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ORIGINAL PAPER

Pollution control in pulp and paper industrial effluents using integrated chemical–biological treatment sequences

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Abstract The main objective of the present study was to improve the quality of pulp and paper industrial wastewater of two local mills RAKTA and El-Ahlia, Alexandria, Egypt, and to bring their pollutant contents to safe discharge levels. Quality improvement was carried out using integrated chemical and biological treatment approaches after their optimization. Chemical treatment (alum, lime, and ferric chloride) was followed by oxidation using hydrogen peroxide and finally biological treatment using activated sludge (90 min for RAKTA and 60 min for El-Ahlia effluents). Chemical coagulation produced low-quality effluents, while pH adjustment during coagulation treatment did not enhance the quality of the effluents. Maximum removal of the tested pollutants was achieved using the integrated treatment and the pollutants recorded residual concentrations (RCs) of 34.67, 17.33, 0.13, and 0.43 mg/l and 15.0, 11.0, 0.0, and 0.13 mg/l for chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), tannin and lignin, and silica in RAKTA and El-Ahlia effluents, respectively, all of which were below their maximum permissible limits (MPLs) for the safe discharge into water courses. Specific oxygen uptake rate (SOUR) and sludge volume index (SVI) values reflect good conditions and healthy activated sludge. Based on the previous results, optimized conditions were applied as bench scale on the raw effluents of RAKTA and El-Ahlia via the batch chemical and the biological treatment sequences proposed. For RAKTA effluents, the sequence was as follows: (1) coagulation with 375 mg/l $FeCl_3$, (2) oxidation with 50 mg/l hydrogen peroxide, and (3) biological treatment using activated sludge with 2,000 mg/l initial concentration and 90 min hydraulic retention time (HRT), while for El-Ahlia raw effluents, the sequence was (1) coagulation with 250 mg/l $FeCl_3$, (2) oxidation with 45 mg/l hydrogen peroxide, and (3) biological treatment using activated sludge with 2,000 mg/l initial concentration and 60 min HRT. In conclusion, results confirmed that the application of the proposed sequential treatments removed almost all COD, BOD_5, high molecular weight compounds, and silica from RAKTA and El-Ahlia influents and produced high-quality effluents, thus achieving the main objective of this study.

Keywords Activated sludge · Coagulation · Hydrogen peroxide · Oxidation · Pulp and paper industry · Wastewater treatment

Introduction

The flattened stalks of papyrus reeds were used by the Egyptians as a writing surface some 5,500 years ago.

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Wood consists of two primary components cellulose (the fibrous component of wood used to make pulp and paper) and lignin (glue that holds wood fibers together). Pulping is a process by which wood is reduced to a fibrous mat by separating the cellulose from the lignin, and it is generally carried out chemically, mechanically or semichemically [41, 42]. The high water usage, between 20,000 and 60,000 gallons per ton of product, results in large amounts of wastewater generation [37], which is considered as the third largest polluter in the United States, and it is responsible for 50% of all wastes being dumped into Canada's waters [36]. The effluents from this industry cause slime growth, thermal impacts, scum formation, color problems, and loss of esthetic beauty in the environment. They also increase the amount of toxic substances in the water, which are lethal to the zooplankton and fish and profoundly affect the terrestrial ecosystem. An alternative approach is to treat the wastewater to such an extent that it can be reused within the mill. Indeed, the concept of "zero liquid effluent" has been suggested for mills making certain grades of paper [46] and would be applicable in areas where water sources are extremely limited [26].

Among the different sources of pulp fibers (woods, straws and grasses, bamboos, or canes and reeds), wood is the most abundant source of papermaking fiber. Wood compounds (lignin, carbohydrate, and extractives) are hard to biodegrade and are washed away from the fibers during the washing, dewatering, and screening processes [1]. Pulping (especially chemical) generates a high-strength wastewater containing more than 250 organic and inorganic compounds that are only partly removed (if at all) [1, 23]. Pollutants in these effluents include wood debris, soluble wood materials as well as the most toxic substances, such as chlorinated compounds, resin acids, unsaturated fatty acids, diterpene alcohols, juvaniones, chlorinated resin acids, etc. Among these pollutants, four categories including total suspended solids (TSSs), biochemical oxygen demand (BOD), color, and toxics are considered major aquatic pollutants [12]. A large number of trace organic compounds have been identified in pulp mill effluents, some of which may be carcinogenic and mutagenic, such as dioxins, furans, and polycyclic aromatic hydrocarbons (PAHs). In addition, pulp mill effluents also contain inorganic ions, organic polymers, and biopolymers [3]. Color is largely due to lignin and lignin derivatives and polymerized tannins [9, 31, 32, 40], which are resistant to degradation due to the presence of carbon-to-carbon biphenyl linkages.

However, it is certain that lignin and lignin derivatives are biodegradable by some of microorganisms under proper environmental conditions [8, 19]. Many studies have focused on screening, identifying, and evaluating the ability and effectiveness of fungi on degrading lignins in situ and in vitro. A variety of fungi has been proved to be lignin degraders and was classified into white-rot, soft-rot, and brown-rot fungi based on the type of wood decay carried out by these organisms [20]. Moreover, it is now generally agreed that lignin degradation is not an ability limited to the wood-rotting "white-rot" fungi. As summarized by some authors, numerous bacteria have been reported to decompose lignins and lignin derivatives. These bacteria included *Pseudomonas* spp., *Flavobacteria*, *Xanthomonas* spp., *BacilIus* spp., *Aeromonas* spp., *Cellulomonas* spp., *Chromobacrtia*, etc. [8, 20].

The main objectives of the present work were to evaluate the efficiency of the integrated chemical–biological treatment approach (coagulation, hydrogen peroxide oxidation, and biological treatment using activated sludge treatments) for the removal of organic and inorganic compounds from RAKTA and El-Ahlia pulp and paper mills effluents, especially those compounds that contribute to color and also silica. Additional objective was to design and optimize sequence bench scale treatment systems for the contaminated effluents for large-scale implementation and application in pulp and paper industry.

Materials and methods

Case study

Wastewaters of RAKTA Paper and El-Ahlia National Paper Mills, Alexandria, Egypt, are discharged into Abu Qir Drain and then to Abu Qir Bay on the Mediterranean Coast of Egypt via El-Tabia pump station. El-Ahlia effluents are discharged within 50 m from El-Tabia pumping station except water from one of its two pulping mills, while RAKTA effluents are discharged within 250 m from El-Tabia pumping station. RAKTA Paper is a chemical pulping mill using rice straw, sugarcane bagasse, and wastepaper as raw materials for the production of writing paper, bag paper, linerboard, and duplex board. El-Ahlia National Paper mill is a mechanical pulping mill using rice straw and scrap papers as raw materials to produce printing and writing paper, machine glazed paper, linerboard, corrugating medium, and low-grade board. Consequently, they consume different amounts of water in their processing and generate different types and amounts of pollutants (Table 1) and make RAKTA effluents much stronger than those of El-Ahlia. Therefore, the main goal of this study is to compare among the two effluents of the same industry and evaluate the efficiency of the proposed system to treat wastewater from the two common processes of the pulping and paper-manufacturing industry.

Table 1 Physicochemical characteristics of RAKTA and El-Ahlia wastewater collected from the main discharge outlet

Parameter	Average concentration		MPL[a]
	RAKTA	El-Ahlia	
pH	7.39	7.80	6–9
TDS (mg/l)	470	834	2,000
TSS (mg/l)	673	1,979	60
TS (mg/l)	1,230	2,827	–
BOD_5 (mg/l)	185	270	60
COD (mg/l)	552	792	100
Turbidity (NTU)	231	592	50
Tannin and lignin (mg/l)	12.2	27.3	–
Silica (mg/l)	89	208	–
Fecal coliform MPN/100 ml	20	20	5,000
Fe (mg/l)	0.946	1.066	1.5
Al (mg/l)	0.0	0.0415	3.0
Pb (mg/l)	0.030	0.055	0.5
Cd (mg/l)	0.005	0.0045	0.05
Cr (mg/l)	0.013	0.0125	1
Zn (mg/l)	0.064	0.0885	5
Cu (mg/l)	0.034	0.031	1.5
Mn (mg/l)	0.158	0.366	1
Ni (mg/l)	0.013	0.0195	0.1

[a] MPL stated by the Egyptian Environmental Law no. 4/1994 for safe discharge into the marine environment

Experimental layout

The following four integrated chemical–biological treatment processes were successively carried out: chemical coagulation, chemical coagulation with pH adjustment, oxidation with hydrogen peroxide, and biological treatment using activated sludge.

Treatment by chemical coagulants

Aluminum sulfate or alum [$AI_2(SO_4)_3 \cdot 16H_2O$], ferric chloride ($FeCl_3$), and hydrated lime [$Ca(OH)_2$] were selected and their efficiencies for coagulation and precipitation of organic compounds from RAKTA and El-Ahlia Paper mill effluents were optimized and compared. Different doses of each coagulant (125, 250, 375, and 500 mg/l) were tested to identify their optimum doses for maximum effluent treatment. The dissolved concentrations of Al and Fe resulted during the coagulation were determined. Jar test experiments were carried out using grab samples of the raw RAKTA and El-Ahlia National Paper Mills wastewater after the addition of the tested dosages of each of the selected coagulants. A multiple stirrer unit consisting of a series sample containers stirred by individual mechanical stirrers was used for coagulation tests to allow an adequate amount of work to be completed in reasonable time. Also, 2,000-ml capacity beakers were used to allow satisfactory settlement of wastewater samples. Two basic stirring speeds were applied, a fast speed of 100 rpm for approximately 5 min for the initial addition and mixing of the coagulant chemicals followed by slow (gentle) stirring at 25 rpm for 15 min capable of promoting flocculation. Then, treated samples were allowed to settle for 30 min before quality analysis. The optimum dose for each coagulant was determined, as well as the most efficient coagulant for the treatment of the targeted effluents.

Chemical treatment (coagulation) with pH adjustment

RAKTA and El-Ahlia (National) Paper Mills wastewater were treated by alum and ferric chloride at their optimum doses before and after pH adjustment at 6.2 and 8.7, respectively, to get the least dissolved concentration of aluminum and iron. The efficiency of both coagulants with and without pH adjustment was compared.

Treatment by oxidation with hydrogen peroxide

Because of the presence of high molecular weight compounds in the chemically treated effluents of the tested paper mills, the proposed biological treatment (activated sludge) would not be sufficient for efficient treatment of the target effluents and production of good quality wastewater. To overcome this obstacle, oxidation with hydrogen peroxide was carried out to degrade these molecules into smaller molecules readily attacked and oxidized by microorganisms during the activated sludge process. This was performed through oxidation of alum and ferric chloride-treated (at their optimum doses) effluents of RAKTA and El-Ahlia Paper Mills with and without pH adjustment using hydrogen peroxide. Different hydrogen peroxide doses ranging from 25 to 100 mg/l were examined for RAKTA mill and from 15 to 60 mg/l for El-Ahlia Mill using 30% volume solution, and the oxidation took place at different exposure times ranging from 15 to 60 min. The initial pH was adjusted to 3.0 using 1 N H_2SO_4 addition to achieve optimum operating pH condition.

Biological treatment using activated sludge

Activated sludge was used to integrate the treatment of RAKTA and El-Ahlia fiber-rich wastewater as integrated approach to produce environmentally acceptable effluents. Sludge inocula were received from Edko domestic wastewater treatment plant. Prior to use, the sludge was allowed to settle at room temperature, and the supernatant was decanted to provide a concentrated sludge.

Sludge acclimation The required sludge volume was mixed with the specific effluent in a ratio of one part sludge to approximately two parts effluent. The appropriate amounts of nutrients were added on a basis of COD:N:P ratio of l00:3:1 [15, 16, 21]. The sludge/effluent/nutrient mixture was placed in lab scale unit 30 × 20 × 22 cm^3. The unit contents were stirred mechanically at 50 rpm to obtain a homogenous mixture and keep the activated sludge suspended. The unit was provided with an air pump to maintain dissolved oxygen content above 4 mg/l. After 24 h, the stirrer and air pump were removed and the mixture was allowed to settle, after which the supernatant was decanted. Fresh effluent was added to provide the same volume as the original total volume of the mixture. Fresh nutrients were added. The procedure of settling, decanting, addition of new effluent and nutrients was repeated at 24-h interval until the desired acclimation time had been achieved (about 3 months).

Nutrient addition Nutrients supplemented in the all experiments were nitrogen and phosphorus. Nitrogen was added in the form of urea (H_2NCONH_2) and phosphorus in the form of 85% ortho-phosphoric acid (H_3PO_4). Nutrient addition is commonly done based on a BOD_5:N:P ratio. However, since only chemical oxygen demand (COD) measurements were performed directly, nutrients were added on the basis of COD:N:P ratio as l00:3:1. In both cases, solutions of the compounds were prepared at appropriate concentrations, which would allow for the addition of the small quantities whenever required. Solutions were stored at 2–4 °C.

Control batch experiment (aeration only) To confirm that any increase and/or reduction in COD observed in the experiments were due to the presence of the sludge, control (blank) experiment, using only the raw mill effluent containing no sludge, was carried out in the proposed unit with a working volume of 10 l under the same conditions of agitation and aeration. The raw effluent was incubated for 48 h at room temperature and samples were taken at various time intervals (usually 0–48 h) to measure the COD, BOD_5, turbidity, lignin, and silica. The treated samples were allowed to settle for 30 min before analysis.

Optimization of activated sludge conditions for efficient treatment Optimization parameters included the initial sludge concentration and the hydraulic retention time (HRT). Optimizing the initial sludge concentration or the sludge inoculum was carried out in 2,000-ml beakers containing different sludge concentrations (500–4000) stirred at 185 rpm using a rotary shaker. The beakers were incubated for 48 h at room temperature and samples were taken at 48 h to measure the COD after 30-min settling. Sludge concentration that achieved the highest removal efficiency (RE%) for COD levels for RAKTA and El-Ahlia effluents was considered as the optimum concentration. The optimum HRT for each effluent was determined using a bench scale reactor (30 × 20 × 22 cm^3) with a working volume of 10 l. Nutrients were added and the effluent of RAKTA or El-Ahlia was poured in the reactor. Aeration and agitation (50 rpm) were supplemented, and optimum activated sludge concentration was added to the reactor. Complex mixing of the reactor contents was assumed to be achieved within 5 min. The first sample was then drawn after that mixing and that was considered as the zero time-sample. The reactor was incubated for 48 h at room temperature, where samples were drawn at various time intervals (usually 0–48 h). At each sampling time, COD, BOD_5, turbidity, lignin, silica, specific oxygen uptake rate (SOUR), sludge volume index (SVI) and MLSS were determined. According to the removal efficiencies of the recorded contaminants, the optimum retention time (residence in the reactor in contact with the activated sludge) for each effluent was determined.

Remediation bioassay of the contaminated effluents using activated sludge The raw as well as chemically treated (coagulation and H_2O_2 oxidation) effluents of RAKTA and El-Ahlia were investigated using the proposed unit at their optimum operation conditions. Working volume of each effluent in each run was 10 l. Reactor was operated for 10 runs for each effluent (RAKTA and El-Ahlia), where samples were withdrawn at definite time intervals for quality analysis. Removal efficiencies of the different contaminants in each effluent were calculated and averaged.

Quality analyses

The wastewaters were analyzed for physical, chemical, and biological quality criteria before and after treatment using all the examined technologies (chemical and biological) to determine the efficiency of the treatment and statistically interpreted. All quality analyses were performed according to the standard procedures described in the “Standard Methods for the Examination of Water and Wastewater” [6]. Quality parameters included pH, total dissolved solid (TDS), TSS, total solid (TS), turbidity, dissolved oxygen (DO), BOD_5, COD, tannin and lignin, silica, and heavy metals (Fe, Al, Pb, Cd, Cr, Zn, Cu, Mn, and Ni). Fecal coliform was determined using the most probable number (MPN) technique [6, 15]. In addition, sludge characteristics included SOUR and SVI, were determined following the standard procedures [6] to ensure proper conditions for efficient treatment.

Statistical analysis

The obtained data were analyzed statistically using ANOVA (analysis of variance). The differences between mean probability levels were analyzed using Duncan's test. The software CoStat Version 6.311 was used as described by Cohort Software 2005 [7].

Results and discussion

Characterization of the selected raw effluents

Results revealed higher pollution load in RAKTA wastewater compared to that of El-Ahlia (Table 1). RAKTA consumes between 81,500 and 137,200 m^3 water/day, which generates huge amount of wastewater. The effluent was characterized by neutral pH (7.3–8.30) and high TDS, TSS, TS, BOD$_5$, COD, tannin and lignin, silica, and turbidity ranges (742–962, 1,052–2,906, 1,982–3,672, 185–236, 729–855, 21.3–33.3, 130–285 mg/l, and 493–690 NTU, respectively). El-Ahlia mill consumes between 66,500 and 110,400 m^3 water/day for its processes. Its effluent was characterized by neutral pH (7.11–7.23) with high TDS, TDS, SS, TS, BOD$_5$, COD, tannin and lignin, silica, and turbidity ranges (428–541, 657–779, 1,114–1,370, 152–217, 491–613, 11.1–13.3, 68.5–109.7 mg/l, and 200–261 NTU, respectively). The recorded levels of the contaminants in RAKTA and El-Ahlia effluents are all exceeding their maximum permissible limits (MPLs) stated by the Egyptian Environmental Law no. 4/1994 for safe discharge into the marine environment. Fecal coliform and heavy metals content (Fe, Al, Pb, Cd, Cr, Zn, Cu, Mn, and Ni) in RAKTA and El-Ahlia effluents recorded much lower levels than their MPLs.

Comparing the two effluents confirmed that RAKTA and El-Ahlia effluents can be classified as strong wastewater according to Metcalf and Eddy, Inc. [24] with RAKTA wastewater considered much stronger. The presence of the high silica content in the black liquor results in two major problems. These include prevention of the recovery of chemical compounds used to digest nonwood raw materials as well as precipitation and scaling of pipes in the evaporators and the recovery boiler, which in turn reduces their efficiency and adds to the maintenance cost [11, 45]. Therefore, for the process to be economically and environmentally beneficial, silica must be removed from the black liquor. These effluents represent a major contaminant source and impose severe pollution load on the receiving water systems (Abu Qir Bay), where they damage aquatic life due to both very high levels of toxic pollutants and the huge amounts of wastewater generated and discharged [2, 30, 48]. On the other hand, due to the high concentrations of tannin, lignin, and the high molecular weight (MW > 1,000 g/mol) organic compounds in the bleaching effluents, which are derived from lignin derivatives, both effluents are characterized by color (thus it is called black liquor), which is stronger in RAKTA effluent. The high levels of organic substances produced cause high BOD$_5$ and COD loads on the receiving water. However, the low densities of fecal coliform in both effluents are attributed mainly to the toxic chemicals produced in the effluent from different processes that effectively inhibit bacterial growth. Similarly, the low levels of the heavy metals in the effluent resulted from the nature of the raw materials used in the mill.

Treatment approaches

Chemical treatment (coagulation)

Coagulation treatment decreased to some extent levels of pollutants in both RAKTA and El-Ahlia effluents (Figs. 1, 2) achieving the following:

1. The highest average removal efficiency (RE) of TSS (98.59 and 97.23%) from RAKTA wastewater was achieved by ferric chloride and alum, respectively, equivalent to residual concentration (RC) of 24 and 43 mg/l, respectively (<MPL of 60 mg/l) compared to lime (47.43% RE and 859.33 mg/l RC). Ferric chloride (250 mg/l) only could achieve highest average RE of TSS of El-Ahlia effluent (95.33%) with RC acceptable by the law (33.67 mg/l), while none of the alum or lime achieved at their highest RE%, residual TSS levels (63.67 and 111 mg/l, respectively) below the MPL.
2. Residual BOD$_5$ concentrations at the highest achieved BOD$_5$ RE% recorded 160.33, 161.67, 196.67 mg/l by ferric chloride, alum and lime respectively in RAKTA treated wastewater and 108.67, 115.00 and 122.33 mg/l by using lime, alum and ferric chloride respectively) in El-Ahlia treated wastewater.
3. Similarly, the highest average removal efficiency of COD (61.34%) achieved with ferric chloride in RAKTA treated wastewater left COD value of 310.67 mg/l. In addition, 203.33, 222.33 and 242.66 mg COD/l were using ferric chloride, Alum and Lime respectively in El-Ahlia treated effluent, all of which are highly exceeded the MPL of 100 mg/l.
4. The residual turbidity levels in RAKTA-treated effluents were lower than the MPL (50 mg/l), except with lime, recording 8.67, 6.33 and 171.67 mg/l with alum, ferric chloride, and lime, respectively, at their highest removal efficiency. For El-Ahlia-treated effluent, all the turbidity levels were lower than the MPL, recording 7.67, 15.67, and 26.67 mg/l with ferric chloride, alum,

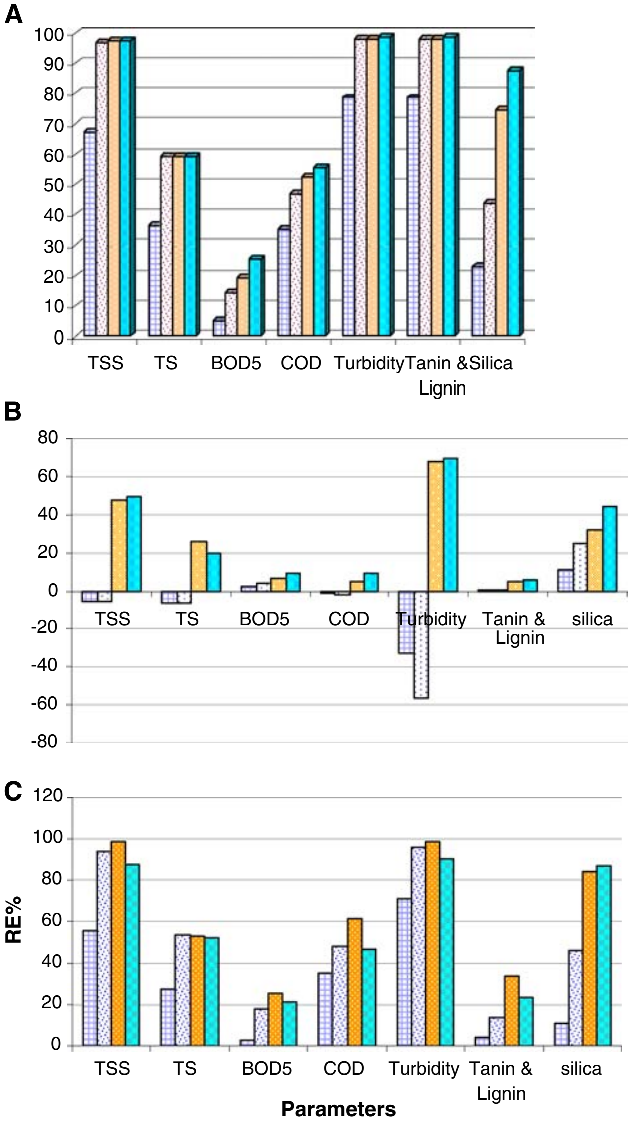

Fig. 1 Average removal efficiency % of the selected contaminants in RAKTA effluent treated with different concentrations of (**a**) alum, (**b**) lime, and (**c**) ferric chloride

and lime, respectively, at their highest removal efficiency.

5. All the recorded averages of dissolved Fe in both RAKTA- and El-Ahlia-treated effluents at all doses were higher than the MPL (1.5 mg/l), while those of Al were all below that limit (3.0 mg/l).
6. The optimum dose of alum and ferric chloride recorded 375 and 250 mg/l for treating RAKTA and El-Ahlia effluents, respectively, after which no further improvement in the RE was achieved. This may be attributed to the floc breakup due to charge reversal and dispersion when there is an excessive or overdosing of the coagulant [28, 41].
7. In conclusion, although solids contents (TSS) were reduced by coagulation than their MPL, it is clear that the three selected coagulants produced low-quality effluents concerning the organic load (high molecular weight tannin and lignin), turbidity and dissolved metals. Thus, it is unsafe to discharge such effluents into surface water systems without further treatment.

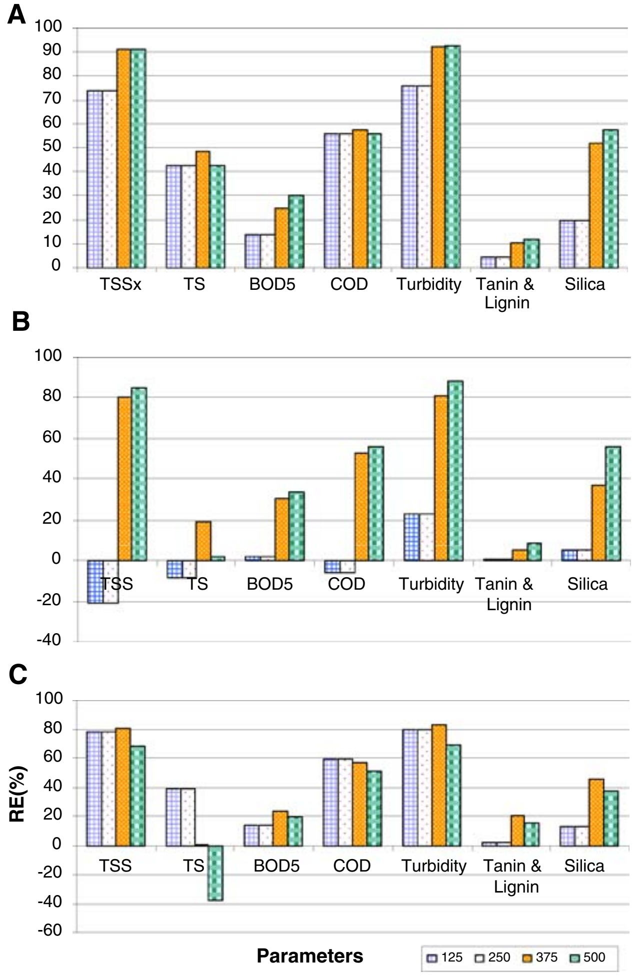

Fig. 2 Average removal efficiency % of the selected contaminants in El-Ahlia effluent treated with different concentrations of (**d**) alum, (**e**) lime, and (**f**) ferric chloride

The higher removal efficiency of the hydrolyzing metal salts (alum and ferric chloride) is due to the increase in valence of the positive counter ions of Al^{3+} and Fe^{3+} compared to Ca^{2+} referring to the double layer compression, which reduces repulsive electrostatic force and leads to neutralizing the colloidal charge followed by colloid destabilization and precipitation of the metal cations, organic anions, and colloids [5, 10, 18, 24, 28, 35, 38, 47]. Iron and aluminum were reported to have a strong tendency to form insoluble complexes with a number of ligands, especially with polar molecules and with oxygen-containing functional groups such as hydroxyl or carboxyl groups, which provide local reacting negative charges [5, 10, 35, 38, 47]. Dissolved organic compounds are removed primarily by sorption onto the hydroxide surfaces. The high tannin and lignin levels in both effluents contributed significantly to the residual BOD_5 and COD (precipitated organic matter) that are not easily biodegradable and considered resistant to biological degradation. The low removal efficiency for tannin and lignin by the tested coagulants is probably due to the prevailing of lower molecular mass fractions (<5,000 g/mol) of lignin in both effluents and mainly due to its nature as an amorphous, branched polydisperse macromolecular substance. The building blocks in these polymers are phenylpropane units. The lignin contains several functional groups such as phenolic hydroxyl, benzylic hydroxyl, carbonyl, and catechol groups [35]. The ionization of these groups is essential to make the lignin water soluble [14], which is a prerequisite for removing lignin during cooking and washing. The lignin gets partly degraded during cooking operation, becomes water soluble, and also remains in colloidal form [43]. Lindström, 1980 [22] showed that lignin (contains negative groups) is coagulated in the presence of multivalent metal cations, by forming stable complexes but only the high molecular mass fraction of lignin [22, 27]. High molecular weight fraction (above 5,000 g/mol) precipitates almost completely, medium molecular mass (1,000–5,000) precipitates partly, while low molecular mass lignin (<1,000) remains in the effluent [39]. This is mainly attributed to van der Waals attractive forces, which have more wide range for larger molecules/colloid particles than for small molecules [13].

Both alum and ferric chloride had greater removal efficiency of silica than lime, which is attributed to the existence of silica (SiO_2) in many crystalline and amorphous forms [33, 34] with very low solubility in water (6.0 mg/l SiO_2) of crystalline forms. Amorphous silica has a much higher solubility of 100–140 mg/l SiO_2. Two of the main disadvantages of metal salts used in chemical coagulation are the high concentrations of salt required, and the elevated and potentially toxic levels of dissolved metals in the treated effluent [38].

Coagulation with pH adjustment

Coagulation treatment with alum and ferric chloride without and with pH adjustment at 6.2 (in case of alum) and 8.7 (in case of ferric chloride) for treating RAKTA effluent (375 mg/l) and El-Ahlia effluent (250 mg/l) was investigated for the removal of BOD_5, COD, turbidity, tannin and lignin, silica and dissolved Fe and Al (Fig. 3a, b). Results indicated the following:

1. Ferric chloride coagulation was more efficient than alum for removing BOD_5, COD, turbidity, tannin and lignin, and silica from RAKTA wastewater, with and without pH adjustment and from El-Ahlia wastewater without pH adjustment. With pH adjustment, alum was more efficient than ferric chloride for the removing of BOD_5, COD, turbidity, and silica, while both were almost equal for tannin and lignin.
2. Using $FeCl_3$ without pH adjustment achieved average RE% for BOD_5, COD, turbidity, tannin and lignin, and silica of 30.4, 61.0, 98.7, 38.8, and 88.3%, respectively, from RAKTA wastewater compared to 29.0, 60.3, 96.5, 21.7, and 67.8% from El-Ahlia wastewater (Fig. 3b). $FeCl_3$ resulted in an average increase in dissolved Fe recording 194.7% (X RC = 3.279 mg/l) and 255.3% (X RC = 2.7 mg/l) in RAKTA- and El-Ahlia-treated effluents, both of which exceeded the MPL (1.5 mg/l) due to the using of high doses (375 and 250 mg/l) of $FeCl_3$, respectively.
3. With pH adjustment, $FeCl_3$ reduced the RE% of all the investigated parameters except the dissolved Fe concentration, which decreased from 1.168 to 0.365 mg/l with an average RE% of 65.2 (RAKTA) and from 0.76 to 0.12 mg/l with an average RE% of 84.2 (El-Ahlia), reaching lower values than Fe MPL (Fig. 3b). The average RE% for BOD_5, COD, turbidity, tannin and lignin, and silica after pH adjustment recorded 26.1, 59.1, 97.7, 33.1, and 85.8%, respectively, for RAKTA wastewater and 5.2, 46.7, 88.6, 13.6, and 43.6%, respectively, for El-Ahlia wastewater.

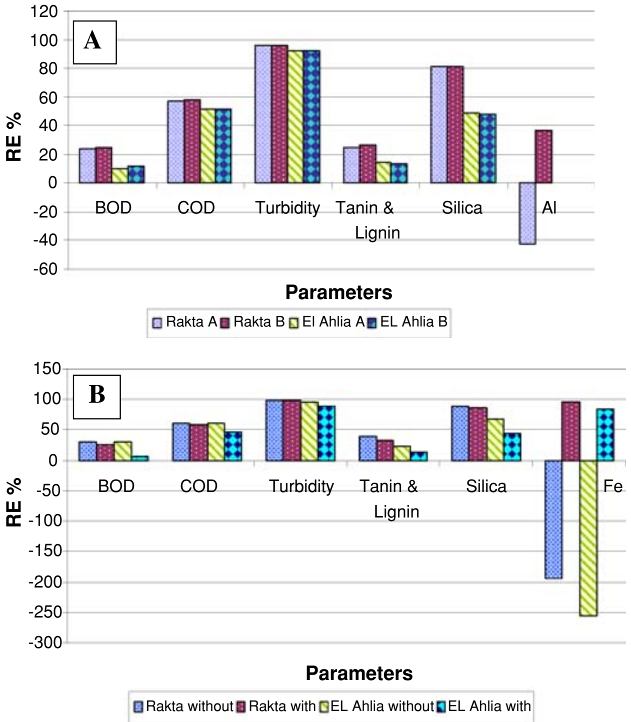

Fig. 3 The treatability effects of (**a**) alum and (**b**) ferric chloride, with and without pH adjustment on the removal efficiency % of the selected contaminants in RAKTA and El-Ahlia effluents

4. Concerning alum treatment (Fig. 3a), no significant differences were recorded in the RE% of the investigated parameters, with and without pH adjustment except for dissolved Al content. BOD_5, COD, turbidity, tannin and lignin, and silica recorded average RE% of 23.8, 57.1, 95.7, 24.1, and 81.2, respectively, without pH adjustment, compared to 24.4, 57.9, 96.1, 26.0, and 81.2% in RAKTA effluent treated with alum and pH adjustment. Similarly, RE% of 9.7, 51.5, 92.0, 13.9, and 48.6% was recorded for BOD_5, COD, turbidity, tannin and lignin, and silica, respectively, in El-Ahlia effluent treated with alum only, compared to RE(%) of 11.7, 51.3, 92.0, 13.3 and 47.7% in the effluent treated with alum and pH adjustment. Al content in RAKTA effluent increased with alum treatment from 0.028 to 0.836 mg/l, while alum and pH adjustment recorded much lower levels of 0.044 mg/l, which is still higher than the initial concentration in the raw effluent (0.028 mg/l). In El-Ahlia effluent, Al content that was not detected in the raw influent increased with alum treatment only to 0.06 mg/l and to 0.03 mg/l with alum treatment under pH adjustment, both of which are much lower than its MPL of 3 mg/l (Fig. 3a).
5. Both alum and $FeCl_3$, with and without pH adjustment, produced effluents with much higher BOD_5 and COD levels compared to their MPLs. Therefore, it was concluded that pH adjustment during coagulation treatment did not enhance the quality of the effluents and has no significant effects, and thus pH adjustment was omitted from the present treatment sequence.

Treatment by oxidation with hydrogen peroxide

Hydrogen peroxide was applied to the chemically treated effluent of RAKTA and El-Ahlia to enhance the RE% of COD, turbidity, tannin and lignin, silica as well as the dissolved concentration of Al and Fe. It was applied as 25, 50, 75, and 100 mg/l (RAKTA) and as 15, 30, 45, and 60 mg/l (El-Ahlia) at different exposure times (0, 20, 40, 60, and 80 min). Results (data are not shown) indicated the following:

1. Hydrogen peroxide (H_2O_2) is a strong oxidant and has high ability to destruct toxic organic compounds to harmless components such as CO_2, water, and inorganic salts or to simpler compounds, which can be subsequently degraded biologically using activated sludge.
2. Oxidation of $FeCl_3$-treated effluents (without pH adjustment) using hydrogen peroxide at all concentrations and exposure times produced the highest removal efficiencies of the tested parameters compared to the previous treatments.
3. The optimum exposure time for hydrogen peroxide oxidation recorded 20 min, after which no significant removals of the tested parameters were achieved.
4. Oxidation of $FeCl_3$-treated effluent of RAKTA (without pH adjustment) with 50 mg/l hydrogen peroxide for 20 min achieved 61.4, 77.3, 91.5, 78.9, and 98.2% RE for COD, turbidity, tannin and lignin, silica, and dissolved concentration of Fe, respectively (X RC = 124 mg/l, 1.5 NTU, 1.4, 4.8, and 0.1 mg/l, respectively).
5. The same treatment with 45 mg/l hydrogen peroxide for 20 min for $FeCl_3$-treated effluent of El-Ahlia achieved 70, 75, 100, 79.6, and 91.5% RE for COD, turbidity, tannin and lignin, silica, and dissolved concentration of Fe, respectively (X RC = 61 mg/l, 2 NTU, 0.0, 6.4, and 0.23 mg/l, respectively).
6. Hydrogen peroxide treatment reduced the iron concentration to levels below the MPL, which confirmed that there was no need for pH adjustment to get minimum Fe solubility.
7. Therefore, based on the previous treatment approaches, results confirmed that coagulation using $FeCl_3$ without pH adjustment followed by oxidation with 50 mg/l (RAKTA) and 45 mg/l (El-Ahlia) hydrogen peroxide for 20 min is the most efficient treatment for the removal of almost all the tested parameters and decreasing their load in both effluents. However, RCs of some parameters, especially the organic load, were still higher than their MPLs and required further treatment especially in RAKTA effluent. Taking into consideration that El-Ahlia effluent characterized by lower pollution strength compared to that of RAKTA effluent, this treatment showed high efficiency even for organic matter content recording levels lower than their MPLs.

Hydrogen peroxide (H_2O_2) was selected, since it is an efficient oxidant (oxidation potential E0 1.76 V) that can destruct toxic organic compounds into harmless components, e.g., CO_2, water, and inorganic salts, or transform them into simpler metabolites, which can be biodegraded later by activated sludge [17]. The high efficiency of H_2O_2 for COD removal in the presence of high Fe levels could be explained by Fenton's reagent (a strong oxidizing reagent), which generates hydroxyl free radicals through the addition of ferrous or ferric iron with H_2O_2. The hydroxyl free radical is more powerful as oxidant than ozone or H_2O_2 and is only surpassed by fluorine [44]. The ferrous ions produced from the above reactions can react with hydroxide ions to form ferric hydroxocomplexes that can coagulate and form large amounts of small flocs. If the concentrations of reactants are not limiting, the organics can be completely detoxified by full conversion to CO_2 and water [25]. The high efficiency of H_2O_2 oxidation for the removal of almost all

Al and Fe is due to the formation of coagulated metal hydroxocomplexes and thus, precipitate Al and Fe [29].

The combination of hydrogen peroxide with $FeCl_3$ without pH adjustment had more efficiency than other chemical treatments for turbidity and color removal due to the generation of hydroxyl free radicals [44]. H_2O_2 removed almost all the lignin and silica present in both effluents within the first 20 min due to their precipitation at the lower pH levels with 0.0 mg/l H_2O_2, since the isoelectric point for Kraft lignin was determined to be at pH 1.0. Consequently, turbidity decreased due to lignin precipitation [6]. However, some contaminants such as the organic load were still higher than their MPLs even with aeration; therefore, biological treatment using bench-scale-activated sludge unit was carried out to get rid of the noncoagulated, nonoxidized contaminants.

Biological treatment using activated sludge

Aeration of raw and chemically treated effluents Only aeration was not enough for the removal of most of the selected parameters, especially organic matter (COD and BOD_5) and color (tannin and lignin), to bring them into acceptable discharging limits even after the chemical treatment with coagulants and oxidizing agents. However, aeration of chemically treated RAKTA and El-Ahlia effluents produced better quality and higher RE% compared to that resulted from the raw effluent, although still not in agreement with the law (Figs. 4, 5).

Optimization of activated sludge treatment To enhance the ability of the activated sludge technique for producing high-quality effluents, operation conditions including the initial sludge concentration and HRT were optimized.

Optimization of the activated sludge concentration Different sludge inocula were tested (500–4,000 mg/l) to determine the appropriate amount of activated sludge for the optimum treatment (Fig. 6). COD removal increased gradually with increasing biomass concentration, approaching a maximum level at 2,000 mg/l for 48 h, which is considered as the optimum dosage of the sludge followed by RE decrease in both raw and treated effluents. Results confirmed that activated sludge is greatly responsible (or the main cause) for COD removal reaching 84.91 and 55.94% for RAKTA raw and treated effluents, respectively, compared to the low efficiency (32.57 and 4.44%, respectively) obtained with only aeration, under the same conditions (Fig. 4). It is also important to notice that chemical treatment is a vital and integrated approach that must be performed prior to the activated sludge treatment to achieve an overall acceptable wastewater quality. This was confirmed by the lowest achieved COD RCs of 24 and 345 mg/l with and without chemical treatment, respectively. Similarly, activated sludge integrated with chemical treatment performed the highest removal of organic matter (as COD) from El-Ahlia wastewater. COD RE recorded 45.86 and 0.52% from the raw and treated effluents, respectively, when only aeration was applied (Fig. 5) compared to 70.05 and 79.27%, respectively, when aeration and activated sludge (2,000 mg/l) were integrated for 48 h as treatment. These results indicated that activated sludge as well as aeration cannot reach acceptable removal limits for COD when applied individually even at longer exposure times and must be applied integrally.

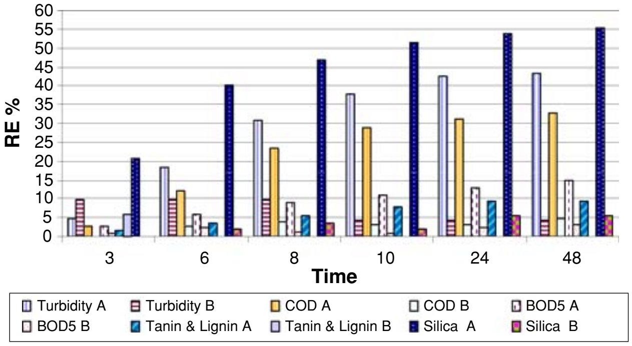

Fig. 4 Effect of aeration at different exposure times on the removal of pollutants from RAKTA raw (**a**) and chemically (**b**) treated effluents

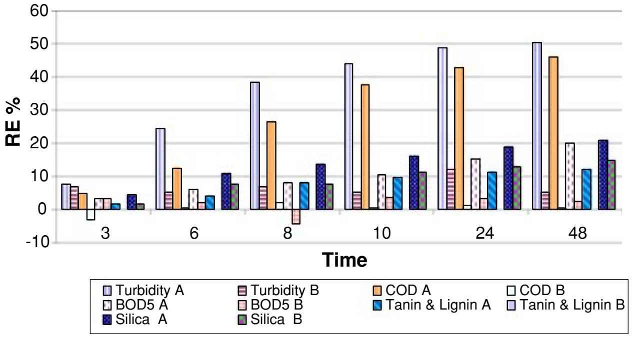

Fig. 5 Effect of aeration at different exposure times on the removal of pollutants from El-Ahlia raw (**a**) and chemically (**b**) treated effluents

Optimization of the hydraulic retention time Optimization of the HRT was carried out at various HRTs (0–48 h) using the chemically treated effluents of RAKTA and El-Ahlia (Table 2). Optimization of the treatment was measured as RE% of COD, BOD_5, tannin and lignin, silica, and mixed liquor suspended solid (MLSS, maximum growth of the sludge) as well as SOUR and SVI. For RAKTA, the highest RE for COD, BOD_5, tannin and lignin, and silica (77.35, 86.72, 92.31, and ≈100%, respectively) were achieved using activated sludge treatment during the first 90–120 min HRT. Similarly, 81.40, 81.97, 100, and 100%, respectively, were recorded as the maximum RE for the same parameters from El-Ahlia effluent within the first 120 min, although 60 min was enough to bring the effluent

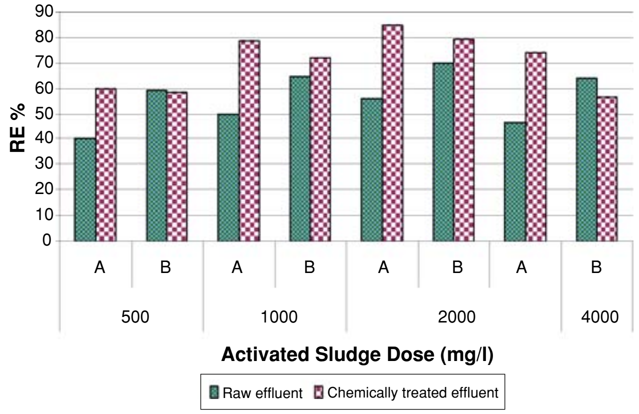

Fig. 6 Optimization of activated sludge dose measured as COD RE% for 48 h using (**a**) RAKTA and (**b**) El-Ahlia effluents

to excellent quality (Table 2). Results indicated that biological treatment of the chemically treated effluents could successfully reach acceptable contaminant limits for safe discharge and fill the deficiency of the chemical treatment. For both effluents, increasing the HRT for 24 and 48 h did not enhance the removal of the target contaminants; moreover, it might increase their levels. The amount of the sludge grown per amount of food consumed (MLSS) were increasing up to 60 and 90 min for RAKTA and El-Ahlia effluents, respectively, due to the presence of plenty of food as organic matter content. Increasing the HRT for 24 and 48 h did not enhance the biomass growth but led to a lessening in the sludge concentration. The SOUR (an indication of biomass activity) decreased as the HRT increased with rapid rate until 120 and 90 min for RAKTA and El-Ahlia effluents, respectively, and then the rate was slowed down. Increasing the HRT for 24 and 48 h did not enhance the biomass growth but led to a decrease in the sludge concentration; thus, the rate of oxygen consumption was decreased. SVI is inversely proportional to TSS; thus, excessive amounts of sludge lead to poor settling. All SVI recorded (a measure of sludge settleability) during activated sludge treatment were below 100 ml/g up to 120 and 90 min HRT for RAKTA and El-Ahlia effluents, respectively, after which there was a decline in its values up to the highest tested HRT (48 h) due to the decrease in the microbial biomass. These results indicated a very good settling characteristic of the sludge without sludge bulking (good sludge has an index of 50–100 ml/g and a bulked sludge may have an index of 200 ml/g or more).

The increase in the sludge concentration increased COD removal except at 4,000 mg/l for both RAKTA and El-Ahlia effluents, respectively. This is mainly related to the lower food to microorganism ratio, which means that at

Table 2 Optimization of hydraulic retention time (HRT) of the activated sludge treatment for 48 h using the chemically treated (ferric chloride: 375 and 250 mg/l and hydrogen peroxide oxidation: 50 and 45 mg/l) RAKTA and El-Ahlia wffluents

Parameters	RAKTA Inf.	Time											
		30 min		60 min		90 min		120 min		24 h		48 h	
		Eff.	RE%	Eff.	RE%	Eff.	RE%	Eff.	RE%	Eff.	RE%	Eff.	RE%
COD (mg/l)	148.67	60.00	59.64	43.67	70.63	34.67	76.68	33.67	77.35	37.67	74.66	39.33	−73.55
BOD_5 (mg/l)	123.00	28.33	76.97	21.67	82.38	17.33	85.91	16.33	86.72	24.67	79.94	27.0	−78.05
MLSS (mg/l)	2,000	2,225	–	2,754	–	2,797	–	2,748	–	1,742	–	1,546	–
Tannin and lignin (mg/l)	1.73	0.90	47.98	0.47	72.83	0.13	92.31	0.13	92.49	0.13	92.49	0.10	94.22
Silica (mg/l)	4.67	3.70	20.77	2.07	55.67	0.43	90.71	0.07	98.50	0.00	100.0	0.00	100.0
SOUR (mg O_2/g TSS h)	30.67	26.33	–	22.33	–	12.0	–	7.00	–	5	–	3.67	–
SVI (ml/g)	62.33	67.33	–	72.67	–	79.33	–	83.33	–	57.33	–	51.33	–

Parameters	El-Ahlia Inf.	Time											
		30 min		60 min		90 min		120 min		24 h		48 h	
		Eff.	RE%	Eff.	RE%	Eff.	RE%	Eff.	RE%	Eff.	RE%	Eff.	RE%
COD (mg/l)	71.67	41.00	42.79	15.00	79.07	13.33	81.40	13.67	80.93	22.33	68.84	30.00	58.14
BOD_5 (mg/l)	61	30	50.82	11	81.97	11	81.97	11	81.97	16	73.77	19	68.85
MLSS (mg/l)	2,000	2,253	–	2,815	–	2,744	–	2,514	–	1,819	–	1,466	–
Tannin and lignin (mg/l)	0.03	0.03	0.00	0	100.00	0	100.00	0	100.00	0	100.00	0	100.00
Silica (mg/l)	2.10	0.73	65.24	0.13	93.81	0.03	98.57	0.00	100.00	0.00	100.00	0.00	100.00
SOUR (mg O_2/g TSS h)	32.33	26.33	–	18.33	–	12.67	–	10.33	–	6.00	–	3.33	–
SVI (ml/g)	56.67	59.33	–	65.33	–	69.00	–	54.67	–	49.67	–	46.00	–

Each reading is an average of three runs the lower sludge concentrations the organic matter available in the effluent (substrate or food) are enough for both the growth and sustaining the degrading microorganisms, but at the higher concentrations of the sludge (biomass), food is only available for sustaining these microorganisms. This fact also explained the relation between COD, BOD_5, and MLSS, where the amount of sludge grown per amount of food consumed reached the maximum capacity for substrate degradation until 120 and 60 min for both effluents, respectively. Increasing the HRT to 48 h did not lead to further growth of the sludge, but conversely, led to a reduction in the biomass concentration. Limitation of microbial growth at higher HRT leads to a decrease in the COD RE%, which is mainly because of the fact that after 120 and 60 min, respectively, biodegradable organic matter (substrate) started to deplete and became not sufficient to support the growth of the sludge leading to a reduction in the biomass concentrations, which in turn reduced COD and BOD_5 removal. Therefore, 60–90 min was considered the optimum HRT of the activated sludge for achieving its maximum capacity for COD and BOD removal.

Moreover, COD removal from both effluents was found to be a result of the integrated chemical–biological treatment and cannot be achieved by one-step process even when applied for longer exposures. This finding is mainly due to the high toxicity of black liquor to the activated sludge even with acclimation for relatively long periods and also due to the fact that not all compounds present in the black liquor were biodegradable.

Activated sludge treatment of both effluents revealed that COD removal is much higher in the chemically treated effluents than their corresponding raw forms. This is mainly due to the presence of large amount of biodegradable compounds in the effluent after hydrogen peroxide oxidation than in the raw effluent. Also, transition metal salts in the coagulation process are strong oxidants for refractory contaminants such as highly molecular weight chlorinated aromatic compounds (e.g. lignin derivatives). Oxidation can be effectively used for the destruction of toxic wastes and nonbiodegradable effluents to render them more suitable for a secondary biological treatment [4]. Therefore, it is concluded that coagulation reduced the toxicity of black liquor against the activated sludge, while H_2O_2 oxidation destructed the toxic wastes and nonbiodegradable effluents, both of which highly facilitated the treatment process and allowed the activated sludge to produce high-quality effluents with acceptable limits for all the prevailed contaminants. Most of the COD removal took place within in the first 120 and 60 min for RAKTA and El-Ahlia effluents, respectively, followed by a decline, which may be a result of the contamination from aeration as well as the prevalence of sludge endogenous phase, where a lot of free swimming microbial and sludge cells begin to lyse.

Two general mechanisms, by which microorganisms might degrade lignin components, have been proposed: (1) depolymerization of lignin macromolecules with release of monomeric and dimeric lignin fragments, which are transported into microbial cells where they are degraded, and (2) dearomatization of the intact polymer by cleavage of rings, while they are still bound in the macromolecule, followed by the erosion of the resulting polymeric, aliphatic network [8]. Activated sludge was able to remove almost all silica present in the sample after 120 min. Removal mechanisms involve mainly adsorption and complexation with the microorganisms in the activated sludge similar to the removal of metals due to the interactions between the metal ions and the negatively charged microbial surface. Metals may also be complexed by carboxyl groups found in the microbial polysaccharides, and other polymers, or adsorbed by protein material in biological the cell [24].

Application of the optimized operation conditions using batch reactor treatments for the contaminated effluents

Based on the previous results, optimized operational conditions for the batch chemical and the continuous biological treatment sequences were proposed. These conditions were applied as bench scale on the raw effluents of RAKTA and El-Ahlia. The sequences are as follows:

1. Coagulation treatment with 375 and 250 mg/l $FeCl_3$ for RAKTA and El-Ahlia, respectively.
2. Oxidation with 50 and 45 mg/l hydrogen peroxide for 20 min for RAKTA and El-Ahlia, respectively.
3. Activated sludge treatment with 2,000 mg/l initial sludge inoculum for 90 and 60 min HRT for RAKTA and El-Ahlia, respectively.

Application of this treatment sequence for RAKTA and El-Ahlia raw effluents (Table 3) revealed the following:

1. RAKTA raw effluents (stronger than that of El-Ahlia) were characterized by high levels of COD (761–855 mg/l), BOD_5 (209–305 mg/l), tannin and lignin (21.3–31.4 mg/l), turbidity (513–690 NTU), TSS (2014–2906 mg/l), and silica (152–201 mg/l). El-Ahlia raw effluents were characterized by COD (504–613 mg/l), BOD_5 (152–188 mg/l), tannin and lignin (11.2–13.3 mg/l), turbidity (223–253 NTU), TSS (721–797 mg/l), and silica (68.5–91.5 mg/l).
2. Pollution load in RAKTA and El-Ahlia raw effluents decreased gradually stepwise as the treatment proceeded according to the above mentioned schedule.
3. With the final step (activated sludge treatment), all the effluent contaminants reached values much lower than their MPLs that are fully acceptable for safe discharging of this kind of effluents. The RC ranges of the vari-

Table 3 Effects of the sequential integrated chemical–biological treatments on the removal of the different contaminants polluting RAKTA and El-Ahlia raw effluents

Parameters	RAKTA raw effluents	Residual concentration (mg/l) in the treated effluents		
		Coagulation with 375 mg/l $FeCl_3$	Oxidation with 50 mg/l H_2O_2	Activated sludge (90 min)
COD (mg/l)	761–855	281–390	88–167	21–44
BOD_5 (mg/l)	209–355	149–213	71–153	13–25
Tannin and lignin (mg/l)	31.4–21.3	15.3–22.8	0.9–2.3	0.0–0.2
Turbidity (NTU)	513–690	7–12	1.2–2.3	–
TSS (mg/l)	2,014–2,906	17.8–41.7	–	–
Silica (mg/l)	152–201	28.8–63.8	3.3–6.3	0.0–0.4
MLSS (mg/l)	–	–	–	2,376–2,741
SOUR (mg O_2/g TSS h)	–	–	–	8–15
SVI (ml/g)	–	–	–	52–88

Parameters	El-Ahlia raw effluents	Residual concentration (mg/l) in the treated effluents		
		Coagulation with 250 mg/l $FeCl_3$	Oxidation with 45 mg/l H_2O_2	Activated sludge (60 min)
COD (mg/l)	504–613	187–332	53–88	15–31
BOD_5 (mg/l)	152–188	109–140	42–67	8–25
Tannin and lignin (mg/l)	11.2–13.3	7.5–10.1	0.0–0.1	0.0–0.0
Turbidity (NTU)	223–253	5–14	1.1–2.6	–
TSS (mg/l)	721–797	14.3–28.1	–	–
Silica (mg/l)	68.5–91.5	18.3–33.3	2.8–9.1	0.0–0.0
MLSS (mg/l)	–	–	–	2,200–2,665
SOUR (mg O_2/g TSS h)	–	–	–	8–22
SVI (ml/g)	–	–	–	54–78

Each reading is an average of three runs

ous contaminants in the final treated RAKTA effluent recorded 21–44, 13–25, 0–0.2, and 0.0–0.4 mg/l for COD, BOD_5, tannin and lignin, and silica, respectively, while 15–31, 8–25, 0.0–0.0, and 0.0–0.0 mg/l were recorded as the RCs ranges for COD, BOD_5, tannin and lignin, and silica of final treated effluents El-Ahlia, respectively. Moreover, the SVI values during both treatments indicated a good settling quality of the sludge.

Therefore, the application of the sequential treatments confirmed the high quality of the produced effluent and the removal of the organic load as well as high molecular weight compounds and silica and achieving the main objective of this study.

Conclusion

In conclusion, results clearly showed that the proposed treatment sequences were able to remove almost all the COD, BOD_5, high molecular weight compounds, and silica of RAKTA and El-Ahlia raw effluents. Results also confirmed that activated sludge treatment of RAKTA and El-Ahlia effluents achieved the optimum operational conditions for the maximum removal of organic loads with initial sludge inoculum of 2,000 mg/l and HRT of 90 and 60 min, respectively. Therefore, the application of the integrated sequential treatments confirmed the high quality of the produced effluent for the safe discharge into natural water courses. It is also economical, easy to maintain and scale up for application in the large industries.

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