

Full Length Research Paper

Wastewater COD removal using sol-gel immobilized humic acid

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In this study, humic acid which contains both hydrophobic and hydrophilic moieties is successfully entrapped in sol-gel matrix which is used to reduce the chemical oxygen demand (COD) of Gaza wastewater. The method was very efficient in which more than 90% reduction of the COD had been achieved, it was found that contact time with the matrix, temperature, pH, particles size, adsorbent dose, and agitation speed effect the COD reduction.

Key words: Wastewater, humic acid, COD, sol-gel.

INTRODUCTION

Pollution of water by organic and inorganic chemicals is of serious environmental concern. The organic content of wastewater is traditionally measured using lumped parameters such as biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS). These parameters as such do not show any chemical identity of organic matter. In recent years, increasing awareness of the environmental impact of COD has prompted a demand for the purification of wastewaters prior to discharge into natural waters (Emmanuel, 2008).

This has led to the introduction of a number of conventional treatment technologies have been considered for treatment of wastewater contaminated with organic substances. Among them, adsorption process is found to be the most effective method. Adsorption as a wastewater treatment process has aroused considerable interest during recent years. Commercial activated carbon is regarded as an effective material for controlling the organic load (Badmus, 2007).

Granular activated carbon was utilized to reduce COD in which about 60% reductions was accomplished

(Suntud, 1999).

Clay was used to reduce COD in wastewater and an efficiency of 50% was achieved (Didik, 2007).

It was concluded that combination of ozone with hydrogen peroxide reduces the COD of wastewater by 70% using a dose of 1:1 mol ratio O_3/H_2O_2 (Tünay, 2006).

Sol-gel was used as an inert matrix to immobilize various humic acids (HAs), and then used to study the interactions of several polycyclic aromatic hydrocarbons (PAHs) with the entrapped HA (Armon et al., 2000).

In this study the sol-gel immobilize humic acid will be used as adsorption matrix to reduce the chemical oxygen demand in Gaza sewage water.

Humic substances are natural complexed mixtures of organic compounds originated from the decomposition of plant and animal residues. These compounds are ubiquitous in soils, sediments, surface waters and groundwater. They contain both hydrophobic and hydrophilic moieties, able to interact with hydrophobic organic contaminants and with heavy metals. These sorption interactions play a crucial role in contaminants fate and transport and sol-gel glasses are formed at room temperature *via* the polymerization of molecular precursors such as metal alkoxides. Proteins can be added to the solution of precursors. Hydrolysis and condensation then lead to the formation of an oxide network in which biomolecules remain trapped. Small analytes can diffuse through the pores allowing bioreactions to be performed inside the sol-gel glass.

Trapped enzymes still retain their biocatalytic activity

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Abbreviations: COD, Chemical oxygen demand; TSS, total suspended solids; BOD, biological oxygen demand; HAs, humic acids.

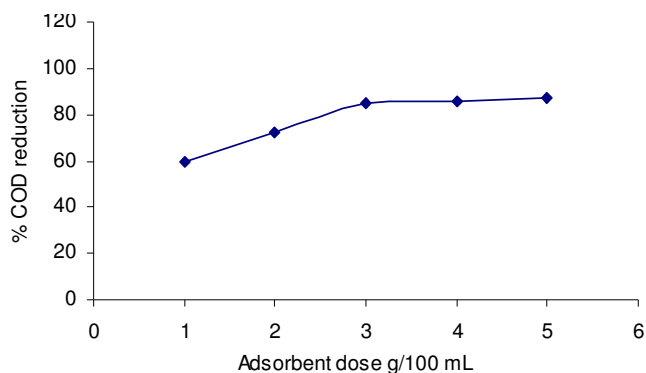


Figure 1. Effect of adsorbent dose on the % COD reduction. At room temperature, at pH 7.0 and after 4 h.

and may even be stabilized within the sol-gel cage. A wide range of biological species such as antibodies and whole cells have been trapped within sol-gel matrices. They usually retain their activity but weak interactions with the silica cage actually occur that can change their behavior (Weetall, 1985; Dave, 1994).

METHODOLOGY

Humic acid and tetraethoxysilane (TEOS) were obtained from Acros Belgium. Wastewater samples were collected from the effluent of Gaza wastewater treatment unit. Samples were stored at temperature below 4°C to avoid any change in the physic-chemical characteristics. The COD of the samples were estimated before and after adsorption COD was measured according the standard method (Standard methods, 1980).

Preparation of sol stock solution

Using 20 ml pipette, 13.5 ml of TEOS were transferred into 50.0 ml glass vial followed by addition of 4.2 ml of 10^{-4} M HCl. The vial was firmly corked and stirred by means of magnetic stirrer for three hours. A homogeneous sol, due to partial hydrolysis of TEOS was obtained. This was stored in a desiccator for further use (Helles, 2008).

Humic acid entrapment system

A 10 ml portion of phosphate buffer, pH 5.0, containing 20% (w/v) humic acid was mixed with 10 ml TEOS sol in 50 ml glass vial. The mixture was shaken gently in which a gel of homogeneously entrapped humic acid was formed in about 3 - 5 min. The gel was allowed to dry for three weeks. A monolith containing entrapped humic acid resulted which was powdered, washed several times with small portions, 50 ml each, of 1 M sodium chloride. Followed by washing three times with plenty of distilled water. Finally the entrapped HA was left in the desired buffer for equilibration before use for one hour, and left to dry for a week at room temperature (Helles, 2008).

Adsorption studies

All the experiments were carried out at room temperature in batch

mode. Batch mode was selected because of its relative simplicity. The batch experiments were run in different glass flask of 200 ml capacity using average speed shaker. Prior to each experiment, a predetermined amount of adsorbent was added to each flask. The stirring was kept constant for each run throughout the experiment ensuring equal mixing. The desired pH was maintained using dilute 0.10 M NaOH/ 0.10 M HCl solutions. Each flask was filled with a 100 ml of sewage water sample having desired pH. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered through whatmann No. 44 filter paper.

Experimental conditions

Study for contact time

These studies were conducted by agitating 100 ml sample with initial COD concentration 1350 ppm, a known amount of sol-gel immobilized humic as an adsorbent was agitated different time period, 30 - 300 min. After the predetermined time intervals, the sample were withdrawn, filtered and determined the residual COD concentration.

Study for pH

pH effect was performed taking a specific concentration, adsorbent dose, and contact time and varying the pH values from 1 - 12 using 0.10 M NaOH/ 0.10 M HCl solutions. The samples were agitated for specific time, filtered and then analyzed for the residual COD concentration.

Study for adsorbent dose: the studies were carried out by varying the amount of adsorbent. A 100 ml of the sample was treated with different doses of sol-gel immobilized humic acid, 1.0 - 4.0 g/100 ml. The samples were agitated for 240 min., filtered and then analyzed for the residual COD.

Study for initial COD concentration

This study were performed by keeping all the conditions constant except changing the initial COD concentration by diluting the waste water sample to obtain samples with initial COD concentration ranging from 200 - 1100 ppm. Studies for agitation time were: performed by varying agitation speed from 100 rpm to 400 rpm and keeping all conditions constant. Finally the samples were analyzed for residual COD concentration. Similarly, studies for adsorbent particle size were performed by keeping all conditions constant and varying the particle size. The residual COD concentration was determined after each run. The removal of COD was quoted (as %) relative to the values measured for the untreated effluent.

The results obtained are an average of three replicates and relative standard deviation ranged from 3.0 - 5.5 was observed.

RESULTS AND DISCUSSION

Figure 1 represents the effect of adsorbent dose on the percent COD reduction by sol-gel immobilized humic acid. It was observed that maximum removal occurs at a dose of 4 g/100 ml. The results showed the tremendous increase in percent COD removal with the increment of adsorbent dose, owing to the increase in the number of sites (Mancy, 1964). At lower doses, the significant small adsorption is possibly due to the saturation of surface active sites with the adsorbate molecules.

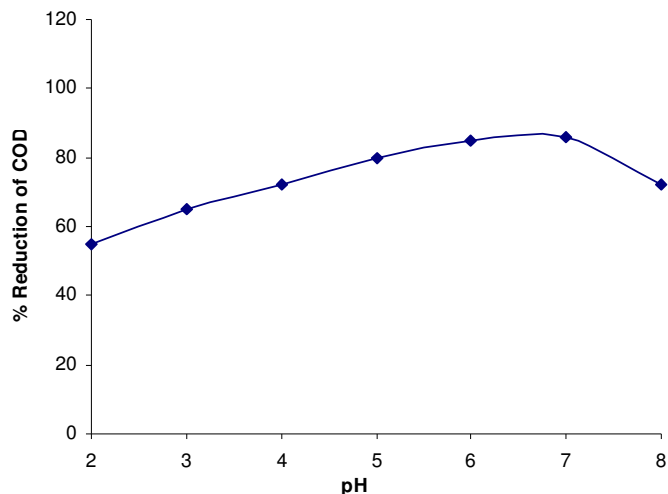


Figure 2. Effect of pH on % COD reduction by sol-gel immobilized humic acid at adsorbent dose 4 g/100 ml, at room temperature and after 4 h.

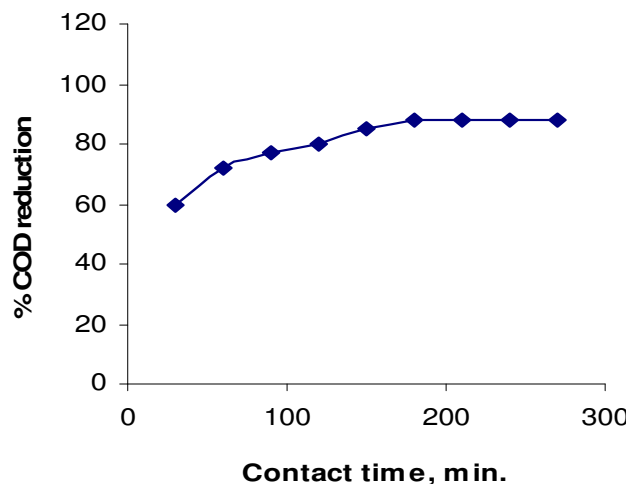


Figure 4. Effect of contact time on % COD reduction at room temperature, pH 7.0, adsorbent dose 4 g/100, after 4 h.

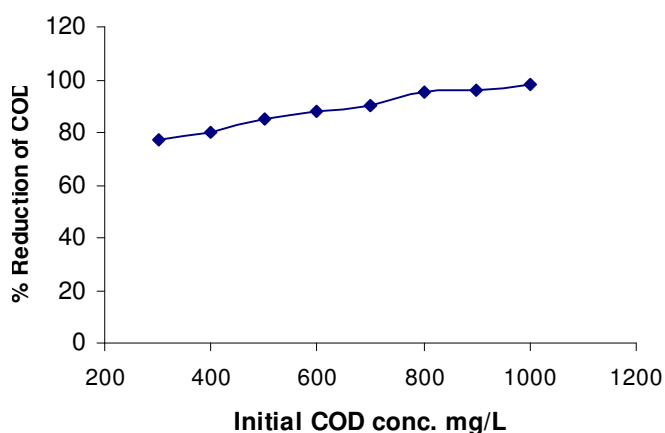


Figure 3. Effect of initial concentration %COD reduction at room temperature, pH 7.0 adsorbent dose 4 g/100 ml and after 4 h.

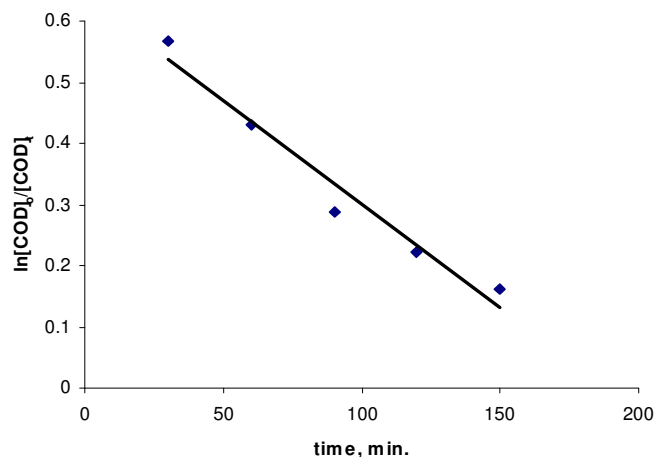


Figure 5. Adsorption order study of organic matter by sol-gel immobilized humic acid at room temperature, at pH 7.0 and after 4 h.

Figure 2 depicts the effect of pH on percent COD reduction sol-gel immobilized humic acid. The runs were taken at constant initial COD concentration, adsorbent dose and the contact time. The results indicate that at all pH levels below 6.0, the sol-gel immobilized humic has consistently lower adsorption capacity for COD this could be due to deprotonation of carboxylic groups on humic acid which enhances the adsorption capacity of the matrix. Higher pH values were not examined due to instability of the matrix in highly basic medium.

Figure 3 represents the effect of initial COD conc. on % COD reduction by sol-gel immobilized humic acid at the optimum pH, adsorbent dose and after three hours contact time as predicted from the figure at lower initial concentration the ratio of initial number of moles of organic species available for adsorption to the adsorbent surface area is low and subsequently the fractional

adsorption becomes independent of initial concentration. At higher concentrations, the available sites of adsorption become fewer and hence the % removal of COD depends upon the initial concentration.

Figure 4 represents the percent removal of COD for different contact time by sol-gel immobilized humic acid. It seems that COD removal had been achieved to an extent of more than 90% by sol-gel immobilized humic acid at a maximum time period of 250 minutes, it has been seen that equilibrium attained in 250 minutes. The smooth and independent nature of curve indicates formation of monolayer cover of the adsorbate on the outer surface of the adsorbent. The adsorption process for the studied adsorbent follows first order kinetics and Freundlich adsorption pattern.

Figure 5 represents plotting of $\ln[\text{COD}]_0 / \ln[\text{COD}]_t$

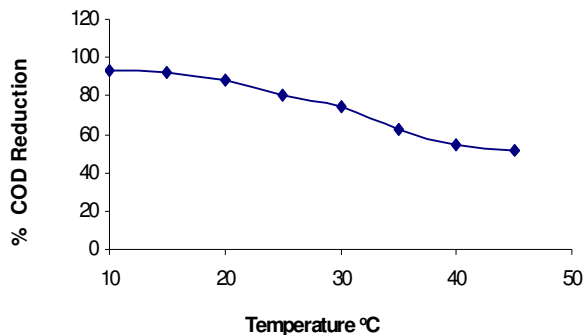


Figure 6. Effect of temperature on the % COD reduction by immobilized humic acid.

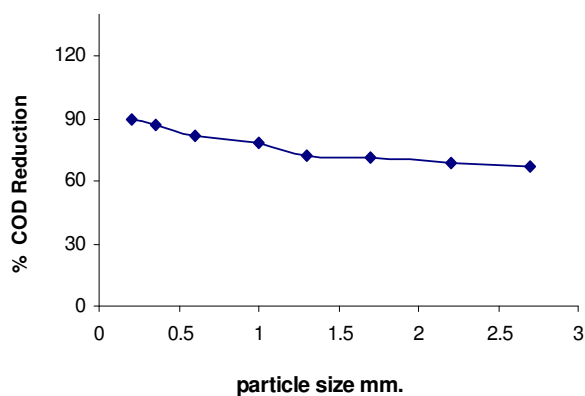


Figure 7. Effect of particle size on COD % reduction by immobilized humic acid, at pH 7.0 adsorbent dose 4 g/l and after 4h.

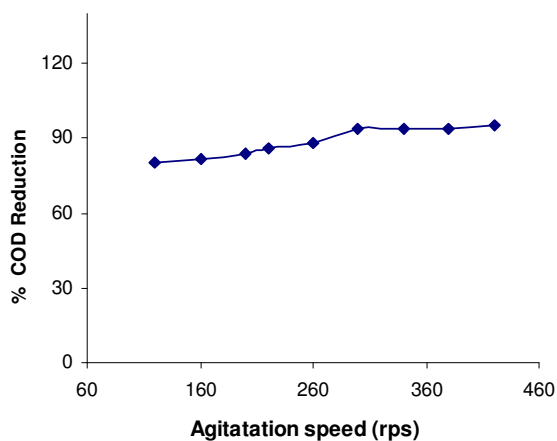


Figure 8. Effect of agitation speed on COD % reduction by immobilized humic acid, at pH 7.0, at room temperature, adsorbent dose 4 g/l and after 4h.

against time gives straight line which confirm that the adsorption rate is first order.

The effect of temperature on the % reduction in COD by sol-gel immobilized is illustrated in Figure 6 at optimum condition of pH, contact time, adsorbent dose

and initial COD concentration as shown from the figure increasing temperature decreasing the percentage reduction in COD that is; at 10°C 92% removal of COD was observed, while only 52% reduction in COD was obtained at 45°C suggesting a physical adsorption on the surface of immobilized humic acid (Figure 6).

Figure 7 represents the effect of particle size on % COD reduction. It was observed that the extent of adsorption decreased with increasing particle size.

However, the surface area per unit mass of adsorbent as well as diffusional transport might be larger in case of smaller particles, which increases the adsorption rate.

Figure 8 represents the effect of agitation speed on the % reduction in COD; the agitation speed was varied from 100 - 420 rps.

The results indicate that there is a definite improvement in the extent of adsorption with increasing the speed of agitation and then equilibrium was set up after 300 rpm.

Conclusion

It is revealed from the studies that the treatment of domestic wastewater by sol-gel immobilized humic acid can be utilized with good performance and at optimum conditions the 90 % reduction of COD can be achieved which open a new process to reduce the organic load of wastewater.

REFERENCES

- Armon R, Zolkov CH, Laor Y (2000). Immobilizing humic acid in a sol-gel matrix: a new tool to study humic-contaminants sorption interactions. *J. Sol-Gel Sci. Technol.* 19: 95-100.
- Badmus MAO, Audu TOK, Anyata BU (2007). Removal of Copper from Industrial Wastewaters by Activated Carbon Prepared from Periwinkle Shells. *Korean J. Chem. Eng.* 24: 246-252.
- Dave B, Dunn B, Valrntine, Zink J (1994). Synthesis of sol-gel encapsulated heme proteins with chemical sensing properties, *Anal. Chem.* 66(22): 1120-112.
- Didik S, Sarowko M (2007). Cement and Clay Treatment for Organic Matter Containing Leachate *World Appl. Sci. J.* 2(4); 387-389.
- Emmanuel O. Aluyor, Olalekan AM (2008). Badmus COD removal from industrial wastewater using activated carbon prepared from animal horns *Afr. J. Biotechnol.* 7(21): 3887-3891.
- Helles R, Salem, Ramadan K, Shaheen, Issa M, Nejem C (2008). Chromium and mercury uptake by sol-gel immobilized humic acid *Environmental Science : An Indian J.* 3(3).
- Mancy KH, Gates WE, Eye JD, Deb PK (1964). Adsorption kinetics of ABS on fly ash. In *Proc. 19th Ind. Waste conference, D.E. bloodgood, Ed. Published by purdue university, W. Lafayette, Indiana pp.* 146-160.
- Standard methods (1980). *Standard methods for Examination of Water and Wastewater (15th edn.) Oxygen Demand (Chemical) Method 508-A.* APHA,AWWA and WPCF, Wahington DC.
- Suntud S, Soydoa V, Warea C (1999). Removal of Organic Matters and PhenolCompounds from the Waste Water by Using Granular Activated Carbon Sequence Batch Reactor System, *Thammasatln t.J. Sci. Tech.* 4(1).
- Tünay O, Berker Y, Ölmez T, Kabdasli I (2006). Residual COD reduction in biologically treated leather tanning effluents by advanced treatment processes *American Leather Chemists Association* 101: 123-131.
- Weetall H (1985). *Enzymes and Cells Confined in Silica Nanopores Trends in Biotechnol.* 3: 276.