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Zero Liquid Discharge and Recycling of Paper Mill Industrial Wastewater via Chemical Treatment and Solar Energy in Egypt

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INTEGRATED treatment for recycling of industrial wastewater has become an urgent necessity at present time. Zero Liquid Discharge (ZLD) in combination with solar energy become urgently needed not only to compensate water shortage but also to preserve the recent water resources from pollution. In this work where the waste-paper was collected to be recycled; an integrated system has been applied for wastewater treatment to reuse in process, while the rest is being comply with the regulatory standards to be discharged from the paper factory. Treatment including a lot of coagulants such as alum, ferric chloride, lime and cationic polymer these coagulant used separate or combined .The removal efficiencies of Chemical Oxygen demand (COD) were 84%, 83.5%, 75% and 79.4%, respectively. Consequently Total Suspended Solids (TSS) removal efficiencies were 99.5%, 99.6%, 97.5% and 98.9%. All treated industrial wastewater can be recycled to fulfill the phenomenon of ZLD. On the other hand, the negative impact of produced chemical sludge was diminished via non-conventional technique as a clean post treatment, where an effective design of a solar dryer was used to obtain dry sludge cake and to collect a highly purified water to be recycled in industrial process. Solar energy showed good potential in drying the sludge paper with competitive cost and clean environment. It is found that each square meter of drying surface area can dry 9 kg of wetted sludge paper per day. The presented trapezoidal shape solar dryer can dry daily upto540 kg of wetted sludge paper. Based on the required sludge paper water demand, a large scale solar dryer can be sized accordingly.

Keywords: Paper industry, Industrial wastewater, Chemical treatment, Solar dryer.

Introduction

The 21st century is witnessing the collision of two powerful trends rising human populations coupled with a changing climate. The demand for water is growing exponentially with population growth, while climate change makes rainfall more erratic and less predictable. The reuse of treated industrial wastewater is necessary not only to face water shortage but also to achieve water sustainability [1-2]. In the paper industry, processes involving tissue paper that require paper recycling consumes a large amount of water in the preparation of the feed material, back washing of manufacturing parts and in overall production processes. According to FAO, the world production of paper including tissue paper in 2015 exceeded 390 million ton [3]. Moreover, according to the prognoses, paper and pulp industry was considered the sixth largest polluter that charging a variety of solid, gaseous and producing large amounts of wastewater into the surrounding environment during manufacturing processes [4]. The needed water in paper industry produced one ton of paper is ranged from 10 to 50 m^3 depending on the type of produced paper and the extent of water reuse [5]. Many technologies for paper mill wastewater treatment have been applied these technologies including; physical treatment, chemical treatment by electro-coagulation and inorganic coagulant and biological treatment by activated sludge and SBR followed by Fenton [6-11]. The optimal coagulation/flocculation process for raw water treatment in the River stream and

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industrial wastewater treatment detected in a lot of research work [12-13]. The treated industrial wastewater can be reused as safe usable water and to pay-pack via a novel solar industrial wastewater treatment system [14]. Also solar energy especially in remote and arid areas is the more suitable choice for water desalination and wastewater treatment via systems such as an integrated solar greenhouse [15]. Pulp and paper mill wastewater treatments generate amount of sludge which can be used in other purposes [16]. A lot of research works concluded that the chemical treatment of sludge can be considered as an additional value for environmental protection [17-18].

The main objective of the present work is to introduce an integrated zero waste system for total recycling of the industrial wastewater from paper mill process using hybrid chemical treatment process with solar dryer as a clean dewatering technology.

Materials and Methods

Description of production process

The wastewater was collected from a paper mill factory located in industrial city, East Cairo, which utilized the exclusively recycled paper to produce toilet and tissue papers. The daily product reached 7 ton, while the total amount of resulted wastewater reached100 m^3/day. The main stages of production process are shown in Fig. 1, where waste paper is mixed with water with ratio 1:4. The mixture is pulping by highly rotating screw, and it is screened to pass through channels for more sleeking and to transfer through final screens to reach hot cylindrical drum to produce the dried sheets, to be cut and packed as final product.

Wastewater analysis

Four composite samples were collected along six months representing the variation of production rates for half and full production capacities. Collected wastewater samples have been analyzed according to APHA, 2017 [19]. The selected parameters include: pH, turbidity, TSS, TP, COD, BOD_5, TKN, phenol, and heavy metals, respectively. The selected chemical coagulants, coagulants aid and other used chemicals are of analytical grade. Table1 indicates the physicochemical characterization of raw wastewaters for the four collected samples along the study.

Chemical treatment

To investigate the full efficiency of the proposed treatment, the experimental chemical treatment has been carried out on the highest loaded wastewater as shown in Fig. 2. Chemical treatment has been carried out using different coagulants and coagulant aid. To obtain the optimal doses; a Jar test unit was used. A series of coagulants at their optimal operating conditions, fixed reaction time, selected rpm and at the same settling time were used to choose the most relevant one. Alum, Lime, Ferric Chloride were tried separated or in combination at their optimal doses and same operating conditions. To reduce sludge agglomeration time; a cationic polymer was added after the flash mixing step. The following doses: 200 and 250 mg/l Alum, 700 and 1000 mg/l $FeCl_3$ and 3.0 and 4.0 g/l Lime were added during flash mixing step. The coagulants were mixed with raw wastewater at 250 rpm for 1-2 min as flash, followed by slow stirring with 25-30 rpm for flock's formation. Consequently, a 5 mg/l Cationic polymer was added for each run to enhance the flocks' agglomeration and to reduce the settling time. The mixtures were allowed to settle for 30 min. Turbidity as well as COD and TSS were measured to indicate the efficiencies in each run and to get the optimal coagulant with its operating conditions for this type of wastewater.

Optimal operating conditions for chemical treatment

As a sub-sequential step for chemical treatment; some tests have been carried out on selected coagulant which gave the highest suspended and COD removals. Selected parameters such as pH, coagulant used, mixing rate as rpm and settling time have been carried out. Investigation of optimal operating conditions for chemical treatment achieved; how much the treatment cost beside to predict the needed area for the treatment unit.

Solar drying for chemical sludge and other wet materials

The resulted sludge from chemical treatment is recycled to the first step as added raw material, while the remaining part will be environmentally safe dried via the proposed solar drier as shown in Fig.3.a Using conventional sources of energy like fossil fuels, causing a greenhouse gases emissions in its various forms that have a negative impact on the environment. One of the main successful solutions to overcome these problems is to use solar energy. It is a clean source of energy, available everywhere in Egypt since Egypt is considered one of the best countries received solar radiation with an average value of 5.5 kWh/m^2/day. Solar drying is considered one of the most important solar thermal applications. It presents an alternative and efficient method to dry chemical sludge and other wet materials in a clean, hygienic and sanitary environment. It saves energy and time, improves product quality, time, occupies less area, protects the environment and makes the process more efficient. An efficient built-in trapezoidal shape greenhouse solar dryer is manufactured, and field tested under metrological conditions of National Research Centre, Dokki, Giza, Egypt. It consists of a built-in trapezoidal shape greenhouse solar dryer with 30 m^2 ground area. The south wall is of 1 m height while the north wall is of 2 m height. All walls are made from galvanized steel sheets of 0.7 mm thickness and glass wool insulation with thickness of 5 cm is inserted between the two galvanized steel sheets making a sandwich panel insulated walls. On the south facing width, the absorber plate with dimensions of 5 m x 5 m is fixed on the iron metal support as a built-in solar air collector. It is made from corrugated iron sheet to maximize the absorbing surface area with a thickness of 0.7 mm. It is painted with black color to maximize the heat absorption on the absorber surface. A digital balance meter with sensitivity 1 gram is used to weigh the fresh and dried product regularly. A digital moisture content meter is used to estimate the product hourly moisture content. A digital solar pyrano-meter has been used to measure the total solar radiation falling on the dryer surface area [20]. The resulted sludge was firstly allowed to be filtrated to reduce the water content in the sludge and this will increase the drying rate then it will be dried by using three different conditions as shown in Fig.3 b, in the first and second cases, the sludge will be placed on glassy surface while in the second case, the height of sludge will be twice as the height in the first case. In the third case, the sludge will be placed on surface from gauze.

Why solar dryer is selected?

The solar dryer is selected in order to avoid the negative impact of the produced waste on the environment. The solar drier will save and protect the working area from any source of pollution besides the "Pay-Back" of additional raw material. In order to choose the relevant design and to identify the optimal operating conditions; a series of experimental runs were carried out in the solar dryer as shown in Fig. 3.b. To identify the most relevant drying conditions like thickness and surface area, a series of similar chemically treated sludge were dried in different containers. First run via glass plate with exposed flat area of 133 cm^2, while the second run by a glass plate with exposed flat area of 95 cm^2. The third run was carried out on gauze surface with area 95 cm^2. The performance of all runs was measured by calculating the losses in weights every one hour. The evaporated water with its removal percentage was calculated according to the equation:

$$\%\,\text{Removal} = \frac{\text{wetweight} - \text{driedweight}}{\text{wetweight}} X100$$

Results and Discussion

Chemical treatment

Results showed that all used coagulants achieved high removal efficiencies as shown in Table 2. However, Alum alone or in presence of Polymer is preferable to avoid any produced color in the treated supernatant as well as in the chemically sludge. On the other hand, treated wastewater using $FeCl_3$has residual iron content in supernatant and the brown chemically sludge. Moreover, the treated wastewater using lime has high turbidity and pH-values in the supernatant, in addition to high solids content that considered a disadvantage for using this coagulant. Although the lime was so far efficient for COD and TSS removal, but it wasn't the proper coagulant for this type of wastewater.

Optimal conditions for chemical treatment

Figure 4 indicates the optimum dose of Alum at 250 rpm, 10 minutes reaction time and 30 minutes settling time results showed the highest removal was at dose of 250 mg/l of Alum where removal efficiency was 84%. Figure 5 indicates that the optimum settling time at dose 250 mg/l and 10 minutes reaction time the optimum settling time which gave the highest removal efficiency was 25 minute.

Solar drying of the sludge

The resulted sludge from chemical treatment by using cationic polymer as coagulant was dried in a solar dryer. Sludge dewatering using glass surface with sludge thickness 0.70 cm and 0.40 cm are shown in Fig. 6 and 7 respectively and by using gauze surface (Fig. 8). It is found that the final sludge has a volume 40 cm^3/l; a weight of 30.1 gm/l and the water needed to be removed is about 27.7 gm/l. In the first run; the depth of sludge on the glassy surface was 0.7 cm with surface area 57 cm^2/l, while in the second

TABLE 1. Physico-chemical characteristics of raw wastewater *

Parameter	Unit	Results	Decree 44/ 2000 **	
pH- Value	= =	7.2	6-9.5	
Total suspended solids, TSS	mg/l	2316	800	
Settleable Solids → 10 min	ml/l	145	8.0	
Settleable Solids →30 min	ml/l	106	15.0	
Biological Oxygen Demand, BOD_5	mg/l	364	600	
Chemical Oxygen Demand, COD	mg/l	1540	1100	
Total Kjeldahl Nitrogen, TKN	mg/l	126	100	
Hydrogen Sulphide, H_2S Sol	mg/l	0.3	10	
Total Phosphates, PO_4	mg/l	0.3	25	
Chromium, Cr^{+6}	mg/l	< 0.001	0.5	5.0
Cadmium, Cd	mg/l	< 0.001	0.2	
Lead, Pb	mg/l	< 0.001	1.0	
Mercury, Hg	mg/l	< 0.001	0.2	
Silver, Ag	mg/l	< 0.01	0.5	
Copper, Cu	mg/l	< 0.01	1.5	
Nickel, Ni	mg/l	< 0.001	1.0	
Arsenic, As	mg/l	< 0.001	2.0	
Boron, B	mg/l	0.05	1.0	
Phenols	mg/l	0.2	0.05	
Cyanide, CN	mg/l	ND	0.2	
Oil, grease & resins	mg/l	10	100	

* Average of three successive runs ** Trigger levels in Ministerial Decree No 44 for 2000 that regulating the discharge of industrial wastewater onto sewerage network. ND = not detected

TABLE 2. Comparative results of the selected coagulants *

Coagulant	Dose (mg/l)	Results					
		pH	TSS (mg/l)	SV (30min)	NTU	COD (mg/l)	% R (COD)
Raw wastewater	= =	7.2	2316	106	699	1540	==
Alum	200	7.3	411	110	139	460	70
	250	7.5	11	115	2.5	246	84
Alum+Polymer	200+(5)	7.4	412	70	150	440	71.4
	250+(10)	**7.5**	8	80	7	256	82.8
Ferric chloride	700	5	480	98	60	511	66.8
	1000	4.5	13	88	9	254	83.5
Lime	3000	11	630	198	241	466	69.8
	4000	12.5	56	248	221	375	75
Cationic polymer	5.0	7.7	560	96	270	913	40.7
	10.0	7.9	24	108	131	318	79.4

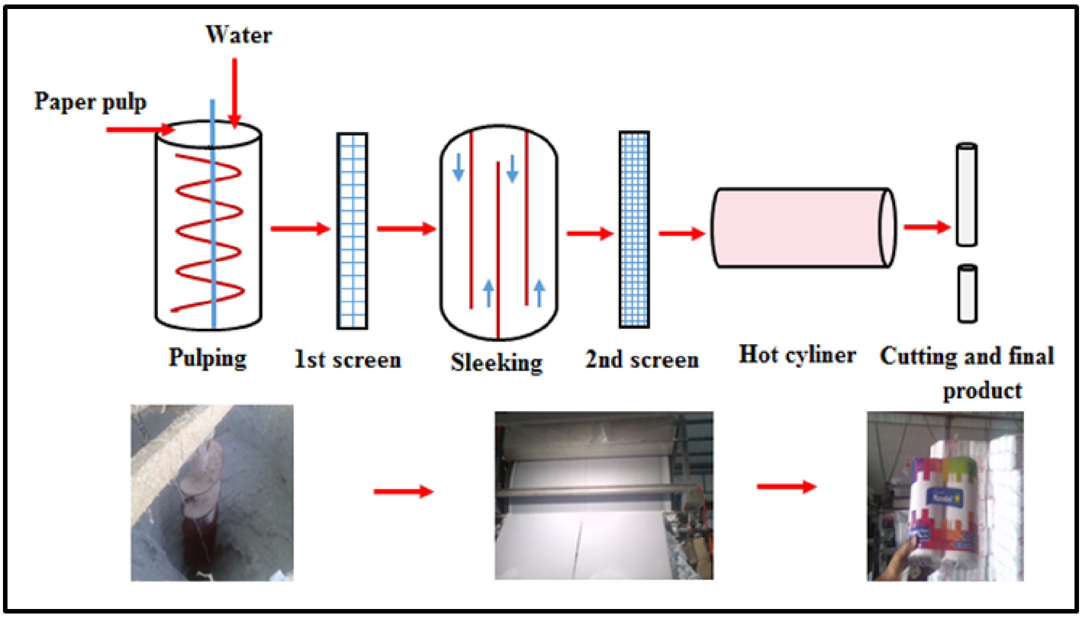

Fig. 1. Different stages of waste paper re-production process

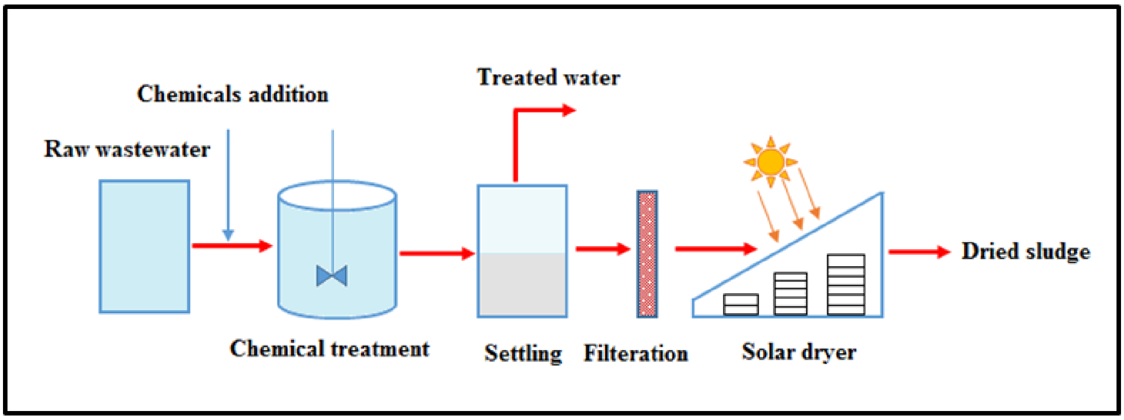

Fig. 2. Schematic diagram of wastewater treatment process

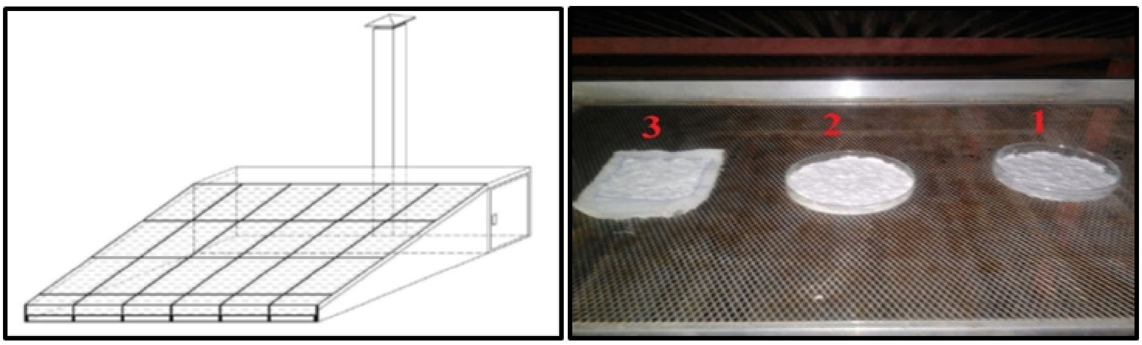

Fig. 3. **a) solar dryer** **b) sludge inside solar dryer**

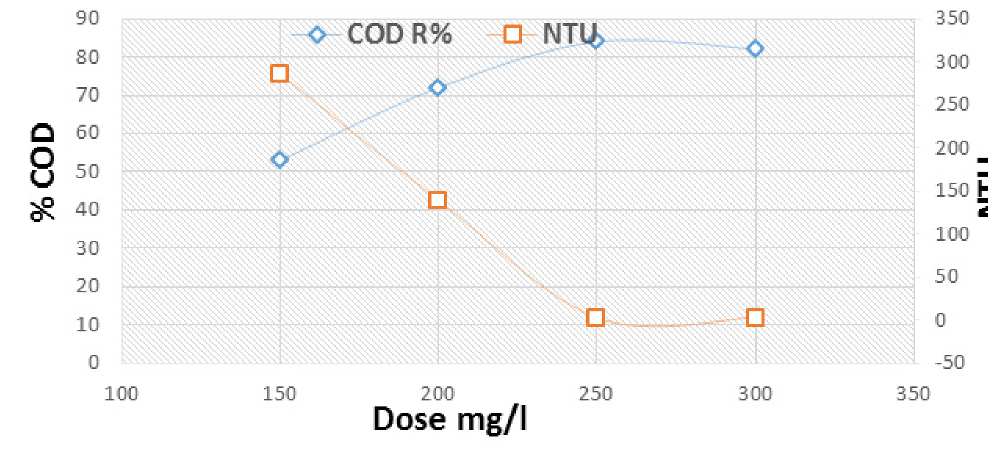

Fig. 4. Detection of the optimal Alum dose

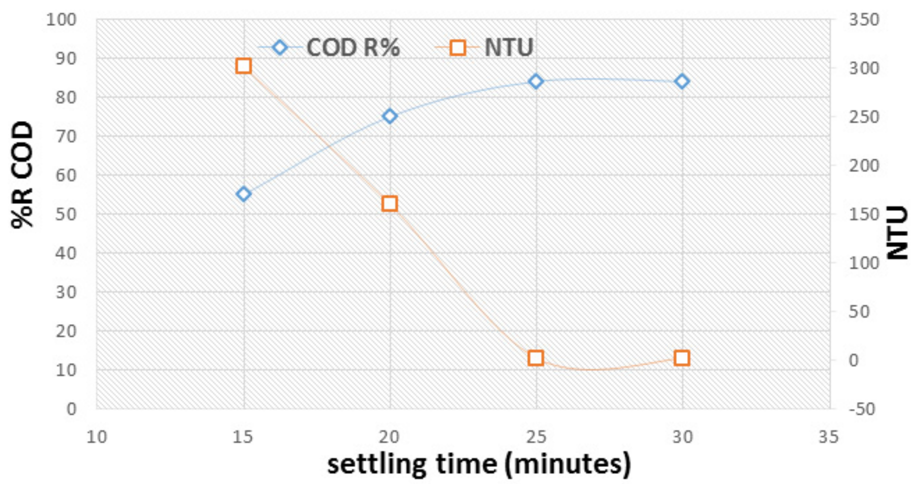

Fig. 5. Detection of the optimal settling time at its optimal dose

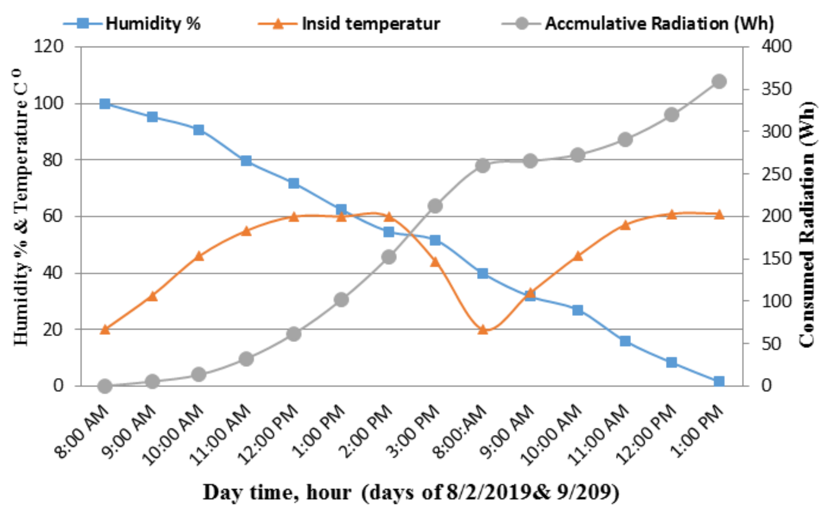

Fig. 6. Detection of the optimal solar exposure time with 0.70 cm sludge thickness

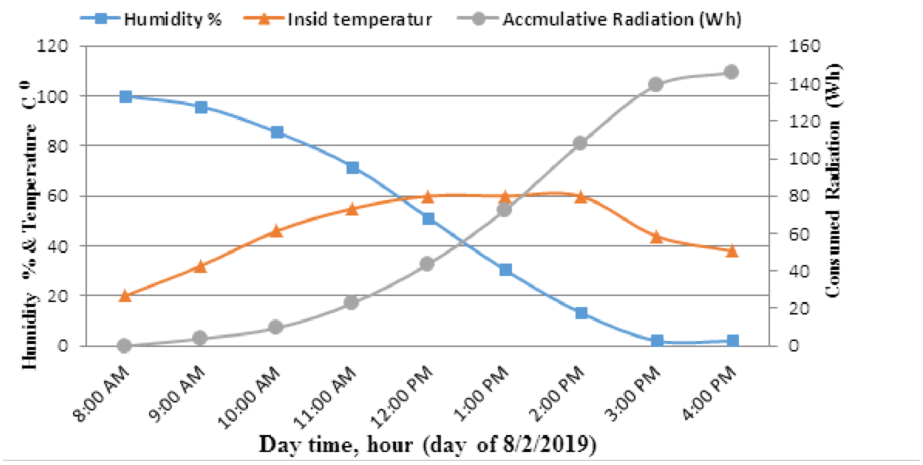

Fig. 7. Sludge dewatering using glass surface with sludge thickness 0.40 cm

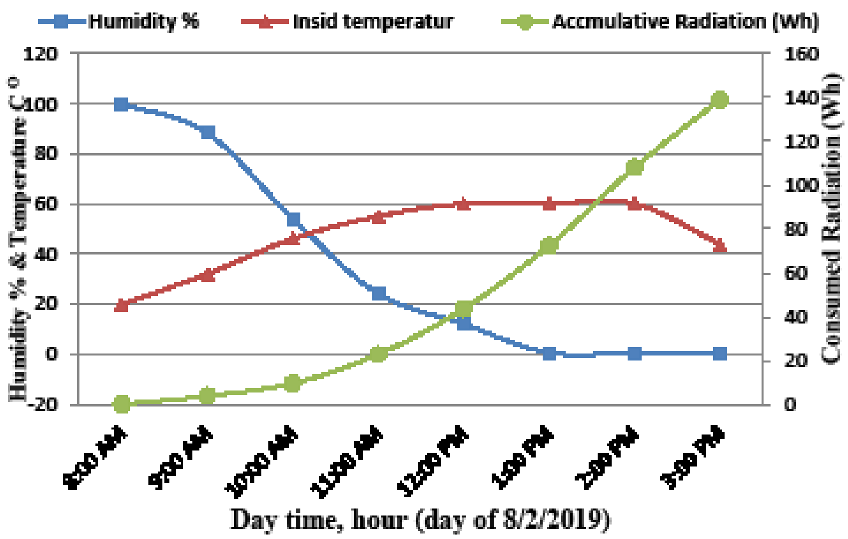

Fig. 8. Water removal in case of gauze

and third runs were 0.4 cm at surface area 100 cm^2/l in. It is found that the depth of sludge layer inside the dryer is directly affect the drying rate where the sludge in first run was totally dried after 13 hours in two days and after 7 hours in the second run. Results showed that using gauze as a surface of drying as shown in Fig.8 is more efficient in water removal from the sludge where it achieved 99.46% removal after 5 hours. Results also showed the consumed solar energy was 360 watt hour, 146 watt hour, and 72 watt hour in first, second and third runs respectively

Cost analysis

In general the main advantage of chemical treatment is the low cost; the main costs of the recent integrated system are about the cost of chemical treatment and the cost of solar drying of sludge as illustrate in Table 3. On the other and if the saving cost of the treated water and the value of dried sludge as a row materials taken into account that will reduce the total cost.

Conclusions

Wastewater from paper recycling mill industry can be efficiently treated by chemical coagulation–flocculation and the treated wastewater can be efficiently reused in the same industrial activities in the purpose of processing water.

It can be environmentally reused for plants irrigation with COD= 245 mg/l.

In case of extra wastewater than needed, it can

TABLE 3. Cost analysis of treatment process

Chemical treatment ($/m^3)			Solar drying of sludge ($/m^3)		Total cost($/m^3)
Coagulant	Labor Cost/m^3	Cost of electricity	Capital cost	Running cost	--
Alum	0.06	0.24	0.09	0	0.39
Alum+Polymer	0.07	0.24	0.09	0	0.40
Ferric chloride	0.63	0.24	0.09	0	0.96
Lime	0.50	0.24	0.09	0	0.83

be discharged with compliance to the regulatory standard to sewerage network or to the agricultural drains.

The treated effluent can be easily flow in irrigation pipes due to the very low suspended solids contents with TSS = 11 mg/l.

Sludge resulted from the coagulation can be dried to zero water content via solar drier and it can recycled in the same factory or reused to produce another grade of paper or cartoons.

Solar energy showed good potential in drying the sludge paper with competitive cost and clean environment.

It is found that each square meter of drying surface area can dry 9 kg of wetted sludge paper per day. Based on the required sludge paper water demand, the presented trapezoidal shape solar dryer can dry daily 540 kg of wetted sludge paper a large scale solar dryer can be sized accordingly.

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