IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.12 No.3 (September 2011) 25-33
ISSN: 1997-4884

University of Baghdad

Aluminum Leachability Evaluation from Oven Dried Alum Sludge

Sami Mohammed Zaboon
University of Baghdad , College of Engineering ,Chemical Engineering Department,Baghdad, Iraq.

Abstract

Phosphorus and dye (direct black) removal for small – scale wastewater applications were investigated using oven dried alum sludge (ODS).The use of alum sludge not only provides a low cost technique but also reduces the hazard and the cost related to the disposal of large amount of alum sludge. Phosphorus and dye removal exceeds 90% for all operating conditions applied in the research.

The residuals generated during the treatment of wastewater were further tested to study the possibility of aluminum leaching from oven dried alum sludge during the adsorption of phosphorus and dye. These tests observed a reduction in aluminum leaching indicating a lower risk imposed on land and surface water based on disposal options rather than on alum sludge disposal.

The leaching of aluminum was observed to be mostly below 1 mg/l for a pH solution of 6 and 7 for both processes of phosphorus and dye removal. However, the pH of 5 seemed to have a concentration of more than 1mg/l of aluminum.

Introduction

Biosolid management is considered very important, as there are considerable amounts of biosolids generated due to anthropogenic reasons. Alum sludge, a biosolid generated in the coagulation process in a water treatment plant, is one ofthem. The reuse of alum sludge in other applications has been considered by many researchers in recent years.Divalent and trivalent cation based materials are known to be effective for phosphorous and dyes removal (Maruf, M., 2006,Sarmad, A., 2009 and Rasha, H., 2010).

Alum sludge is typically known to be a mixture of various forms of aluminium hydroxide (Wang et al., 1992). The use of waste material (alum sludge) not only can provide low cost appropriate technological alternative for small – scale applications, but also can reduce the hazard and the cost of the disposal of large amount of alum sludge.Physical and chemical methods are considered very expensive in terms of energy and reagent consumption. Another account that limits their use is the excessive sludge they generate (Yokubuet al., 2008).Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances.At the present time, there is a growing interest in using low – cost, commercially available materials for the adsorption of phosphorous and dyes.Sarmad(2009) investigated the removal of phosphorous from wastewater by using oven dried alum sludge. The results showed that the oven dried alum sludge were effective for adsorbing phosphorous and the removal percentage was up to 85%.

Rash H. (2010) investigated the removal of dyes from wastewater by using oven dried alum sludge. The results showed that the removal was 92%.

Phosphorous and dyes adsorption onto oven dried alum sludge shown in the researches mentioned earlier provided an environment friendly management option for water treatment residuals . However, the residuals generated during the process of adsorption on oven dried alum sludge are also needed to be managed due to large amount of aluminum in these residuals and aluminum in water has proven to produce chronic toxicity (Allin and Wilson ,1999).

The chemical speciation of aluminum in natural water regulates its mobility, bioaviability and toxicity. Aluminum normally undergoes hydration reaction in aqueous system to an extent governed by the ligand properties and concentrations of aluminum, and hydrogen ion (Faust and Aly, 1999). Hydrolysis increases as the solution pH increases resulting in a series of aluminum hydroxide complexes. Alum sludge is mostly composed of these series of aluminum hydroxide complexes (i.e. $Al(OH)_2^+$, $Al(OH)_3$, $Al(OH)_4$, Al^{+3}, … etc).

The objective of this study was to study the leachability of residuals (i.e. aluminum) generated from adsorption of phosphorous and dyes from small – scale wastewater on alum sludge.

- **Materials**

1. **Adsorbent**

❖ **Alum Sludge**

Alum sludge is a waste material generated during the coagulation / sedimentation process in a drinking water treatment plant. Alum sludge that is generated from drinking water treatment contains precipitated alum hydroxide and the contaminants that are specific to row chemistry. In this research, alum sludge was collected from Al-Qadisiya treatment plant, Baghdad governorate, Iraq. Inorganic materials in alum sludge are presented in table 1.

Table 1, Inorganic materials in alum sludge

Constituent	Weight percent
Aluminum	3.38 %
Iron	0.819 %
Manganese	0.16 %
Chromium	0.013 %
Vanadium	0.002 %
Zinc	0.0098 %
Lead	0.0001 %
Barium	0.0001 %
Arsenic	0.0002 %

The alum sludge used in this research was heated in an oven at 105 C^o for 24 hours. The dried sludge was then cooled to room temperature. The sludge particles were then crushed to produce a particle size of 2.36 mm. The physical properties are listed in table 2.

Table 2, Physical properties of oven dried alum sludge

Item name	Oven dried alum sludge
Bulk density (kg/m^3)	786.7
Particle porosity	0.7
Bed porosity	0.65

2. **Wastewater**

- Orthophosphate(Potassium Dihydrogen Orthophosphate KH_2PO_4) was used in this study to prepare a phosphorus solution. Physical properties of KH_2PO_4 are listed in table3.

Table 3, Main properties of adsorbate

Name of component	Potassium dihydrogen orthophosphate
Chemical symbol	KH_2PO_4
Name of company	The British Drug Houses LTD / England
Molecular weight	136.09 kg / kg.mole
Assay (acidimetric)	99 to 101per cent
Chloride (Cl)	Not more than 0.01 per cent
Sodium (Na)	Not more than 0.2 per cent
Sulphate (SO_4)	Not more than 0.05 per cent
pH (1 percent solution)	4.5 to 4.7

- Deionized water was spiked with KH_2PO_4 to prepare a phosphorus solution of (10) mg/L, this concentration was achieved by 0.0143 mg KH_2PO_4 with liter of water. The phosphorus concentration was chosen as typical phosphorus concentration in many wastewaters. The same thing was used to prepare the dyes solutions.
- Black direct dye of 10 mg/l was used as adsorbate. The concentration of dye was measured with Shimatzu UV Spectrophotometer at wave length corresponding to the maximum absorbance of 566nm.

- **Experimental Arrangements**

The schematic representation of experimental equipment is shown in Figure 1.

- **Adsorption Column**

The fixed bed adsorber studies were carried out in Q.V.F. glass column of 2 in. (50.8 mm) I.D. and 50 cm height.The oven dried alum sludge was confined in the column by fine stainless steel screen at the bottom and a glass cylindrical packing at the top of the bed to ensure a uniform distribution of influent through the alum sludge.The influent solution was introduced to the column through aperforated plate, fixed at the top of the column.

Experiments were carried out at various pH solutions (5 – 7) with keeping other variables constant (i.e. initial phosphorus and dyeconcentration, particle size, flow rate and bed depth).

The experimental procedure for column system experiments is as follow:

- The oven dried alum sludge with particle size of 2.36 mm was placed in the adsorption column for the desired bed length (i.e. 40 cm)
- The wastewater with the desired concentration was prepared in the feed container, using distilled water (i.e. phosphorusconc. 5 ppm and dye conc. 10 ppm).
- The wastewater was pumped to the adsorption column through the calibrated rotameter at the desired flow rate (i.e. 1.67×10^{-6} m^3/s).
- Samples were taken periodically, the concentration of phosphorus, dye, and aluminum in these samples were measured using UV spectrophotometer and atomic absorption.

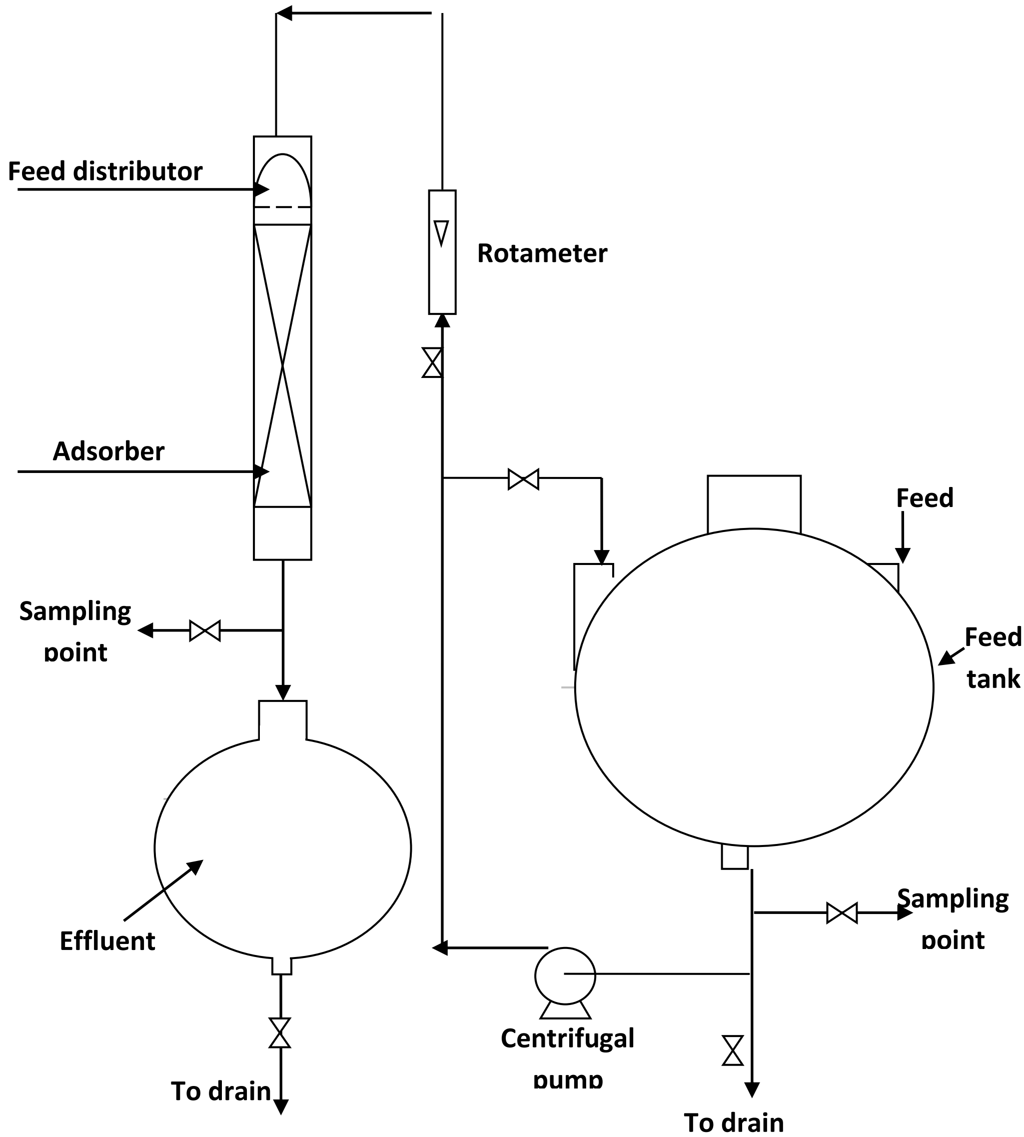

Fig. 1, Schematic representation of experimental equipment

- **Tests for Characterizing Oven Dried Alum Sludge**

a. IR Spectroscopy

The samples for infrared spectra (Bruker Vector FT-IR spectrometers) were prepared with methylene chloride (CH_2C_{l2}) mulls onCsI plates. Vibrational spectra were reported in wavelengths (cm^{-1}) against ranked infrared absorption, where the value of the wavelengths at peak corresponds to the characteristics of the active groups present on the surface of the material. This test was done in the College of Science / Chemistry Dept. and the result is shown in Figure 2.

b. X-Ray Diffraction

X-Ray powder diffraction patterns of ODS were obtained from gently pressed specimens of random powder particles that are less than 0.45 µm.

Powder X-ray diffraction data were collected from 10 to 60° 2δ with a Nicolet X-ray powder diffractometer (graphite monoachromatized Cu KR radiation, 0.05° 2δ step size, and 2-s count time per steps).This test was carried out in theMinistry of Science and Technology and the result obtained is shown in Figure 3.

c. Specific Surface Area

In practice, the method mostly used for determining specific surface area is the BET method (Brunauer, Emmett and Teller) based on the physical adsorption of an inert gas at constant temperature of liquid nitrogen. The principle of measurement consists of determining the point when molecular layer of gas covers the surface (Lepage, 1987).The apparatus of type Carlo-Erabasorptomic series 1800 was connected to computer in which all necessary BET principles were run from the information of the pressure decrease. This test was done in Petroleum Research and Development Center.

The experimental results showed that oven dried alum Sludge had an average specific surface area of 191 m^2/g.

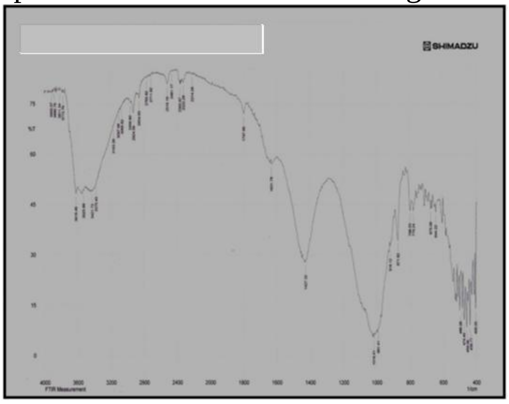

Fig. 2, IR Spectroscopy of ODS

Results and Discussion

To study the possibility of aluminum contaminants leaching from oven dried alum sludge,a series of experimental breakthrough curves were carried out for adsorption of phosphorus and dyes using oven dried alum sludge. The experiments includedstudying the effect of pH solution (5, 6, and 7) on phosphorus and dyes adsorption onto oven dried alum sludge and aluminum leaching from the adsorbent.

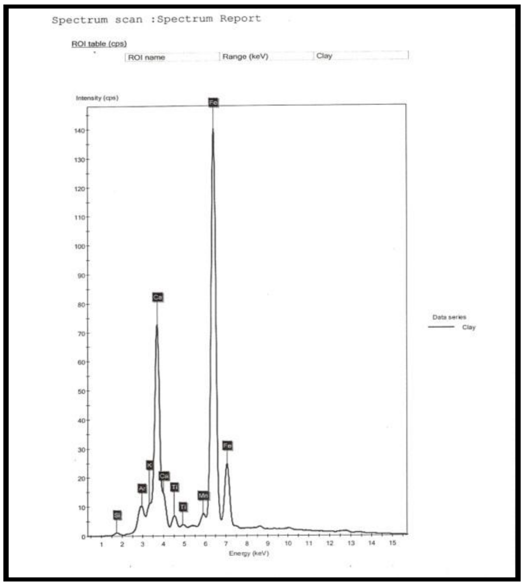

Fig. 3, X-Ray Diffraction of ODS

❖ **Phosphorus Adsorption:**

The removal of phosphorus by using oven dried alum sludge, as a function of different values of pH is presented in Figures4, 6, and 8. Varied values of pH solution are 5, 6 and 7. The other variables (phosphorus concentration 5 ppm, operating temp. 25°C, bed height 40 cm, particle size 2.36 mm) are kept constants.

The results indicate that pH had little effect on the adsorption density. However, pH solution of 6 appeared to produce maximum phosphorus adsorption density.

In the same time, tests conducted on oven dried alum sludge showed lower tendency to leach aluminum. Aluminum leaching was in general high in the beginning of the experiments as shown in Figures 5, 7, and 9. However, over time, aluminum leaching decreased. In many cases, aluminum concentrations were lower than the concentration present in the raw water because of the structural variation in alum sludge surfaces during the drying process. Also, the pH of the system affects both metal ion and waste water solution. The solution suffers protonation as the pH of the system decreases:

$$A^- \underset{-H^+}{\overset{H^+}{\rightleftarrows}} HA^+ \underset{-H^+}{\overset{H^+}{\rightleftarrows}} H_2A$$

If the solution is unable to ionize as a result of the concentration of hydrogen ion, it will not be able to form a complex with a metal ion, and hence extraction will not occur.

The effluent pH was understandably dependent on the influent pH. An influent pH 5 produced effluent pH of (4.7-5.5). Similarly an influent pH 6 generated an effluent pH range (5.6-6.3) and an influent pH 7 generated an effluent pH range of (6.5-7.5). This was due to the adsorption and desorption of H^+ ions during the adsorption of phosphorus on alum sludge. An effluent pH below 4.5 is not suitable for disposal in surface water. The effluent pH can be increased prior to disposal in surface water. However, the cost of chemicals to reduce initial pH and to increase final pH and hazards of dealing with increased amount of sludge would pose negative interest for pH control.

In general, a pH value in the range of 6 – 9 is reasonable for wastewaters before disposal into surface water.

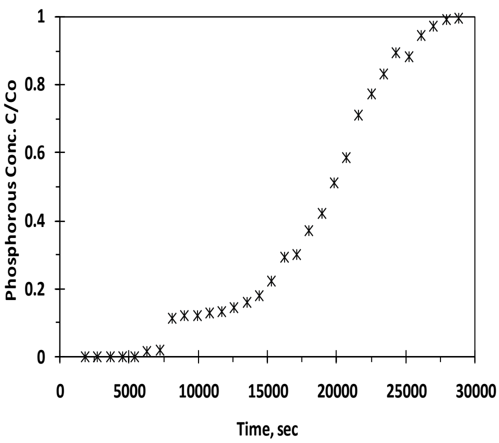

Fig. 4, Phosphorus ratio (C/Co) concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature=25°C, bed height = 40cm, column diameter= 2in., particle size = 2.36 mm, pH=5, $Q=1.67\times10^{-6}$ m^3/s.

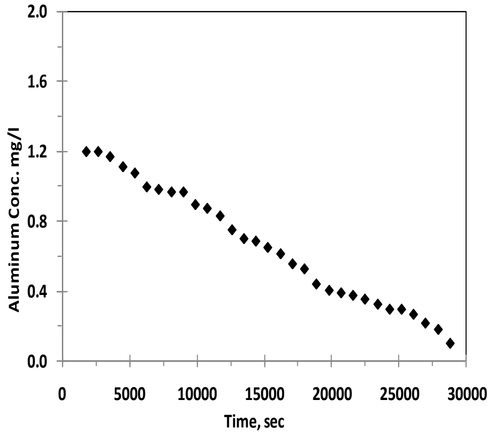

Fig. 5, Aluminum concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature= 25°C, bed height = 40cm, column diameter= 2in., particle size = 2.36 mm, pH=5, $Q=1.67\times10^{-6}$ m^3/s.

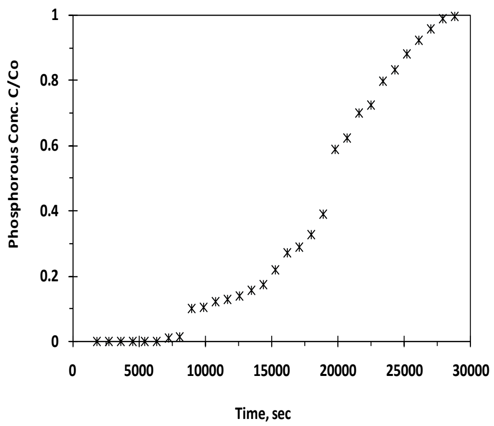

Fig. 6, Phosphorus ratio (C/Co) concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature= 25°C, bed height = 40cm, column diameter= 2in.,particle size = 2.36 mm, pH=6, $Q=1.67\times10^{-6}$ m^3/s.

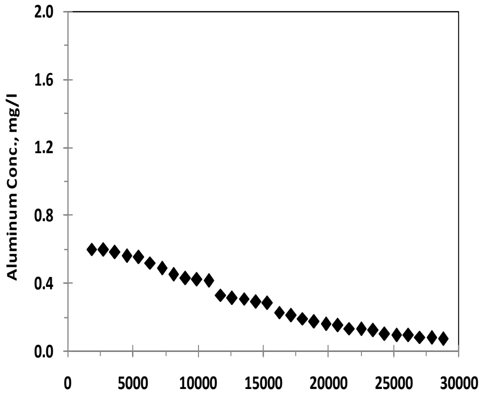

Fig.7, Aluminum concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature= 25°C, bed height = 40cm, column diameter= 2in., particle size = 2.36 mm, pH=6, Q=1.67×10^{-6} m^3/s.

❖ Direct Black Dye Adsorption

The removal of direct black dye by using oven dried alum sludge, as a function of different values of pH is presented in Figures 10, 12, and 14. Varied values of pH are 5, 6, and 7. The other variables (dye concentration 10 ppm, operating temperature 25 °C, bedheight 40 cm, particle size 2.36 mm)are kept constants.

The effluent pH levels were in the range of 5.5 – 7.5 for an is influent pH of 5 – 7 and this mostly suitable for disposal in surface water.The results showed that the oven dried alum sludge was effective in adsorbing dyes with removed efficiency up to 93%.

Aluminum leaching was in general about 1 mg/l in the beginning of the experiments for each pH a shown in the Figures 11, 13, and 15. However, over time, aluminum leaching decreased to less than 0.2 mg/l; this was due to the structural variation in alum sludge surfaces during drying process and the effect of pH solution that discussed previously.

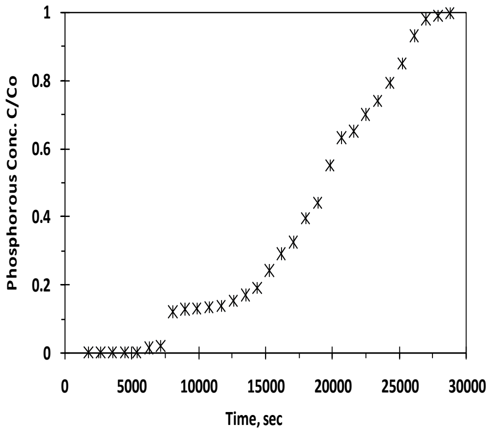

Fig. 8, Phosphorus ratio (C/Co) concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature= 25°C, bed height = 40cm, column diameter= 2in., particle size = 2.36 mm, pH=7, Q=1.67×10^{-6} m^3/s.

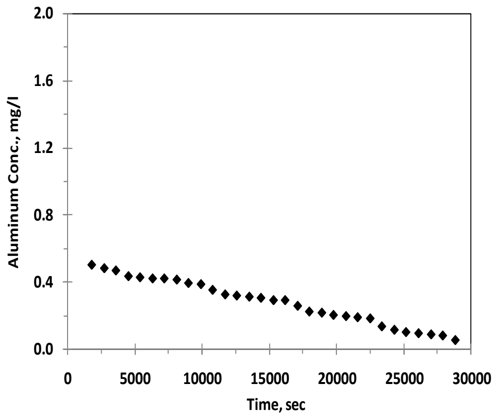

Fig.9, Aluminum concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature= 25°C, bed height = 40cm, column diameter= 2in., particle size = 2.36 mm, pH=7, Q=1.67×10^{-6} m^3/s.

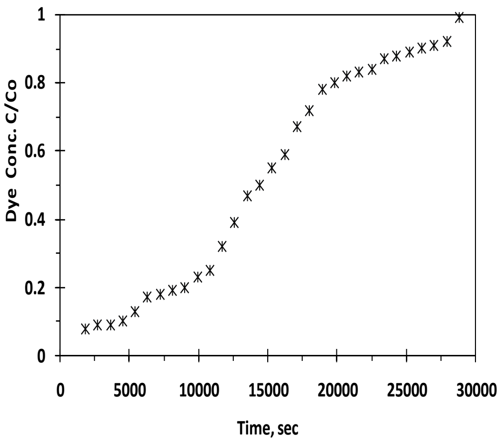

Fig.10, Direct black dye concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature= 25°C, bed height = 40cm, column diameter= 2in., particle size = 2.36 mm, pH=5, Q=1.67×10^{-6} m^3/s.

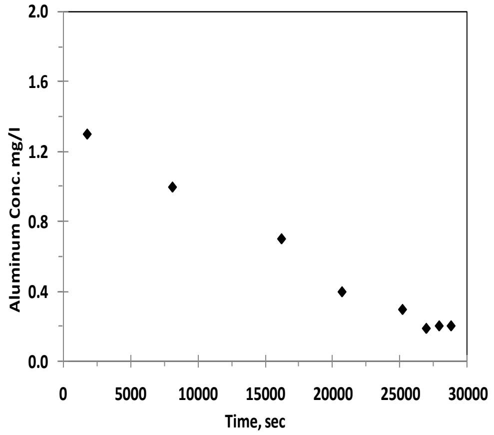

Fig.11, Aluminum concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature= 25°C, bed height = 40cm, column diameter= 2in., particle size = 2.36 mm, pH=5, Q=1.67×10^{-6} m^3/s.

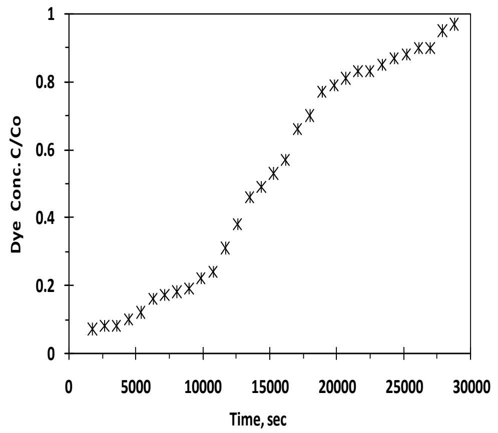

Fig.12, Direct black dye concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature= 25°C, bed height = 40cm, column diameter= 2in., particle size = 2.36 mm, pH=6, Q=1.67×10^{-6} m^3/s.

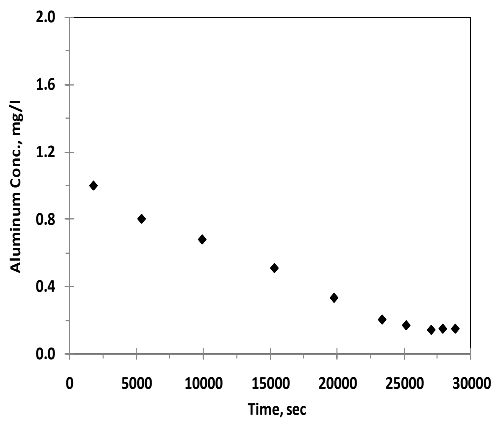

Fig.13, Aluminum concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature= 25°C, bed height = 40cm, column diameter= 2in., particle size = 2.36 mm, pH=6, Q=1.67×10^{-6} m^3/s.

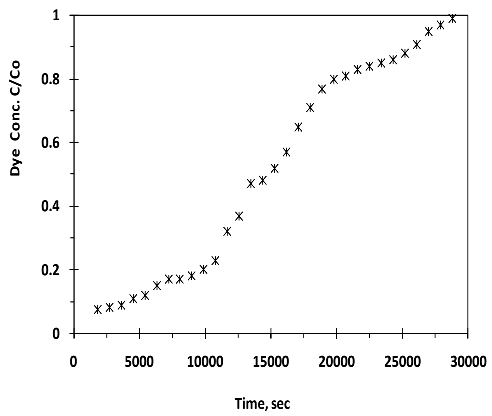

Fig.14, Direct black dye concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature= 25°C, bed height = 40cm, column diameter= 2in., particle size = 2.36 mm, pH=7, Q=1.67×10^{-6} m^3/s.

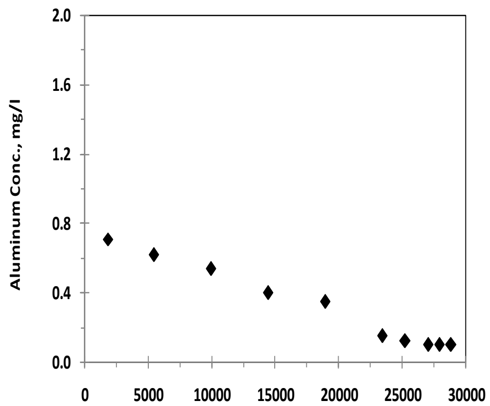

Fig.15, Aluminum concentration with time

Operating Conditions: Phosphorous conc. = 5ppm, operating temperature= 25°C, bed height = 40cm, column diameter= 2in., particle size = 2.36 mm, pH=7, Q=1.67×10^{-6} m^3/s.

Conclusion

- Oven dried alum sludge was effective in adsorbing phosphorus and direct black dye.
- Experimental findings indicated the residuals generated during adsorption of phosphorus and dye on oven dried alum sludge would not cause alarming level of aluminum leaching. Therefore, there were low chances of these residuals being a problem for disposal.

References

- MarufMortula, Meaghan Gibbons, and A. Gagnon, 2006, "Phosphorus Adsorption by Naturally-Occurring Materials and Industrial by-Products", J. Environ. Eng. Sci., 6, pp 157-164.
- Yakubu, M.K., Gumel M.S., and Abdullahi A.M., 2008, "Use of activated carbon from date seeds to treat textile and tannery effluents", African Journal of science and technology (AJST), Science and Eng. Series, 9(1), p. 39 – 49.
- Sarmad, A.R., 2009, "Phosphorus Removal from Wastewater Using Alum", M. Sc. Thesis, University of Baghdad.
- Wang, M.C., Hull, J.Q., Jao, M., Dempsey, B.A., and Cornwell, D.A., 1992,"Engineering behavior of water treatment sludge", Journal of Environmental Engineering, 118 (6), 848 – 864.
- Rasha H. Salman, 2010,"Removal of Dyes from Textile Effluent by Adsorption onto Oven Dried Alum Sludge", Journal of Engineering, No.2, 16 (5249 – 5262).
- Allin, C.J., and Wilson, R.W., 1999,"Behavioral and Metabolic Effects of Chronic Exposure to Sublethal Aluminum in Acidic Soft Water in Juvenile rainbow trout", Canadian Journal of Fisheries and Aquatic Science, 56 (670 – 678).
- Faust, S.D., and Aly, O.M., 1999, "Chemistry of Water Treatment", 2nd edition, Lewis Publishers.