



INDUSTRIAL WASTEWATER TREATMENT IMPROVEMENTS USING LIMESTONE

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ABSTRACT

The discharge limits of industrial wastewater effluents are subjected to regulations which are getting more restricted with time. A previous research was carried out in Port Said city, studied the efficiency of treating industrial wastewater using the first stage A-stage of the multiple-stage plant AB-system. From the results of this research, the effluent treated wastewater has high rates of total dissolved solids TDS and chemical oxygen demand COD. The purpose of this paper is to improve the treatment process in removing TDS and COD. A pilot plant was constructed at wastewater pump station in the industrial area in the south of Port Said city. Experimental work was divided into several runs, by adding powdered limestone with different dosages to wastewater. Furthermore, for each run wastewater was filtered after being mixed with limestone powder. TSS and pH as physical variables were also studied. Significant removals of TDS and COD were observed in these experiments showing that using effective adsorbents can aid such removals to large extent.

Keywords: Adsorption, Filtration, Industrial Wastewater, TDS Removal, and COD Removal

1. INTRODUCTION

A significant growth has occurred in the industries of developing countries in the recent years. These industries discharge wastewater which carries high concentrations of dissolved solids and biochemical oxygen demand, BOD. These effluents should be treated for safe disposals which meets the regulations imposed on industrial sectors. Industrial wastewaters have high concentrations of total dissolved solids, TDS and it has been a difficult task for engineers to remove them from industrial wastewaters [1]. TDS values can exceed 100000 mg/L. Other characteristics such as high values of BOD and TSS are common problems associated with industrial wastewater. BOD values can exceed 200000 mg/L. High amounts of TDS and BOD are associated with different types of industries such as tanning, textile,

milk, cheese, yogurt, buttermilk, distillery, and etc. Food processing industries are one of the major sectors which consume a huge amount of water for their production process; such industries consist of different kinds of production like dairy products, beverages, vegetables and fruits, and meat [2]. Existing wastewater treatment technologies often find it difficult to reduce high BOD and TSS values to meet water quality regulations. There is growing necessity for finding more effective treatment technologies to be used. Adsorption is one such treatment process for different types of water. Removal of organic compounds has been observed using activated carbon, activated alumina, and activated bauxite as adsorbents, and it is one of the technologies in treatment of different water resources or wastewaters which has been frequently used to remove organic pollutants [3]. The objective of this study was to study the effect of using limestone on removal of TDS, BOD, and COD, and to study the effect of using limestone on pH values. Moreover, the objective was to determine the optimum dosage of limestone to obtain optimum TDS and COD removal ratios.

2. METHODS And MATERIALS

2.1. Methods

2.1.1. Adsorption

Industrial wastewater is often contaminated with various compounds such as: phenol, chromium, suspended solids, dissolved organic compounds, high concentrations of dissolved salts and etc. It is imperative to be treated to an environmental acceptable limit. Table 1 shows the characteristics of industrial wastewater.

Table 1. Characteristics of Industrial Wastewater

No.	Wastewater	TDS (mg/L)	BOD₅ (mg/L)	TSS (mg/L)	Ref.
1	Tanning factory	6850	959.66	4200	[4]
2	Textile industry	130450	3900	-	[5]
3	Dairy Industry	-	8239	7175	[6]
4	Cheese Industry	-	3000	1100	[7]
5	Tannery (soaking)	22000-33000	1100-2500	3000-7000	[8]
6	Yogurt and Buttermilk	-	1000	191	[9]
7	Distillery Wastewater	52,000–112,000	36,000–204,000	-	[10]

Adsorption is a fundamental process in the physiochemical treatment of wastewaters, a treatment which can economically meet today's higher effluent standards and water reuse requirements. Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent. The driving force for adsorption process is Surface affinity. Chemical

reactivity, pH, surface area for adsorption per unit volume and reduction in surface tension is key parameter for adsorption.

Adsorption is a sorption operations, in which certain components of a fluid phase, called solutes, are selectively transferred to insoluble, rigid particles suspended in a vessel or packed in a column. Adsorption is a separation process in which certain components of the fluid phase are transferred to the surface of the solid adsorbents. The phenomenon of the enrichment of chemical substances at the surface of a solid is called adsorption. All adsorption performance processes are depends on solid-liquid equilibrium and on mass transfer rates

TYPES OF ADSORPTION:

At molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed.

- Physical adsorption: It is a result of intermolecular forces of attraction between molecules of the adsorbent and adsorbate. Physical adsorption occurs when the intermolecular attractive forces between molecules of a solid and the gas are greater than those between molecules of the gas itself. Furthermore, it occurs lower or close to the critical temperature of the adsorbed substance.

- Chemisorptions: it is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption. Commercial adsorbents rely on physical adsorption; catalysis relies on chemisorptions.

- Chemisorptions occur only as a monolayer and substances chemisorbed on solid surface are hardly removed because of stronger forces.

ADSORPTION DYNAMICS:

It is generally accepted that adsorption dynamics consists of the following consecutive steps:

- Transportation of adsorbate from the bulk solution to external surface of the adsorbent by diffusion through the liquid boundary layer.
- Internal (inter-phase) mass transfer by pore diffusion from the outer surface of the adsorbent to the inner surface the porous structure
- Surface diffusion along the porous surface.
- Adsorption of the adsorbate on the active sites on the internal surface of the pores. [14]

2.1.2. FILTRATION

Wastewater treatment using local available materials such as gravel and charcoal was investigated. The removal of TDS from roughing filters was evaluated for roughing filtration treatment system. Achieved results showed that roughing filters could be considered as a major pre-treatment process for wastewater, since they efficiently separate fine solids particles over prolonged periods without addition of chemicals. Gravel was used as a control medium since it is one of the most commonly used roughing filter. In order to improve the performance of roughing filters, this process can be modified by applying local available material such as charcoal as an alternative filter media. The overall function of the filter in removing parameters such as TDS is accepted using charcoal as an alternative filter media.

2.1.2.1 Types of Filtration Operations

- 1- Cross-flow filtration, in which a septum is responsible for the filtering action (e.g., micro-screens).
- 2-Depth or deep-bed filtration, in which the particles are removed throughout the filter bed or in a significant portion of it, (e.g., sand filters).
- 3- Cake filtration, in which the particles are removed on the surface of a cake formed by the solids accumulating on a septum (e.g., rotary vacuum filters). [15]

2.1.2.2 Classification of Filtration Systems

Filtration systems can be classified according to:

- 1- Type of operation (batch vs. continuous).
- 2- Direction of fluid flow with respect of filter medium (perpendicular vs. parallel)
- 3- Type of filter medium (e.g., screen, deep bed, cake)
- 4- Location within the filter medium where particle deposition occurs.
- 5- Flow rate or pressure control during filtration (e.g., constant pressure drop). [15]

2.2. MATERIALS

Wastewater samples were collected from Port Said pumping station, the influent wastewater to the pilot plant is pumped directly from the wet sump. The Port Said pumping station receives sewage from two sources, municipal wastewater, and industrial wastewater. The industrial input streams come from food and sugar industry, electronics, detergents, metal processing plants and textile industry. Commercially available adsorbent such as limestone powder was used in the experiments.

2.2.1 Limestone as an adsorbent

Limestone is deeply absorbent because of its soft texture. According to Geological Surveys, limestone is very soluble, meaning water dissolves the stone over time. The longer limestone is exposed to the elements, the more porous it becomes. The Great Pyramid in Egypt is partially made of limestone, and recently it is used in wastewater treatment to remove COD, colour, copper, phosphorus and fluoride.

Researchers showed that the major mechanisms for removing P from eutrophic water by constructed wetlands were chemical adsorption and sedimentation by substrates, rather than plant uptake and microbe removal. So, it was very important to select an appropriate substrate material. As calcium ions can form stable and insoluble products with phosphate, calcium-based materials are considered to be one of the potential sorbents for P removal.

Another study showed that LS was one of the ideal substrates for removing P-pollutants from wastewater of low P content such as storm water. The main purpose of this study was to investigate the effect and influencing factors of LS as adsorptive material for P removal, and to establish the parameter for the design of CW using LS as the main substrate when treating effluent from municipal wastewater treatment plant. [16]

2.3 EXPERIMENTAL WORK

A pilot plant was used for this study. It consists of mixing tank ($35 \times 35 \times 60$ cm³ tank made of glass with detention time of one hour) and filtration unit ($35 \times 35 \times 80$ cm³ tank with flow rate = 0.5 m³/m²/hour). Figure 1 shows a sketch of the pilot plant.

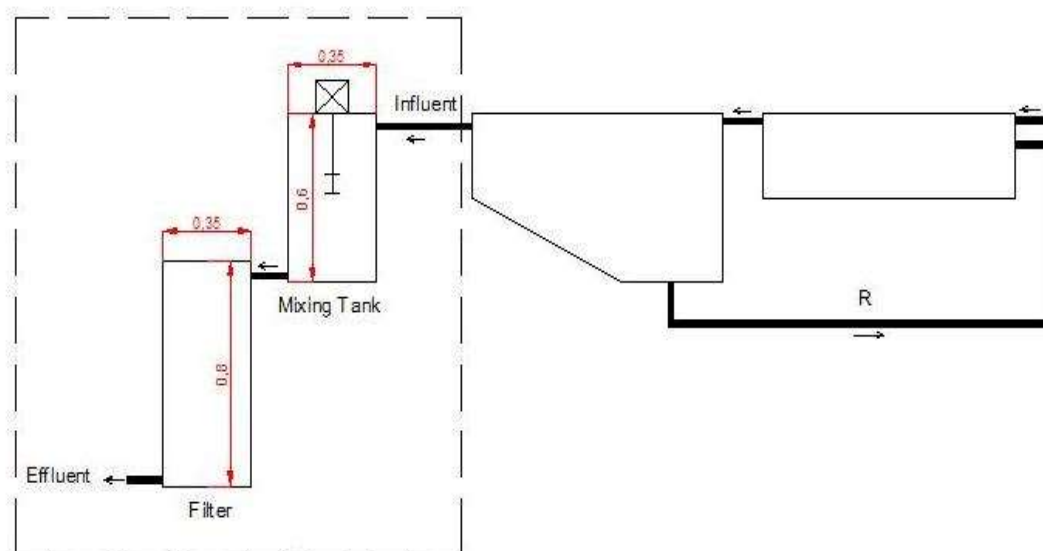


Figure 1 Sketch of the pilot plant.

The dosages of powdered limestone used, in mixing tank, ranged from 4 gm/L to 10 gm/L followed by 1 hour of shaking with speed of 350 rpm. After shaking of the samples they were subjected to analysis. Each dosage was used with adjustment of pH from 6-8 in order to check the effect of pH in TDS removal. 0.1 N of HNO₃ was used as acidic solution to control pH in each run and pH was measured using a standard pH meter in these experiments. After that stage of mixing with adsorbent and adjusting of pH the wastewater goes to the filtration unit.

The experimental work was divided into four groups using limestone (using dosages of 4, 6, 8 and 10 gm/L) each group was carried out in 10 days and samples were collected 3 times each day.

2. RESULTS And DISCUSSION

The observations and the results which were obtained can be summarized as follows: In first group, limestone was added with dosage of 4 gm/L. It reduced the TDS concentration from 132720 mg/L to 20934 mg/L (84.23% removal efficiency). The COD value also was reduced from 3422 mg/L to 873 mg/L (746.75% removal efficiency). TSS removal efficiency was 88.38%.

Table 2. Results of the four groups (average values)

Group	Dosage (gm/l)	Temperature	Q (L/hr)	Average values											
				pH		TDS (mg/L)			TSS (mg/L)			COD (mg/L)			BOD ₅ (mg/L)
				Eff	Inf	Eff	Inf	Eff	η%	Inf	Eff	η%	Inf.	Eff	η%
1	4	26	128	8	12	132720	20934	84.23	773	90	88.38	3422	873	76.75	41
2	6	23	74	9	11	72720	6009	91.74	370	38	89.69	1055	203	82.28	36
3	8	20	72	9	11	114820	12663	89.92	501	94	84.06	2885	826	87.06	39
4	10	19	72	9	10	172350	23324	87.39	752	134	83.83	5647	1451	71.12	42
allowable		35		6~9		<2000 mg/l			<60mg/l			<100mg/l			<60mg/l

Increasing the dosage of powdered limestone (in second group) to 6 gm/L achieved better results in removing TDS and COD. 91.74% of TDS were removed and 82.28% of COD. The efficiency of removing TSS was 89.69%.

More increasing of powdered limestone didn't achieve higher efficiencies in removing TDS or COD, that's what was observed in the third group. Adding 8 gm/L of powdered limestone to each litre of wastewater removed 89.92% of TDS and 78.06% of COD. The efficiency of removing TSS was 84.06%.

Adding 8 gm/L was the chemical dosage used in the fourth group. 87.39%, 83.83% and 71.12% were the efficiencies of TDS, TSS and COD removal respectively.

BOD values of the effluent samples were less than 100 mg/l (i.e. BOD values were within the standard limits).

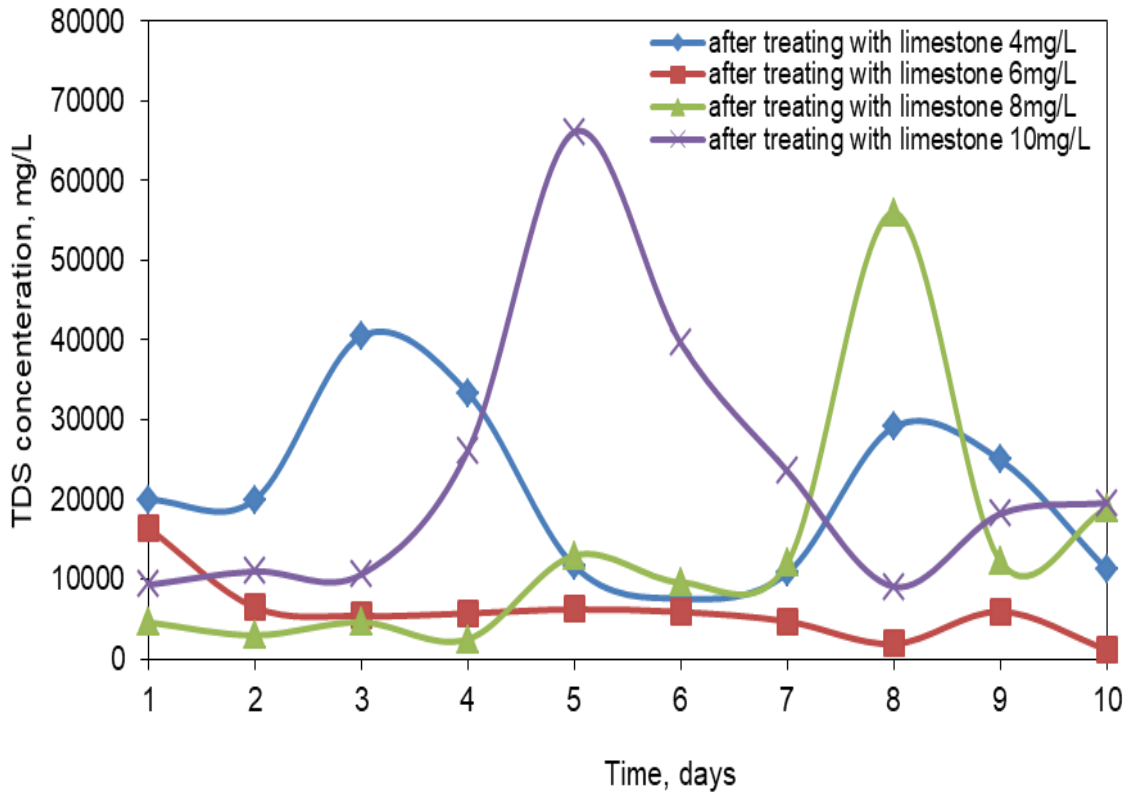


Figure 2 TDS concentrations

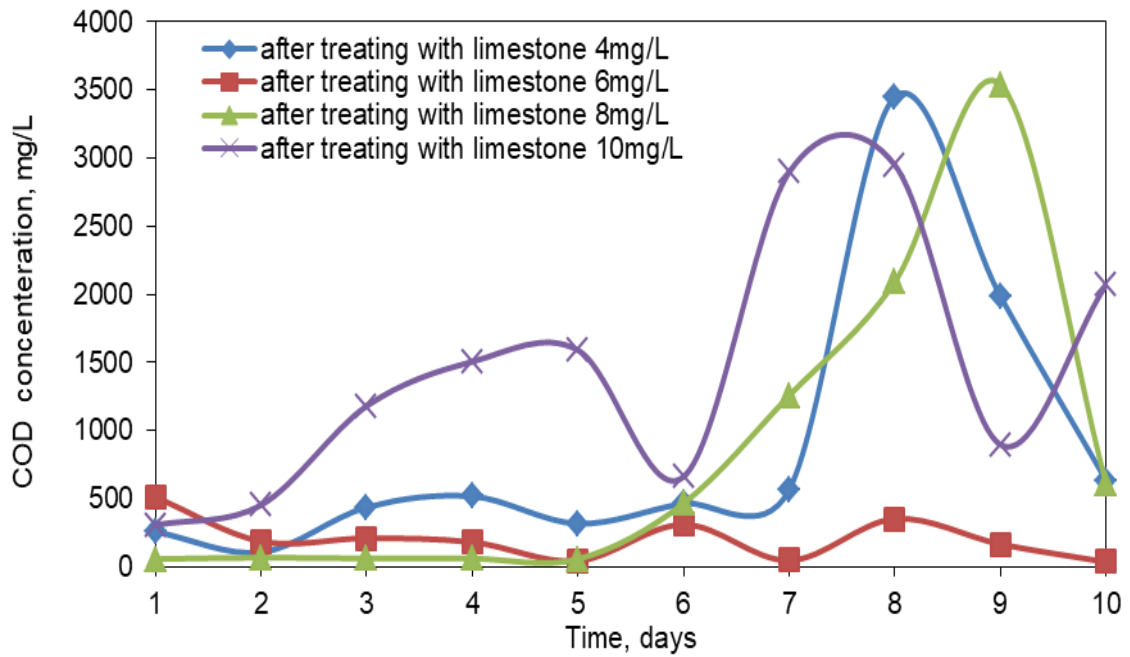


Figure 3 COD concentrations

4. CONCLUSIONS

The most effective dosage in removing TDS was 6 gm/L of limestone. 91.74% of TDS were removed using this dosage, Figure 2.

The highest efficiency of COD removal was observed in the third group (dosage =8 gm/L of limestone end removal efficiency was 87.06%), Figure 3.

The highest efficiency of TSS removal was observed in the second group and equalled 89.69%.

Using limestone raises the alkalinity of the effluent more than activated carbon does.

Based on the observations and the results obtained in this study, the optimum dosage of chemical addition, limestone, was 8 gm of powdered limestone for each litre of wastewater.

It can be stated that the experimental results from the pilot plant are a very good basis for the dimensioning of full-scale plants.

5. REFERENCES

- I.C.A. Basha, P. Ghosh, G2008. Gajalakshmi, "Total dissolved solids removal by electrochemical," *Electrochimica Acta*, vol. 54, pp. 474-483,.
- <http://www.unido.org/>. [Online].
- http://www.unido.org/fileadmin/import/32129_25PollutionfromFoodProcessing.7.pdf
- S. D. Lambert, N. J. D. Graham1995, "Removal of non-specific dissolved organic matter from upland potable water supplies-I.Adsorption," *Wat. Res.*, vol. 29, no. 10, pp. 2421-2426,.
- G.M. Ayoub, A.Hamzeh, L.Semerijan2011, "Post treatment of tannery wastewater using lime/bittern coagulation and activated carbon adsorption," *Desalination*, vol. 273, pp. 359–365,.
- D. H. Ahn, W. S. Chang and T. I. Yoon1999, "dyestuff wastewatertreatment using chemical oxidation, physical adsorption, and fixed bed biofilm process," *Process Biochemistry*, vol. 5, no. 429-439, p. 34,.
- Arbeli, Z. Brenner, A. Abeliovich2006, , "Treatment of high-strength dairy wastewater in an anaerobic deep reservoir: Analysis of the methanogenic fermentation in a moving bed biofilm reactor," *Water sci. Technol*, vol. 45, no. 12, pp. 321-328,.
- O.H. Monroy ,J.P. Guoyot, J.C. Vazquez, F. M. Derramadero1995, "Anaerobic-Aerobic treatment of cheese wastewater with national technology," *Water Sci. Technol*, vol. 32, no. 12, pp. 149-156,.
- J. Raghava Rao, N.K. Chandrababu, C. Muralidharan, Balachandran Unni Nair, P.G. Rao, T. Ramasami 2003 "Recouping the wastewater: a way forward for cleaner leather processing ," *Journal of Cleaner Production*, no. 11, pp. 591–599,.
- Koyuncu, D. Topacik, M. Turan, M. Celik, M. S. Sarikaya2001, "Influence of filtration conditions on the performance of nanofiltration and reverse osmosis membranes in dairy wastewater treatment," *Water Sci. Technol*, no. 1, pp. 117–124,.

- P. Piya-areetham, K. Shenchunthichai, M. Hunsam 2006, "Application of electrooxidation process for treating concentrated wastewater from distillery industry with a voluminous electrode," *Water Research*, vol. 40, pp.2857– 2864,.
- Ullmann's Encyclopedia of Industrial Chemistry Fifth Edition, First International Edition in English by Wolfgang Gehartz.
- Saito Toshihide & Hagiwara Kazuyoshi, *Research survey on adsorbents in wastewater treatment*, (1985).
- Weber WJ (jr) & Smith Eh, *Activated carbon adsorption the state-of-the-art*.(1986)
- Satya Vani Yadla1, V. Sridevi, and M.V.V. Chandana Lakshmi (2012), a Review on Adsorption of Heavy Metals from Aqueous Solution, *Journal of Chemical, Biological and Physical Sciences*.
- *Standard Methods for Examination of Water and Wastewater*, 15th Edition, Washington DC.
- Shan, Q. Chen, C. Yin and C. Hu, *Environ. Sci.*28, 2280 (2007) (translated from Chinese).