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Sulfur Removal from Wastewater and Subsequent Exploitation of the Waste Residue

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Abstract:

Different design parameters can be used to remove the Sulfur contaminant from wastewater by Rice Husk (RH) in adsorption processes. The design parameters studied to adsorb Sulfur using RH as an adsorbent material were the initial concentration of Sulfur, RH absorbance material packing height, pH of the Sulfur feed inlet, treatment time, feed flow rate and feed temperature. The results show that the highest removal efficiency was 95.75 % for Sulfur from an aquatic solution and this efficiency decreased with increasing initial concentration, pH and flow rate while the removal efficiency increased with increasing bed height of the absorbance material and feed temperature. An investigation into the utilisation of the remaining RH by beneficial methods was carried out. One of these methods was conducted by preparing a type of fertiliser for tomato crops. The results showed that the Tomato crop bloomed well and gave a higher weight crop (21 wt%) than tomatoes irrigated with fresh water.

Key words: rice husk, Sulfur, aqueous solutions, adsorption, residue and wastewater

INTRODUCTION

Sulphate is a normal constituent of domestic wastewater and reduced Sulfur compounds are known to be potent inhibitors of plant growth and certain microbial activities [1]. High sulphate wastewaters originate from a number of industrial activities, including pulp and paper manufacture, mineral processing, petrochemical industries and mining activity, i.e., acid mine drainage [2]. Sulphate causes corrosion in the sewers during wastewater discharge, and leads to serious difficulties during on-site anaerobic wastewater treatment, due to the chemical reduction of sulphate to sulphide in various situations, as described below:

1. The production of sulphide is an occupational health and safety issue and a maintenance problem as hydrogen sulphide is a poisonous gas and, when being oxidised to SO_2 and then Sulfuric acid, corrodes concrete and metal structures and gas engines.

2. Sulphide is a wastewater contaminant that influences the amount of BOD, COD and human health [3]. At present, the treatment processes for wastewater containing sulphates, mainly focuses on the removal of sulphate separately. As for sulphate-rich wastewaters, anaerobic biological treatment has been widely used. Under anaerobic conditions, sulphate reducing bacteria (SRB) respire by using sulphate as a terminal electron acceptor at the expense of the oxidation of electron donors. Depending on the strain and species, these SRB can utilise electron donors such as hydrogen, low molecular weight fatty acids and alcohols, and a variety of environmental contaminants to support their metabolism [4]. Therefore, SRB is commonly found in anaerobic processes treating sulphate-rich wastewater [5-6]. The biological sulphate reduction has been recognised as an efficient method for removing sulphate from wastewater. Various aspects of this anaerobic process have been studied [7-8]. When more and more pollutants such as sulphate are discharged together in wastewaters from pharmacy, food, paper making industries and so on, a renewable process that might be capable of simultaneously removing sulphate has received a primary attention [9]. Different strategies have been suggested to control the sulphide

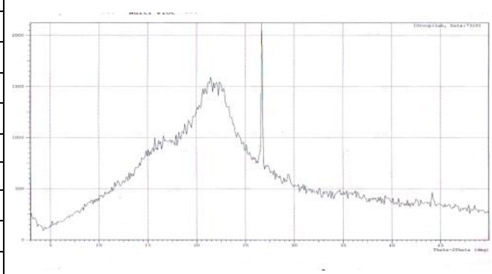
toxicity, including a two-stage treatment with the first stage for sulphate reduction and the second for methanogenesis [10]; sulphide precipitation using iron salts; pH control; use of an anaerobic filter in down flow mode [11] and gas stripping [12]. From these perspectives, a more pragmatic sulphide control technique is needed [10, 13]. Also a high sulphate amount is shown in synthetic seawater [14]. One of the suitable methods for removing sulphate from water and wastewater is by using a surface adsorption process. The aim of this investigation is to study the possibility of using rice husk for removing Sulfur from an aqueous solution, and subsequently benefit from the rice husk residue in an eco-friendly method.

MATERIALS AND METHODS

Rice husk (*adsorbent media*)

Rice husk (RH) was collected from the Al-Shanafia rice fields in the Southern part of Iraq. The rice husk was washed three times with double distilled water. Excess distilled water was used to remove the soluble materials present in the rice husk brought from the field, boiled to remove colour and other fine impurities which may be found in the rice husk, and then dried at 105 °C for 24 hours. The adsorbent thus processed was used in its original piece size. The surface area of RH was measured by BET (Brunauer – Emmett – Teller Sulfur adsorption technique). The characteristics of the RH are presented in **Table 1**. When the RH was heated in an oven, most of the water was removed from the rice husk while the second major mass loss of about 45-65 % was attributed to the breakdown of cellulose constituent char, which is a carbonaceous residue.

Table1: Characterisation properties of Iraqi rice husk

Chemical Composition		XRD of Iraqi Rice Husk
Compound	Composition wt %	
SiO_2	90.7	
Al_2O_3	0.13	
Fe_2O_3	0.06	
TiO_2	0.015	
CaO	0.61	
MgO	0.25	
Na_2O	0.09	
K_2O	2.64	
P_2O_5	0.73	
LOI	4.71	
S.A (m^2/g)	17.5	

Stock solutions

In order to avoid interference with other elements in wastewater, the experiments in this study were carried out using simulated synthetic aqueous solution (SSAS) of different Sulfur concentrations. A 1000 mg/l stock solution of Sulfur was prepared by dissolving a known weight of Na_2SO_4 in one litre of double distilled water. All solutions used in the experiments were prepared by diluting the stock solution with double distilled water to the desired concentration for the experimental work of this investigation. The Sulfur concentrations were measured using spectrophotometer thermo-genesys 10 UV, USA.

Sorption unit

A fixed bed column using continuous mode experiments were conducted in order to test Sulfur removal by treating SSAS containing Sulfur above a desired concentration with the various bed heights of the adsorbent media RH using different flow rates of SSAS containing Sulfur at various pH. The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl solutions. A schematic representation of the sorption unit is shown in **Figure 1** where the flow direction is downward by gravity. The sorption unit consists of two glass containers with an inlet at the top for the SSAS with Sulfur to enter and an outlet at the bottom with a 1 litre capacity. The glass column has 2.54 cm internal diameter (ID) and 150 cm height. The sorption column was packed with adsorbent media to a height of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 cm supported from the top and the bottom by a glass hollow cylinder layer, each cylinder being 0.5 cm ID, 0.1 cm thickness and 1 cm long. Before starting the runs, the packed bed sorption column was rinsed by double distilled water by a down flow through the column.

The RH was packed into the column to the desired depth, and slurry was fed to it by mixing the media RH with distilled water in order to avoid the formation of air bubbles inside the media. After the packed bed sorption column was loaded with the required amount of adsorbent media, the adsorption process was started by allowing the Sulfur SSAS of the required concentration and pH to flow down through the sorption column from the inlet container by gravity at a precise flow rate in an experiment which was adjusted by the valve as shown in **Figure 1**. To determine the best operational conditions, the experiments were carried out at a temperature between 20 to 55 °C, various pH values (1–8) and initial feed concentrations of SSAS of different Sulfur concentrations (1–100) mg/l fed individually and at different flow rates (5–100) ml/min. Outlet samples after treatment in each experiment were collected every 10 minutes from the bottom of the packed column and the unadsorbed concentration of Sulfur in the outflowing SSAS was analysed by spectrophotometer.

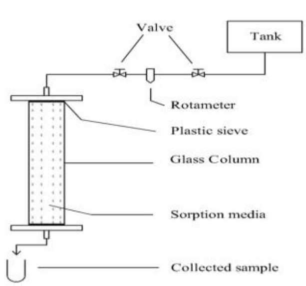


Figure 1: The experimental setup for the adsorption unit

Reusability of rice husk

In order to check the reusability of sorbent media treated RH with different Sulfur concentrations the used RM were firstly dried and tested again in the sorption unit under conditions of the experiment to give the best percentage removal of Sulfur from the aforementioned SSAS. The capacity of the sorbent was found to decrease on repeated use until it became constant at a specific percentage removal after different times of repeated use. The percentage removal and the number of repeated uses were found to be dependent on the Sulfur concentration. It was determined that *eleven times* of sorbent use was seen to be feasible.

RESULTS AND DISCUSSION

The ability of RH to remove Sulfur from SSAS in a fixed bed column of continuous mode was investigated for various parameters such as the pH of the SSAS containing Sulfur (*pH*), height bed of the adsorbent media RH (*h*), flow rates of SSAS (*F*), SSAS temperature (T_{feed}) and time of treatment (*t*). The experiments were undertaken by varying all the above parameters for different initial concentrations (C_o) of SSAS containing Sulfur. The results obtained are explained below.

Effect of Initial Concentration

The results showed that using adsorbent material, the percentage removal of Sulfur decreased when the initial concentration (C_o) of SSAS containing Sulfur increased with the other variables held constant as shown in **Figure 2**. This can be explained by the fact that the initial concentration of Sulfur had a restricting effect on the Sulfur removal capacity. Simultaneously the adsorbent media had a limited number of active sites, which became saturated at a certain concentration.
This led to an increase in the number of Sulfur molecules competing for the available functional groups on the surface of

the adsorbent material. Since a solution of lower concentration has a small amount of Sulfur compared to a solution with a higher concentration, so the percentage removal tended to decrease with increasing initial concentration of Sulfur. For the adsorbent media, the highest percentage removal was 95.75 % for Sulfur at an initial Sulfur concentration of 1 mg/l, so the adsorbent material was found to be efficient for Sulfur removal from SSAS and wastewater.

Effect of pH

The results showed that the percentage removal of Sulfur decreased when the pH of the SSAS containing Sulfur increased with the other variables held constant and using RH as the adsorbent material, as shown in **Figure 3**. This decrease can be explained as follows: The adsorption of Sulfur from SSAS is dependent on the pH of the solution, which affects the surface charge of the adsorbent and the degree of ionisation and speciation of the adsorbate species. This can be attributed to the dependence of Sulfur ionisation on the pH value. In addition, the presence of OH^- ions on the adsorbent prevents the uptake of Sulfur ions. The pH also affects the surface properties of the sorbent i.e. the surface charge of the cells used as a sorbent. At very low pH values, the surface of the sorbent is also surrounded by hydronium ions, which enhance the Sulfur ion interaction with the binding sites of the sorbent by greater attractive forces. Hence its uptake on the polar adsorbent is reduced [7].

Effect of Adsorbent Media Bed Height

The results indicated that when the adsorbent media bed height was increased, the percentage removal of Sulfur increased as well when the other variables were held constant as shown in **Figure 4**. The increase in bed height (h) meant an increase in the amount of adsorbent media RH, thus increasing the surface area of the adsorbent material, hence increasing the number of active sites in the adsorbent material surface i.e. the availability of binding sites for adsorption increases and consequently this increases the Sulfur removal capacity of the RH. This led to increase the ability of the adsorbent media to adsorb a greater amount of Sulfur from the SSAS at different initial concentrations and ultimately the percentage removal of Sulfur increased.

Effect of Flow Rate

The results illustrated that when the flow rate of SSAS containing Sulfur increased, the percentage removal of Sulfur decreased with all the other variables held constant as shown in **Figure 5**. This may be due to the fact that when the flow of SSAS containing Sulfur increased, the velocity of the solution in the column packed with the adsorbent media RH increased as well, so the solution spent a shorter time in the column compared to when a low flow rate was used. With a low flow rate the SSAS containing Sulfur resides in the column for a longer time, and therefore undergoes more treatment with the adsorbent media. Thus with a high flow rate the adsorbent media uptakes a low amount of Sulfur from the SSAS and therefore the percentage removal of Sulfur decreased when the flow rate increased.

Effect of Feed Temperature

The results demonstrated that when the temperature of the feed of the SSAS containing Sulfur increased, the percentage removal of Sulfur also increased with all the other variables held constant as shown in **Figure 6**. The effect of temperature is fairly common and increases the mobility of the acidic ions. Furthermore, increasing temperatures may produce a swelling effect within the internal structure of the adsorbent media enabling Sulfur ions to penetrate further. It is indicated that Sulfur adsorption capacity increased with increasing feed temperature from 5 to 55 °C. This effect may be due to the fact that at higher temperatures an increase in active sites occurs due to bond rupture.

Effect of Treatment Time

The results demonstrated that when the treatment time of SSAS containing Sulfur increased, the percentage removal of Sulfur increased with all the other variables held constant as shown in **Figure 7**. This may be due to the fact that when the time of treatment of SSAS containing Sulfur increased and the velocity of the SSAS in the column packed with the adsorbent material remained constant, the solution spent a longer time in the column than when the time of treatment was decreased. Thus the adsorbent material could uptake a greater amount of Sulfur from the SSAS and therefore the percentage removal of Sulfur from the SSAS increased.

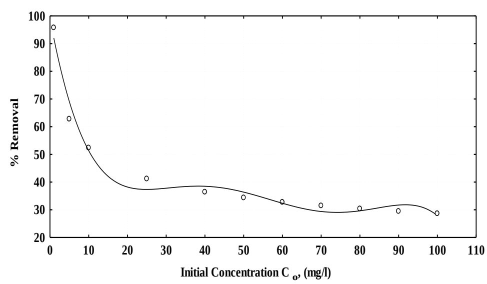


Figure 2: Effect of initial concentration ($C_\circ$) on the percentage removal of Sulfur @ T_f =55 °C, h_b = 1 m, *pH*=1, *t*=60 min. and *F*=5 ml/min.

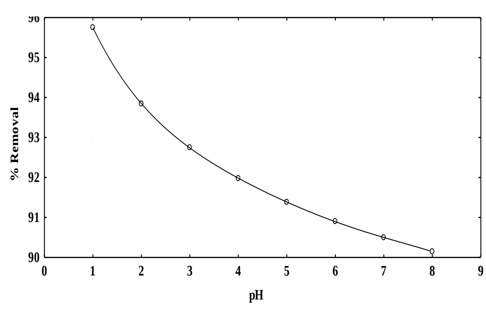


Figure 3: Effect of pH on the percentage removal of Sulfur @ $C_\circ$= 1 mg/l, Tf =55°C, hb = 1 m, t=60 min. and F=5 ml/min.

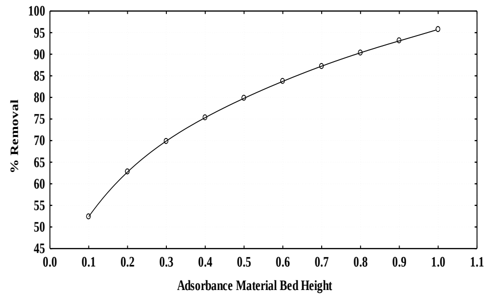


Figure 4: Effect of adsorbent media bed height (hb) on the percentage removal of Sulfur @ $C_{\circ}$= 1 mg/l, pH=1, Tf =55 °C, t=60 min. and F=5 ml/min.

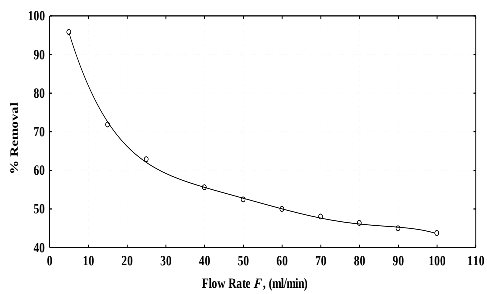


Figure 5: Effect of aqueous solution flow rate (F) on the percentage removal of Sulfur @ $C_{\circ}$= 1 mg/l, pH=1, Tf =55°C, hb = 1 m and t=60 min.

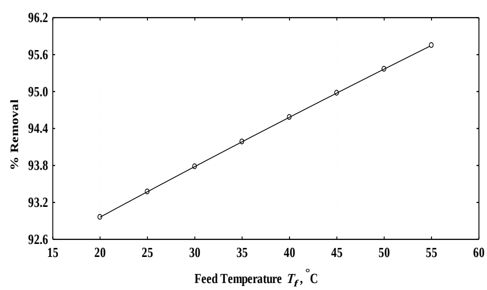


Figure 6: Effect of feed temperature (Tf) on the percentage removal of Sulfur @ $C_{\circ}$= 1 mg/l, pH=1, hb = 1 m, t=60 min. and F=5 ml/mi

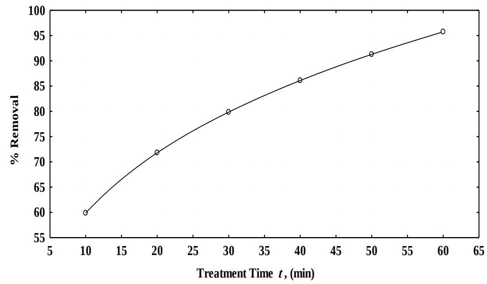


Figure 7: Effect of treatment time (t) on the percentage removal of Sulfur @ $C_{\circ}$= 1 mg/l, Tf =55 °C, pH=1, hb = 1 m, and F=5 ml/min.

Statistical Model

A statistical model was developed based on the experimental results obtained from this study. Regression Analysis and the **π** Theorem were adopted to maintain a relation between the percentage removal of Sulfur and the feed temperature, flow rate, pressure, pH of the feed solution, initial concentration of Sulfur, adsorbent media RH bed height, treatment time and column diameter. These relations are shown in **Equation 1** below, which has a correlation coefficient (R^2) 0.989.

$$\%\boldsymbol{R} = \mathbf{2.3932} \times \mathbf{10^{-6}} \left(\frac{T_f \,.P\,.h_b\,.C_{P_{sol}}\,.t}{F\,.d\,.C_{\circ}\,.g}\right)^{0.262} \left(\frac{1}{pH}\right)^{0.029} \quad \ldots \qquad (1)$$

where:

where:	$\%R$	Percentage Removal of Sulfur from SSAS
	T_f	Feed Temperature, (K)
	P	Pressure, (Pa)
	h_b	Adsorbent Material Bed Height, (m)
	$C_{P_{sol}}$	Heat Capacity of Aqueous Solution, (J/g. K)
	F	Aqueous Solution Flow Rate, (m^3/s)
	d	Internal Diameter of Sorption Column, (m)
	$C_{\circ}$	Initial Concentration of Sulfur , (g/m^3)
	t	Treatment Time, (s)
	g	Acceleration of Gravity, (m/s^2)

Exploitation of used Rice Husk

A huge amount of rice husk remained over after being used for the removal of Sulfur from the SSAS as explained above. Utilisation of this rice husk containing Sulfur can be achieved as follows:

Employment of used rice husk as a fertiliser for tomato crops

Exploitation of the used RH can be achieved by employing it as a fertiliser for tomato crops as follows: RH waste which has previously adsorbed Sulfur from SSAS under different operating conditions was segregated and classified according to its Sulfur content and utilised as a raw material in the synthesis of a fertiliser for tomato crops. The samples had different ratios of Sulfur to RH namely between 0.01 to 0.1 wt % for Sulfur. RH containing different Sulfur ratios was firstly crushed to make powder, the powder completely dissolved in water and the resulting solution used to irrigate the tomato crop. The tomato crop results showed good blooms and gave a higher weight crop (21 wt%) than tomatoes irrigated with fresh water.

It is known that Sulfur tends to increase the yield of crops, vegetables and fruits, produces superior turf, with healthy and deep roots. It enhances the uptake of fertilisers, creates vegetation in saline and poor soils, and promotes ecological balance. This is achieved by enhancing the soil structure and fertility through the addition of vital organic matter in the soil, by the efficient transfer of fertiliser nutrients and micronutrients because of the high chelation and cation exchange proportion of the active Sulfur component, increasing the moisture holding capacity of the soil, increasing microbial activity in the soil and enhancing the plant cell biomass.

Sulfur affects plant growth in different ways. It can affect physically through increasing the water holding capacity, increasing the aeration of soils, improving soil workability, helping resist drought, improving the seed bed, making the soil more friable or crumbly and reducing soil erosion. It can affect chemically by chelating nutrients for uptake by plants, possessing a high ion-exchange capacity, increasing the buffering properties of soils, and increasing the percentage of total Sulfur in soils. Lastly, Sulfur can affect biologically through accelerating plant cell division and promoting growth, increasing germination of seeds and viability, increasing root respiration and formation, stimulating growth and the proliferation of soil microorganisms, and aiding in photosynthesis.

Sulfur is a fungicide that can be used on tomato plants according to the Utah State University Extension. It is a useful preventative for diseases and some pest problems to which tomatoes are susceptible. Alternaria leaf spot - also known as early blight - and powdery mildew are the two fungal diseases that can be treated with Sulfur. Certain pest infestations can also be treated with Sulfur. Sulfur protects new growth from further damage by pests or diseases but should not be applied until a symptom or pest presents itself.

Employment of used rice husk in electric generation as a low value material

In many agricultural countries which are producers of rice, such as Thailand, Malaysia, Sri Lanka and others, residual rice husk is often used in the generation of electrical energy. Hence, it is possible to use rice husk to remove Sulfur from wastewater before being used in the production of electrical power and thus two benefits can be achieved from the use of the rice husks and thus contributes to reducing the use of fossil fuels and preserving the environment in a more convenient and economical way by getting rid of two pollutants by one material.

CONCLUSION

The following conclusions can be drawn:

1. RH has shown good ability to remove Sulfur from SSAS using a fixed bed adsorption unit. Thus, it can be recommended for removal of Sulfur from wastewater in Iraq instead of using other material because it is valid, cheaper, economical, easy and simple to use. It has a

high ability to adsorb Sulfur and can be used several times instead of applying a costly regeneration method. Finally the residue can be used yet again to receive further benefit.

2. The maximum removal of Sulfur was 95.75 % at an initial Sulfur concentration of 1 mg/l.
3. The percentage removal of Sulfur increased with decreasing flow rate of SSAS, pH and initial concentration of Sulfur while the percentage removal increased with increasing treatment time and the height of the adsorbent material RH.
4. The RH residue that has previously adsorbed Sulfur from SSAS can be prepared as a good fertiliser for tomato crops. Thus the polluted waste can be removed by an economic and eco-friendly method.
5. The RH can be used for generating electric power after it has been used to remove the Sulfur from wastewater. Thus two pollutants are removed by one material in an economic and eco-friendly method.

REFERENCES:

(1) A. Wiessner, U. Kappelmeyer, P. Kuschk, M. Kästner, Sulphate reduction and the removal of carbon and ammonia in a laboratory-scale constructed wetland, *Water Research*, 39 (2005) 4643-4650.

(2) A. N. Knobel, A. E. Lewis, A mathematical model of a high sulphate wastewater anaerobic treatment system, Water Research, 36 (2002) 257-265.

(3) S. Tait, W.P. Clarke, J. Keller, D.J. Batstone, Removal of sulfate from high-strength wastewater by crystallisation, Water Research, 43 (2009) 762-772.

(4) S.N. Medírcio, V.A. Leão, M.C. Teixeira, Specific growth rate of sulfate reducing bacteria in the presence of manganese and cadmium, Journal of Hazardous Materials, 143 (2007) 593-596.

(5) P. N. L. Lens, A. Visser, A. J. H. Janssen, L.W. Hulshoff Pol & G. Lettinga, Biotechnological Treatment of Sulfate-Rich Wastewaters, Critical Reviews in Environmental Science and Technology, 28 (1998) 41-88.

(6) B.M. Tebo, A.Y. Obraztsova, Sulfate-reducing bacterium grows with Cr(VI), U(VI), Mn(IV), and Fe(III) as electron acceptors, FEMS Microbiology Letters, 162 (1998) 193-198.

(7) L.W. Hulshoff Pol, P.N.L. Lens, A.J.M. Stams, G. Lettinga, Anaerobic treatment of sulphate-rich wastewaters, Biodegradation, 9 (1998) 213-224.

(8) S. Nagpal, S. Chuichulcherm, A. Livingston, L. Peeva, Ethanol utilization by sulfate-reducing bacteria: An experimental and modeling study, Biotechnology and Bioengineering, 70 (2000) 533-543.

(9) F. Fdz-Polanco, M. Fdz-Polanco, N. Fernandez, M.A. Urueña, P.A. Garcia, S. Villaverde, New process for simultaneous removal of nitrogen and sulfur under anaerobic conditions, *Water Research*, 35 (2001) 1111-1114.

(10) S.K. Khanal, J.-C. Huang, ORP-based oxygenation for sulfide control in anaerobic treatment of high-sulfate wastewater, *Water Research*, 37 (2003) 2053-2062.

(11) L.B. Moody, D.R. Raman, SE--Structures and Environment: A Dual-reactor Anaerobic System for Complete Treatment of a Food Processing Waste, *Journal of Agricultural Engineering Research*, 80 (2001) 293-299.

(12) D. H. ZITOMER and J. D. SHROUT High-Sulfate, High-Chemical Oxygen Demand Wastewater Treatment Using Aerated Methanogenic Fluidized Beds, *Water Environment Research*, 72 (2000) 90-97.

(13) B. Sharifzadeh, B. Vahid, and P. Faeqeh, "Preparation of Polyaniline Nanocomposites for Removal of Sulfate from Wastewater", *2011 2nd International Conference on Chemistry*

and Chemical Engineering, *IPCBEE vol.14 (2011)*, *(2011) IACSIT Press, Singapore*.

(14) L. Zhu, C. B. Granda and M. T. Holtzapple, Prevention of calcium sulfate formation in seawater desalination by ion exchange, Desalination and Water Treatment 36 (2011) 57–64