

**Evaluation and chemical treatment of organic pollution discharged into the River Nile:
Case Study**

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ABSTRACT

The present study deals with the evaluation of the organic pollution by determination of COD in the effluents discharged from Egyptian Sugar and Integrated Industries Company (ESIIC) into the River Nile without any treatment. Then, how we can treat the organic pollution? through the decrease in COD value by use (AC) Activated Carbon, H₂O₂, UV and UV/H₂O₂ effects. The obtained results revealed that the concentration value of COD 36294 mg/l in waste water of ESIIC. The efficiency of (AC), H₂O₂, UV exposure and UV/H₂O₂ are weak in the removal of organic pollution, however the COD values 34843, 33375, 33999 and 16000 mg/l after treatment. The recommended procedure for the removal of organic pollution using (AC) in the first step then UV/H₂O₂ in the second step however the COD value reached to 980 mg/l after treatment.

Keywords: Chemical treatment, organic pollution, River Nile.

INTRODUCTION

Environmental pollution problems are considered the most serious problems that face mankind in the 20th century. It is also, one of the most serious national problems which require great effects at all levels: industrial group, national and international (Marjonoric, 1990). This is especially true with respect to River Nile pollution because it serve as recipient of urban, rural and industrial waste water which contain frequently, hazards contaminants in high concentration (Abdo, 2002).

About 120 industrial activities and gas filling stations occupy nearly 1% of the total Cairo land and are diffusely located throughout the region (Platenburg *et al.*, 1997). The major industries estimating in the region can be classified as shown in Table (1).

Table 1: Types of industries exists in the greater Cairo

No. of factories	Type
23	Chemical industries
27	Textile and Spinning
7	Metals
32	Food Industries
29	Engineering
9	Mining

According to Helwan Waste Water Master Plan (1978), the industrial waste water discharge from Helwan (except El-Badrasheen area) amounts to about 41,314,000 cubic meter per annum. Shoubra El-Kheima area represents one of the highest concentrations of industry in Egypt. The industrial activities include metal production, food processing, detergents and soap manufacturing, textile finishing and paper pulp. Moreover, the electrical power plants use the River Nile water in cooling processes and recoiling water discharged into the Nile causing thermal pollution (Abdo, 2002).

The discharged industrial waste water of 350 industries into the River Nile created numbers of new conditions which are noticed by comparing the pictures upstream and downstream the waste water discharge (El-Sharkawy, 2010).

Many treatment processes, such as chemical precipitation, evaporation, ion exchange, adsorption, electro dialysis and reverse osmosis, are currently used (El-Sharkawy, 2010). Among these methods, adsorption is promising and widely applied method due to its, low cost and effectiveness. Activated carbon is one of the most popular adsorbents for the removal of metals and organic pollutants from aqueous solutions (Abdo *et al.*, 2010). Through the world other material have been used for the production of activated carbon such as Peanut skin, melon seed ,husks, stream, onionskin, tea leaves, line seed fiber and some other agriculture by-products (El-Sharkawy, 2010).

The objective of the present study is studying the factors affecting the uptake of organic pollutants from ESIIC waste water samples using activated carbon developed from locally available materials e.g. Rice straw by one-step steam pyrolysis, followed by advanced oxidation using H₂O₂/UV for removal of organic pollutant through the decrease in Chemical Oxygen Demand (COD) values.

MATERIALS AND METHODS

Historical background of the area under investigation:

According to EAAA (2009), Egyptian Sugar and Integrated Industries Company "ESIIC" is one of the affiliated companies of food industries holding companies. ESIIC has 8 sugar factories that crush annually over 10million tons of cane producing more than 1 million ton of white cane and refined sugar and 450,000 ton of molasses as by-products. The cultivated cane area reaches 325,000 feddans throughout all Upper Egypt governorates, mainly concentrated in El- Minya, Souhag, Qena and Aswan. Approximately 45% of the molasses are manufactured by ESIIC to useful bio-products in biochemical factories belonging to ESIIC; Hawamdia Dsitillery Factory (HDF), Hawamdia Chemical Factory (HCF) and Abu Korkas Distillery Factory (AKFD). Molasses, the main raw material for biological products, contain sugars, minerals and organic non-sugar compounds. The sugars in molasses are fermented in different processes to ethyl alcohol, yeast, acetone, butanol and CO₂ products. After separating these products in pure form, the waste residuals are collectively called Vinasse. The Vinass liquor (VL) causes a serious polluting problem, due to its high hydraulic, biological, mineral loads, high temperature degrees and violating brown color. The daily average volume of Vinasse all over the year is 2550 ton. Violating parameters of Vinasse liquor: Color: dark brown, BOD: 22000mg/l, COD: 44400 mg/l and ash (on dry materials): 13000mg/l.

Vinasse has serious impact on water quality of the River Nile, resource consumption and worker safety if not environmentally managed. As world wide experience has shown in adequate consideration of the environmental impact of alcohol production can lead damage. On the other hand, the major progress has been made by the industry in last four decades, and modern technologies for the treatment of effluents have greatly reduced their volume and impact. Great awareness about the importance of environmental risk management was based upon the economic development, health and quality of life, using the (4R) technical package (Reduce-Reuse-Recovery).

Sampling program:

Sub surface water samples were collected during four sampling campaigns at three sites of ESIIC along the River Nile. The three sites (I, II and III) are:

I: From the River Nile before 2 km of ESIIC (upstream).

II: Discharged point of ESIIC waste water into the River Nile.

III: The next site after the ESIIC discharged into the River Nile (downstream).

Water analysis:**Field measurements:**

The electrical conductivity (EC) of water sample ($\mu\text{S}/\text{cm}$), temperature ($^{\circ}\text{C}$), and pH values were measured in the field using Hydrolab, Model "Multi 340I/SET". Alkalinity CO_3^{2-} and HCO_3^- were measured titrimetrically on spot, where samples were titrated against standard H_2SO_4 (0.025 N) using phenol phthalin and methyl orange indicators. Also, dissolved oxygen (DO) content was determined by Azide modification method as specified in APHA (2008).

Laboratory measurements:

Water samples were analyzed for all selected variables according to procedures specified in the standard method of American Public Health Association APHA (2008). Total solid (TS) was measured by evaporating a known volume of well mixed sample at 105°C . Chemical oxygen demand (COD) was performed by refluxing flask and $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation and Biochemical oxygen demand (BOD) by 5 days incubation method. Cl^- was determined by argenometric method and SO_4^{2-} by turbidity method. Na^+ and K^+ were measured directly using flame photometer Model "Jenway PFP, UK". Ca^{+2} and Mg^{+2} were determined by EDTA titrimetric method. Concentrations of NO_2^- , NO_3^- , NH_3 , Orthophosphate (ortho-P) and reactive silicate in water were determined using the colorimetric techniques with formation of reddish purpleazo-dye, Cd-reduction, Phenate, stannous chloride reduction and molybdo silicate method, respectively. Total Phosphorous (total-P) was measured as reactive phosphate after ammonium persulphate digestion technique.

Preparation of the active carbon from rice straw:**One- step steam pyrolysis of rice straw:**

The fluidized bed reactor was heated until the bed temperature reach to 150°C . 0.5 Kg of dried rice straw was injected into the reactor and subjected to heating rate of $150^{\circ}\text{C}/10\text{min}$ under inert environment of nitrogen. The flow rate of nitrogen used was sufficient to provide good mixing of the rice straw within the reactor (300ml/min). When the temperature of the furnace reach to 350°C , the steam produced by steam generator entered the reactor at a rate of approximately $5\text{cm}^3/\text{min}$ and at this temperature heating was continue up to final temperature of 750°C , holds at this temperature for one hour. After the treatment, the sample was left to cool down and the steam flow is interrupted at temperature $250\text{-}300^{\circ}\text{C}$, then the sample was drown from the reactor and weighed. This gives adsorbent two, C-2 (EL-Sharkawy, 2001).

Removal of organic pollutants from ESIIC waste water:

The target was to removal of organic pollutants and to achieve the permissible levels of COD in ESIIC effluent using adsorbent C-2. In this concern, four trials were applied:

- 1- Effect of adsorbent mass (C-2)
- 2- Effect of H_2O_2
- 3- Using UV exposure
- 4- Using UV/ H_2O_2

A Hewlett Pack'rd Diode array spectrophotometer (Model 8451 A) was used to measure the UV/Vis absorbance for raw and treated water samples. A micro-processor pH meter HANNA (Model HI-9321) was used for pH measurements. A water bath shaker of American Optical Corporation (Model Buffalo, Newyork) was used for all the adsorption experiments.

RESULTS AND DISCUSSION

Water quality of the River Nile studied area at ESIIC:

The water quality is largely affected by natural processes (weathering and soil erosion) as well as anthropogenic impact (municipal and industrial waste water discharge). The anthropogenic discharges represent a constant polluting source, whereas surface runoff is a seasonal phenomenon largely affected by climatic conditions (Najafpour *et al.*, 2008).

In view of the Table (2) we can declare that the physico-chemical parameters of water quality increased at station II and slightly increased at III and decreased values at station I. The mean

concentration values of TS; 3577 mg/l, BOD; 2403 mg/l and COD; 3558 mg/l respectively. This is mainly attributed to the waste water of ESIIC included great amount of suspended matter and other organic pollutants discharged into the River Nile at this station. Also, the increase in water temperature (40 °C) at station II was related to the thermal pollution discharged from ESIIC into the River Nile at this area. On the other hand, all physical and chemical parameters concentration values were recorded at stations I & III are within the permissible limits of water quality standard values (AWWA, 1991). Therefore, the main problem is represented in the high values of COD at station II, that related to the effluent effects of ESIIC and the target was to improve the efficiency of removal of organic pollutants matter in ESIIC (COD; 36294 mg/l).

Table 2: The mean values of water quality parameters of the area under investigation

Stations		I	II	III
Parameters				
Physical parameters	Air Temp °C	21	23	24
	Water Temp °C	20	32	30
	Transp. cm	85	40	43
	EC µS/cm	400	617	501
	TS mg/l	264	3577	669
Chemical parameters	pH	8.3	7.5	7.8
	DO mg/l	10.0	7.0	8.0
	BOD mg/l	5.0	2463	36
	COD mg/l	19.0	3558	125
	CO ₃ ⁻² mg/l	7.8	nil	3.8
	HCO ₃ ⁻ mg/l	214	300	236
	SO ₄ ²⁻ mg/l	28	46	36
	Cl ⁻ mg/l	27	27	25
	Ca ⁺² mg/l	33	104	39
	Mg ⁺² mg/l	15	25	16
	Na ⁺ mg/l	34	35	33
	K ⁺ mg/l	5	7	6
	NO ₂ ⁻ µg/l	14	17	17
	NO ₃ ⁻ µg/l	40	59	38
	NH ₄ ⁺ µg/l	520	3250	2090
	SiO ₃ ⁻ mg/l	4.3	5.89	5.27
	PO ₄ ³⁻ µg/l	85	546	137
	TP µg/l	135	832	216

Characterization of prepared activated carbon:

Some physical and chemical properties of the prepared activated carbon are shown in Table (3). In this concern, there are two types of densities associated with activated carbon called apparent and packed (bulk) density.

Table 3: Physical and chemical properties of the prepared activated carbon (C-2)

parameters	unit	C-2
Apparent density	g/ml	0.21
Bulk (packed) density	g/ml	0.28
Ash content	%	40
BET- surface area	m ² /g	63
Pore volume	CC/g	1.35
Pore diameter	Å ^o	16.5
Methylene blue (MB) index	mg/g	41
pH		9.07

The apparent density of a solid is defined as the mass of unit volume of the carbon particle indicating its pore system. While in bulk density, is defined as the mass of unit

volume of the sample including both the pore system and the voids among the particles. The American water works Association (AWWA, 1991) has set a lower limit on the bulk density at 0-25 g/ml GACs to be of particle use. The high bulk density is explained by the high lignin of precursors.

The ash content of the carbon is the residue that remains when the carbonaceous material is burned off. The ash content of the adsorbent depends on the chemical composition of the raw material (mainly inorganic compounds) and the degree of carbonization (Zanzi, 2001). The specific surface area was estimated by applying the BET- equation to get the BET-surface area, the total pore volume, V_p from nitrogen held as liquid at relative pressure $p/p_0 = 0-95$, and an average pore radius from the empirical relation $r = 2V_p/S_{BET}$ (Villar-Rodile *et al.*, 2002).

Table (3) indicates that the adsorbent C-2 has lower surface area ($63m^2/g$), higher pore volume ($1.35cc/g$) and the diameter ($16.5A^\circ$). The dye adsorption (MB) was used to determine the capacity of the activated carbon to adsorb molecules of a particle size (Yenisory-Karakas *et al.*, 2004); the uptake of MB by C-2 ($41/ mg/g$) is acceptable. The pH measurement it is well established that steam activation at high temperatures ($800-1000^\circ C$) from alkalinoxide, which have chromene and pyron type structure (Pereira *et al.*, 2003). The most activated carbons are usually alkaline ($pH \approx 8$) and probably the high ash content might additionally raise the basicity e.g. C-2.

Treatment of organic matter of ESIIC waste water:

In this concern, advanced oxidation process involving hydroxyl radicals OH^\cdot , represent a new treatment concept and have gained increasing interest in treatment of industrial and drinking wastewater to remove organic contaminants. So, four trials were applied to get the recommended procedure to decrease the organic pollutants and achieve the permissible level of COD in ESIIC effluents.

1st trial "C-2 mass effect":

The effect of adsorbent mass was tested in removal of organic pollutants matter due to COD values. As shown in Table (4), as the adsorbent amount of C-2 Activated Carbon(AC) increases, the % R values increases.

Table 4: % R of organic pollutants related to COD values in the ESIIC effluents using C-2.

Serial no.	C-2AC (Adsorbent mass)	Initial concentration Of COD C^0	Final concentration of COD C_e	% R
1	19/e C-2 AC	36294	36058	0.65
2	29/e C-2 AC		35791	1.38
3	39/e C-2 AC		35295	2.75
4	49/l C-2 AC		34964	3.66
5	59/e C-2 AC		34843	4.00

However, a steady-state condition was apparent indicating that 5g/l of C-2 AC increases the %R achieved 4% removal of organic matter pollutants in ESIIC effluents. Excess of AC will inhibit good mixing and in turn prevent the organic matter pollution to reach all the AC particles i.e. of no use (Niragu and Simmons, 1994).

2nd trial "H₂O₂ effect":

The presence of H₂O₂ has a great influence in the reduction of organic pollution concentration in waste water. Moreover, it is necessary to decide the amount of H₂O₂ to fulfill the lowest possible value of COD. This is due to the much higher H₂O₂ concentration will be (1) economically undesirable (Shen *et al.*, 1996) and (2) scavengers for hydroxyl radical. The residual of H₂O₂ in solution was determined by the KI titration method.

Figures (1&2) show the ratio between H₂O₂ /Slope (v/v) and contact time to achieve the maximum (%R) of COD.

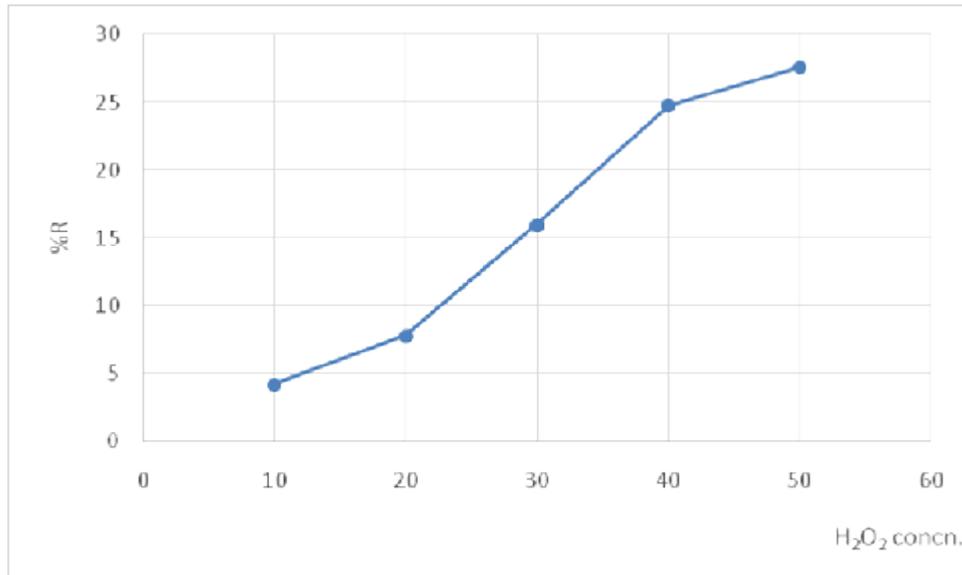


Fig. 1: %R of the COD in the ESIIC effluents using H₂O₂ (various concentrations).

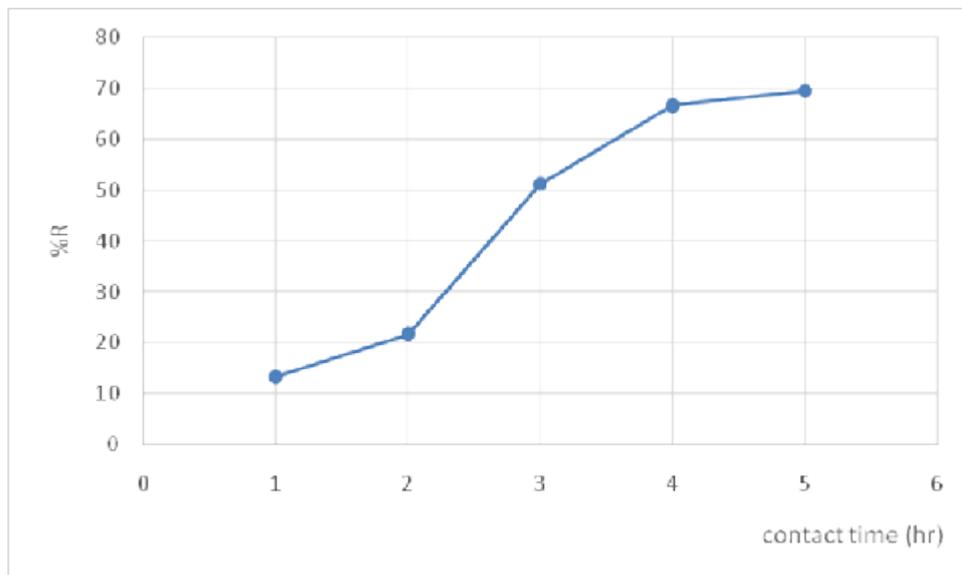


Fig. 2: %R of the COD in the ESIIC effluents using H₂O₂ (various contact time)

3rd trial "UV exposure"

The presence of UV light has an influence on the reduction of the organic pollution concentration in wastewater. But, it is limited without presence of an H₂O₂ full file the lowest possible value of COD shown in Fig. (3).

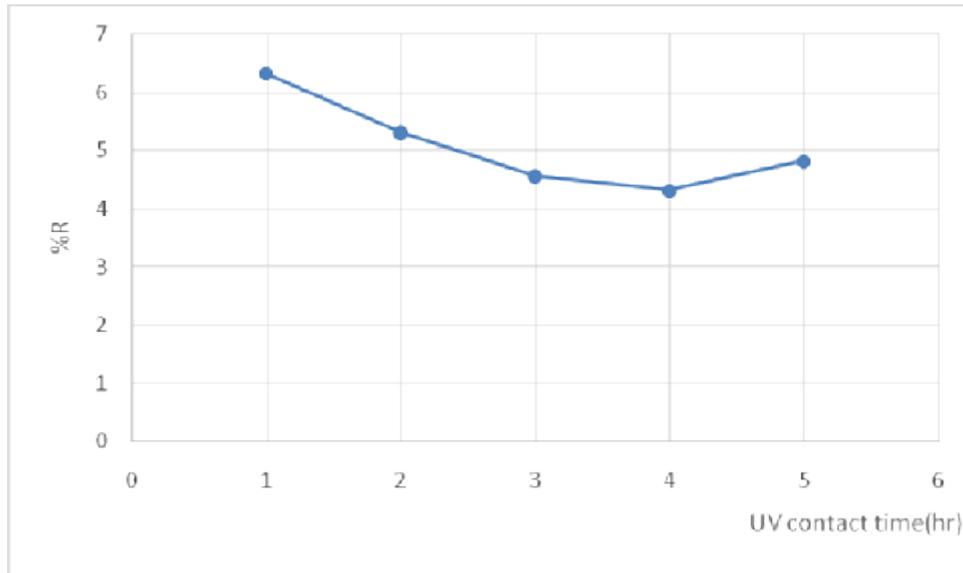
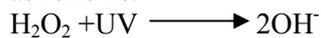


Fig. 3: %R of the COD in the ESIIC effluents using UV exposure (various contact time).

4th trial "UV/ H₂O₂ effect"

In the presence of H₂O₂ photocatalytic and radiation with $\lambda > 300$ nm, the radiation was as follows:



The reduction of the COD in the ESIIC effluents was rapid; there was a 97.2% reduction of COD using UV system after one hour exposure and reaction with 30% H₂O₂ as shown in Fig. (4).

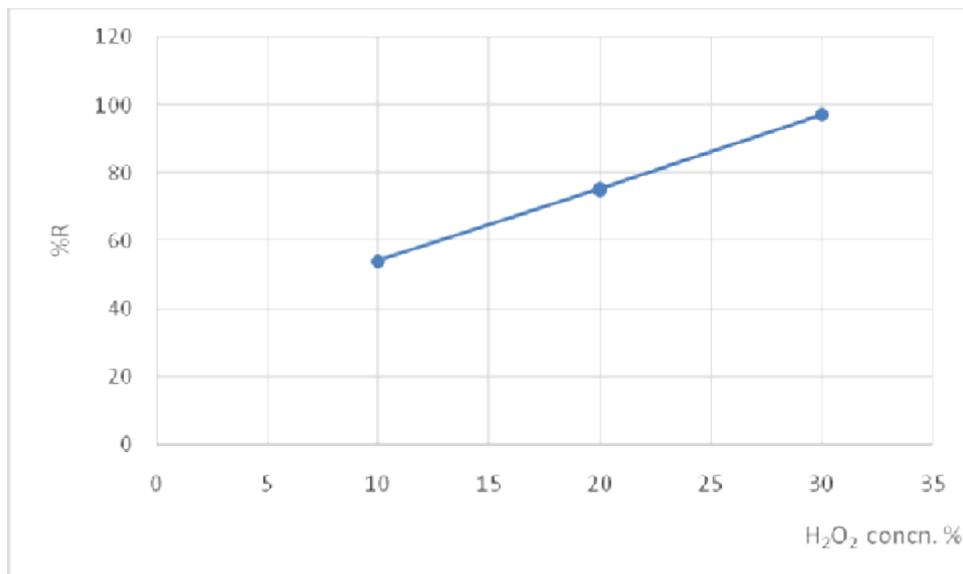
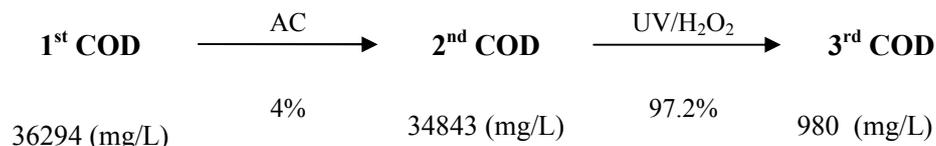


Fig. 4: %R of the COD in the ESIIC effluents using UV/H₂O₂

CONCLUSION AND RECOMMENDATION

In this concern, treatment of wastewater by mixing with C-2 activated carbon was assessed, followed by advanced oxidation with UV and H₂O₂. As a measure of extent treatment we used the % removal at chemical oxygen demand (COD) before and after the treatment.

Based on the results of the experiments, the amount of AC C-2 (5 g/l) was used. In case of the 2nd step (photo-oxidation using UV/H₂O₂), the ratio of the H₂O₂ to the contaminate was 3:10 and the exposure time required for complete degradation was one hour. So,



On the basis of the adsorption and advanced oxidation process (AOPs) studies, a pilot plant for the treatment of organic pollutions in ESIIC effluents can be established to achieve the permissible level of COD. We can conclude that the ESIIC wastewater carrying heavy load of organic pollution is mostly has serious effect on the River Nile water quality, and we recommended applying the present chemical treatment procedure to remove this organic pollutants from ESIIC effluents to save the River Nile water quality at this area.

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ARABIC SUMMARY

التقييم والمعالجة الكيميائية للتلوث العضوي المنصرف في نهر النيل – دراسة حالة

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تهدف هذه الدراسة الي تقييم وتأثير الملوثات العضوية علي جودة مياه نهر النيل وكيفية عمل معالجة كيميائية عن طريق دراسة حالة وهي شركة الحوامديه للمصناعات التكاملية. والتي تصب مخلفاتها مباشرة في نهر النيل والذي يؤدي الي حدوث تغير جوهري في البيئه المائيه لنهر النيل. وقد استهدفت الدراسة عمل معالجة لهذه المخافات العضويه باستخدام عدة طرق منها قش الارز المعالج حراريا وكذلك استخدام الاشعة الفوق بنفسجية وكذلك استخدام فوق اكسيد الهيدروجين كموا د مؤكسده. وكان الهدف هو تقليل قيمة وتركيز الاكسجين المستهلك كيميائيا في مخافات شركة الحوامديه. وقد اوصت الدراسه باستخدام الكربون النشط المعالج حراريا من قش الارز في المرحلة الاولى ثم استخدام فوق اكسيد الهيدروجين مع الاشعة فوق البنفسجية في المرحلة الثانية لتقليل قيمة وتركيز الاكسجين المستهلك كيميائيا.