irdemez, N.Demircioglu; Sulu Ortamlardan Fosfat Giderme Metotlari, I. Ulusal Erciyes Sempozyumu, Kayseri **(2003)**.

[6] G.Tchobanoglous, L.F.Burton; Wastewater Engineering Treatment, Disposal, Reuse, 315, Mc. Graw Hill International Edition Civil Engineering Series, New York **(1991)**.

[7] L.D.Benefield, (JR) J.F.Judkins, B.L.Weand; Process chemistry for water and wastewater treatment. Prentice Hall.New Jersey **(1982)**.

[8] Y.S.Yildiz; Endüstriyel Atiksulardan MF-PAC Prosesi ile Fenol Giderimi, Fen Bilimleri Enstitüsü, Master thesis, Atatürk University, Erzurum **(1998)**.

[9] O.Bayat; Characterization of Turkish fly ashes, Fuel, **77**, 1059 **(1998)**.

[10] APHA, AWWA, WPCF, Standard Methods for Water and Wastewater Examination, New York, 16th Edition, **(1985)**.