STUDY OF EQUILIBRIUM ADSORPTION OF ORTHOPHOSPHATE ON ALUMINA ADSORBENTS

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ABSTRACT

This work is a part of a comprehensive study on economic re-utilization of a phosphate contaminated industrial water stream in a typical petrochemical plant in the Kingdom of Saudi Arabia. The experimental study is primarily the adsorption of orthophosphate at equilibrium conditions on 28x48 mesh Alcan Alumina AA 400G. A fixed amount of orthophosphate solution containing 10 mg/L of phosphorus is added to varying amounts of alumina adsorbent. The mixture is allowed to equilibrate over a period of time in excess of 24 hours. The phosphorous content is obtained by forming a molybdate complex and analyzed on the visible range of UV Spectrophotometer at 700 μm. The equilibrium isotherm data are obtained at pH of 4.5 and 6. A peak adsorption capacity of 12 -14 mg elemental phosphorus per gram adsorbent is observed. The data is fitted to both Freudlich and Sigmoidal Isotherm. Effect of activation and pH are presented.

Keywords: *Waste water, Phosphate Removal, Activated Alumina, Adsorption*

1. INTRODUCTION

Contaminants in water are a major problem faced by technologist and environmentalist alike. The former is interested in minimizing them for the down stream processing while the latter for health and ecological reasons. Contaminants in water arise from different sources. In industrial plants, contaminants in steam condensate may be as a result of a side reaction, thus reducing it to a non-usable effluent stream. Generally these impurities are at low-level concentration but still need to be further reduced to levels acceptable by various destinations in the plant, the most rigid among them being the boiler feed water. Fresh process water introduced in various streams meets all the requirements but when this water is recycled it is necessary to ensure that there is no contaminant build up.

In general, treated water is an expensive commodity; hence there is a need to ensure its economical usage. Contamination in industrial process water stream is selective and process dependant, hence the water treatment process is also quite specific. One such generic case is that of steam used in catalytic reactions. The resulting condensate will carry along the soluble reactants, products and catalyst components. Consider the reaction of ethanol production from ethylene and steam using phosphoric acid catalyst on silica gel carrier. The resulting steam condensate has small amounts (400 ppm) of organic and inorganic phosphates. This limits the re-use of the water stream till it is treated to concentration level of < 10 ppm. In a present day plant, the flow rate of such a non-reusable stream is several thousand cubic meters per day, which results in higher production costs. A suitable treatment process for removing phosphates is desirable.

Water treatment for phosphate removal is a very old and established process, although most of the processes are dedicated to drinking and sewage water treatments. Little attention has been given to the industrial wastewater contamination since these processes are quite specific in nature. A brief review of the literature on phosphorous removal from water streams clearly indicates the availability of wide range of processes [De Renzo, 1981]. Most of these processes however were established and dedicated to municipal wastewater treatment where the emphasis is more on ecological considerations. Industrial wastewater treatment is done with a dual motive of environmental as well as economic consideration. In order to have a feasible industrial process, the treatment should be cost effective, so also the involvement of secondary treatment should be minimal.

2. LITERATURE REVIEW

Removal of phosphate from wastewater has been practiced for a long time in order to prevent eutrophication of lakes and water bodies. Presently economical means of removing phosphates in wastewater treatment plant is precipitation of the phosphates using metal salts, i.e. alum, ferric chloride, or lime and subsequent sedimentation of the phosphate floc in the

treatment plant clarifiers. Application of alumina in water treatment is quite common [Fleming, 1986]. Concentration can be reduced to 1 mg/L by use of this method. Further reduction is possible with the use of activated alumina but it is a relatively expensive process for municipal wastewater. The main disadvantages of chemical precipitation are the high sensitivity to pH, increase in the electrolyte concentrations and problems associated with sludge handling while a major advantage of using activated alumina are no sludge. Further the alumina can be regenerated using sodium hydroxide solution.

The adsorption of phosphates on activated alumina occurs through an ion exchange mechanism. The ion exchange selectivity sequence for activated alumina has been determined for a range of typical cations and anions as follows [Fleming, 1990]:

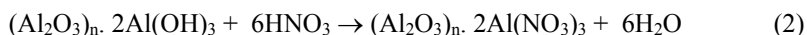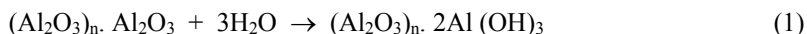$$OH^- > PO_4^{3-} > C_2O_4^{2-} > F^- > CrO_4^{2-} > SO_4^{2-} > Cr_2O_7^{2-} > Cl^- > NO_3^-$$
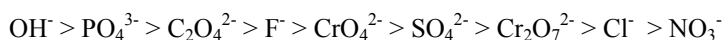
This sequence indicates that only hydroxyl ions are preferentially adsorbed to phosphate ions from water. Activated aluminas are high surface area, porous aluminas prepared by low temperature calcinations of alumina hydroxide compounds such as the trihydroxides (gibbsite, bayarite) and oxyhydroxides (boehmite, pseudoboehmite). Their adsorbent properties lead to a wide variety of applications including catalyst, catalyst supports, desiccants and water purification.

By varying the type of pelletisers and production technique it is possible to produce activated alumina products with a very wide range of physical characteristics; typical examples include the Alcan standard grades AA300 and AA400. AA300 is stronger, has higher density and is less macro porous – an ideal combination for application as a desiccant. AA400 has higher macro porosity and is thus better suited to applications in catalysts, catalyst support or general adsorbent.

Activated alumina have a strong affinity for water. When placed in water, surface hydroxyls are formed by chemisorption. A further layer of water is bound to these hydroxyls by hydrogen bonding. The surface of activated alumina is very heterogeneous in terms of groupings of cations, hydroxyls and oxygen ion vacancies and this leads to the surface hydroxyls ranging from very basic to partially acidic. The surfaces are also amphotric in nature, as the surface hydroxyls can be protonated in acidic media giving a positively charged surface and deprotonated in basic media to give a negatively charged surface. This behavior can be modified by incorporation of other ions.

Activated alumina has been examined as a phosphorus selective adsorbent for the removal of orthophosphate from aqueous solutions and effluents of biological treatment of domestic sewage and numerous studies have indicated the technical feasibility of activated alumina as

an adsorbent for phosphate removal [Fleming, 1990, Yee, 1966, Nufeld & Thodos, 1969, Ames & Dean, 1970, Narkis & Mordehai, 1981, Urano & Tachikawa, 1991, 1992]. The use of conventional ion exchange resins for selective phosphorus removal from effluents is not practical for the removal of phosphates alone, because of the extensive removal of nearly all other anions, which reduces the efficiency and capacity of the resins to remove phosphates. Also these resins have a high sensitivity towards the pH [Ames & Dean, 1970]. It seems that the pH, the activated alumina granule size and the column length are very important parameters in minimizing the operating costs of a fixed-bed system for phosphorus removal. One of the earliest techno-economic study for selective removal of mixed phosphates on activated alumina was done by Yee [Yee, 1966]. The forms of phosphates studied for removal from wastewater included sodium orthophosphates and a variety of mixed polyphosphates. Three types of alumina varying in properties and with surface area ranging from 250 – 500 m^2/g were deployed. Exhausted column were regenerated in a three step process of re-circulating 1M NaOH solution followed by re-acidification with HNO_3. Polyphosphates were hydrolyzed to convert to orthophosphates for accurate analysis. 99% of orthophosphate was removed for 3000 bed volumes (BV) and isotherm capacities up to 30 mg. PO_4^- /g adsorbent were reached. 12 BV of waste NaOH solution is generated during regeneration, which indicates the high volume reduction factor (rate of product water to regenerated waste) that can be achieved. Yee [Yee, 1966] indicated that the acidified activation of alumina is a necessary prerequisite to phosphate removal. The alumina is prepared by first washing with distilled water, and then with 1N nitric acid. Hence the following surface reactions are postulated:

$$(Al_2O_3)_n. \ Al_2O_3 \ + \ 3H_2O \ \rightarrow \ (Al_2O_3)_n. \ 2Al \ (OH)_3 \qquad\qquad (1)$$

$$(Al_2O_3)_n. \ 2Al(OH)_3 + \ 6HNO_3 \rightarrow (Al_2O_3)_n. \ 2Al(NO_3)_3 + \ 6H_2O \qquad\qquad (2)$$

Then the phosphate ions will exchange with the nitrate ions present on the solid activated alumina. The adsorption capacity of activated alumina can be increased by adding aluminum sulphate or iron sulphate to form complex salts on their surface[Purshottam & Yee, 1970]. In particular, activated alumina combined with 2.0 x 10^{-4} mol of aluminum sulphate/g, has a good phosphate adsorption capacity in a pH range of 4 to 7.

The concentration measurements of orthophosphate type are determined by colorimetry or ion chromatography. Concentrations of phosphite, hypophosphate and tripolyphosphate types are determined by colorimetry after changing to orthophosphate. The orthophosphate are mixed with stannous chloride and ammonium molybdate solution and the resulting mixture analyzed by a spectrophotometer at wavelength of 690 mμ. Standard procedures are available [ASTM, 1992].

The basic data needed for a good design of a packed bed adsorption system includes the equilibrium and kinetic parameters. The equilibrium data is a relation between the solute concentrations in the adsorbent to that in the liquid phase. This data of q (solute concentration in the liquid phase) versus C (solute concentration in the fluid phase) is normally fitted to one or more standard "isotherm" equations. Among the isotherms the most widely applicable for the liquid phase adsorption are the Langmuir Isotherm and the more widely used Freundlich Isotherm. The Langmuir isotherm is normally represented as follows

$$\frac{q}{q_m} = \frac{bC}{1 + bC}$$

(3)

and the main assumptions are the mono layer coverage, defined sites, equal energy of adsorption and no interaction forces between adjacent sites. The Freundlich isotherm is normally represented as follows

$$\frac{q}{q_m} = KC^{1/n}$$

(4)

where n is a constant which is usually greater than 1. The main assumptions are that energy distribution for the adsorption sites is essentially of exponential type and coverage need not be monolayer coverage. Other isotherms used include the extended Langmuir-Freundlich Isotherm, which has three parameters, and the Radke-Praunitz isotherm, which is asymptotic to Henry's Law, and Freundlich isotherm at extreme concentration. These isotherms have a wider applicability. Cooney [Conney, 1999] has presented a summary discussion on this subject. The foregoing isotherms were limited to single solute and in case of multi solute adsorption, these isotherms are extended for mixtures. The extended two solute Langmuir isotherm is represented as

$$\frac{q_1}{q_{m1}} = \frac{b_1 C_1}{1 + b_1 C_1 + b_2 C_2}$$

(5)

$$\frac{q_2}{q_{m2}} = \frac{b_2 C_2}{1 + b_1 C_1 + b_2 C_2}$$

(6)

and the extended two solute Freundlich Isotherm is represented as

$$q_1 = \frac{a_1 C_1^{1/n_{11}}}{b_1 C_1^{1/n_{12}} + b_2 C_2^{1/n_{13}}}$$

(7)

$$q_2 = \frac{a_2 C_2^{1/n_{21}}}{b_1 C_1^{1/n_{22}} + b_2 C_2^{1/n_{23}}}$$

(8)

In the present work, data is obtained by equilibrating orthophosphate solution with activated alumina till equilibrium is achieved and subsequently analyzing the solution for its phosphate content.

3. EXPERIMENTAL

The first set of experiments was to prepare the calibration curves. For this purpose, samples of orthophosphate solutions with concentration of elemental phosphorous varying from 0 to 0.2 mg/L were prepared and its transmittance obtained on the spectrophotometer. 25 ml of the solution was mixed with 1 ml. of ammonium molybdate/ sulfuric acid solution and 2 drops of stannous chloride/ glycerol solution. The resulting blue colored complex was analyzed by the visible range colorimetry method on a Shimadzu spectrophotometer at a wavelength of 700 μm. The resulting calibration curve was used for obtaining phosphate concentration of the experimental samples.

Experimental studies for obtaining equilibrium isotherms were done by equilibrating the model solution of 10-mg/L phosphates content with varying amounts of Activated Alumina. A period of 24 hours was established for such an operation. The model solution was prepared primarily by adding 1.532 gm of Orthophosphoric acid (85% by wt., specific gravity = 1.69) to water so that the total volume of this stock solution is 2000-ml. A part of this stock solution is diluted to 2000-ml. to obtain an elemental phosphorus concentration of 10 mg/L.

A typical set of experiment comprised of preparing samples by adding 100 ml of 10mg/ L solution to flask containing activated alumina powder ranging from 0.05, 0.1, 0.5, 1 and 5 g. The flasks were put on a shaker at 25 °C for a period in excess of 24 hours. The suspension was then filtered and analyzed for phosphorous content as indicated above. The experimental sample was diluted appropriately to obtain a reading within the range of the spectrophotometer. The wavelength used was 700 μm. pH was measured and controlled using 0.1 M buffer solutions of sulfuric acid and NaOH respectively as required.

4. RESULTS AND DISCUSSION

Since the work is still on going, only a limited set of data has been collected, primarily exploratory in nature and a base for subsequent experimentation. This limited set of data has been useful to establish trend regards activation, pH, and isotherm behavior. Since a sealed packet of alumina AA400G was used, the first set of experimentation was performed without activation. The result of this run is shown in Figure 1. A maximum capacity of 4 mg per gram adsorbent could be achieved. The level of equilibrium adsorption capacity was much lower than expected. Subsequently, the adsorbent was activated by a flowing nitrogen stream at 70°C for a period of 24 hours. The above set was repeated and a dramatic increase in the capacity up to 14 mg / g adsorbent was observed as shown in Figure 2. The pH of the solution

was not maintained at a fixed value for the different samples in the set. A value of pH ranged from 3.7 at the start of the run and was at a value ranging from 4 to 5.9 at equilibrium. Final pH increased monotonically with the ratio of adsorbent to adsorbate. As seen from the Figure 2 all the samples had the same final equilibrium concentration suggesting a limiting concentration under varying pH conditions. This observation indicates that similar amounts of phosphate have been adsorbed in spite of varying quantities of adsorbent. This trend is justified due to the fact that at higher pH the adsorption capacity decreases. Hence samples with larger ratio of adsorbent to adsorbate exhibit higher pH and hence lesser capacity thereby adsorbing same amount as those with lesser ratio of adsorbent to adsorbate, which exhibits, lower pH. A significant conclusion could be postulated, subject to further experimentation that if pH were not controlled than the final exit concentration of the influent in a flow process would be limiting value of around 3 mg/ L for an inlet concentration of 10 mg/L.

The third and fourth sets of runs were carried out under controlled pH conditions of 4.5 and 6. The results are shown in Figure 3 and 4 respectively. The pH varied with time and it was intermittently monitored and controlled by the buffer solutions. A coarse control of pH at 4.5 did result in an expected trend as observed in Figure 3. The data in Figure 4 at a pH 6 indicates a similar trend. . A peak capacity of about 14 mg per gram adsorbent is reached Also the difference in capacity at two levels of pH is not very prominent.

For the case, when adsorption occurs from a liquid solution, the Freundlich and Langmuir Freundlich isotherms are commonly used to fit the data as found in the literature [Urano & Tachikawa, 1991, Cooney, 1999]. Urano and Tachikawa [Urano & Tachikawa, 1991] fitted the data for adsorption of bi-phosphate on activated alumina using a Freundlich isotherm. as follows:

$$q = 20 \, C^{0.04}$$

where q is mg P/ g alumina and C is equilibrium concentration in mg/L. The present data appeared to suggest a BET type or sigmoidal type isotherm. The data is fitted using both Freundlich as well as sigmoidal isotherms. The Freundlich equation is displayed on the respective diagram. For the Sigmoidal type Isotherm the equation is as follows:

$$q = \frac{C^n}{K + C^n}$$

The value of *K* and *n* is 300 and 6 for the curve in Figure 3 and 300 and 5 Figure 4 respectively. Further investigation, especially a finer pH control, is necessary to analyze the results at a better confidence level.

ACKNOWLEDGEMENT

NOMENCLATURE

b, b_i	Constant in Langmuir Isotherm
C, C_i	Liquid Phase Concentration
n, n_i	Exponents in Freundlich, Sigmoidal Isotherm
q, q_i	Solid Phase Concentration
q_m	Saturated Solid Phase Concentration

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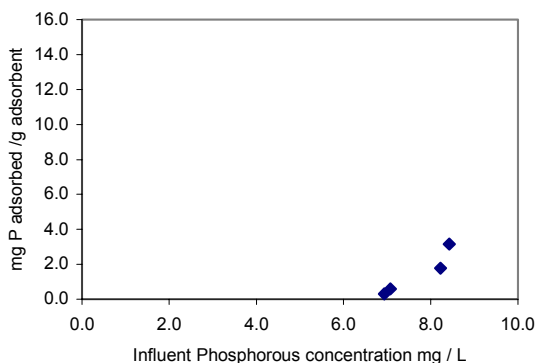
Fig. 1 Adsorption of Phosphorus on Activated Alumina
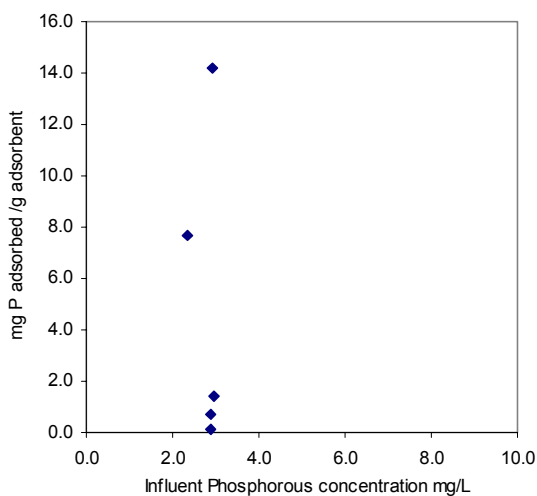AA400G
(before Activation)

Fig 2. Adsorption of Phosphorus on Alumina AA400G
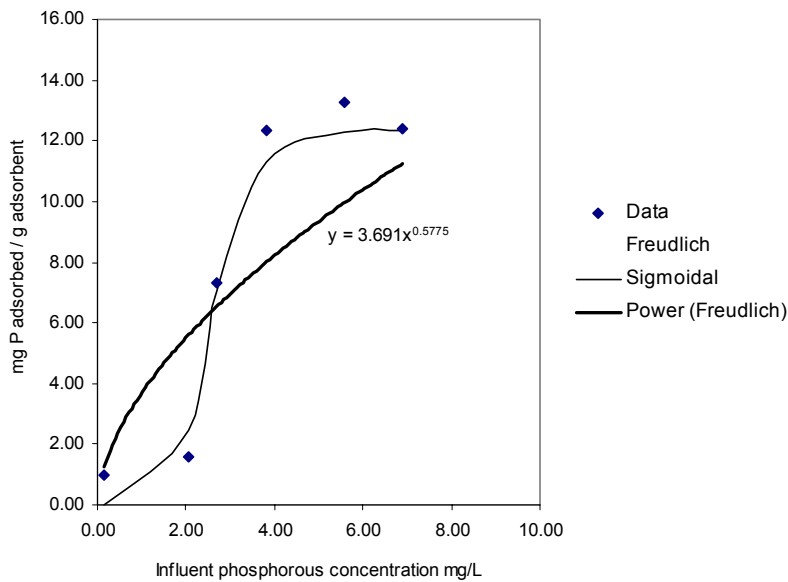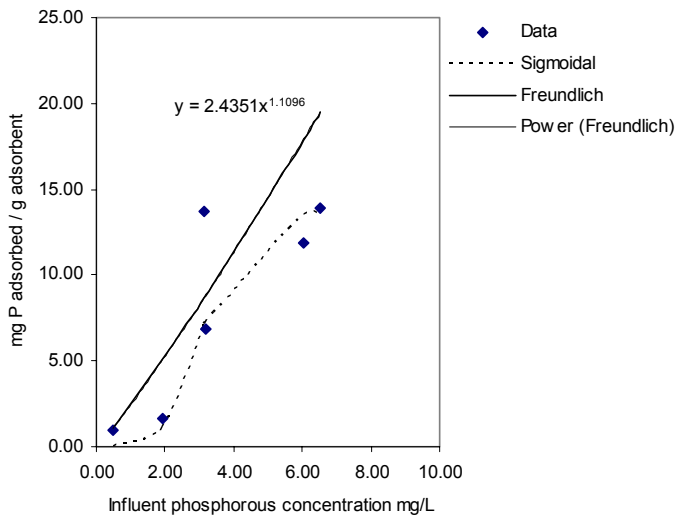(after Activation)

Fig. 3 Adsorption of Phosphorous on Alumina AA 400G at pH 4.5

Fig. 4 Adsorption of Phosphorous on Alumina AA 400G at pH 6