Original article

Inhibiting effect of textile wastewater on the activity of sludge from the biological treatment process of the activated sludge plant

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ABSTRACT

Textile industry represents an important source of toxic substances rejected in environment. Indeed, effluent of these industries contains dyes and chemicals. They are rejected in environment without any treatment. The aim of this work is to evaluate ecotoxicological effect of industrial textile effluents on the sludge harvested from activated sludge treatment plant of Marrakech city (Morocco). For this, we are interested in determining the inhibition condition that corresponds to 50% decrease of bacterial activity in sludge. Obtained results showed that inhibition percentage of bacterial activity depends narrowly on contact time and on added effluent volume, until a limit concentration where there is no degradation of substratum. In fact, substratum degradation speed shows about 65 times decrease when 80% (v/v) of textile wastewater is added, in comparison with the controlled one. Consequently the inhibition constant (Ki) that corresponds to 50% of bacterial inhibition activity is estimated to 0.65 mg l^{-1} of dye. These studies confirm a real ecotoxicological risk of these effluents. Therefore, a treatment is mandatory before their rejection in environment.

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1. Introduction

Approximately 1.84 billion metric tonnes of texitle-dyeing wastewater was produced in the Chinese in 2015 according to the China Environment Statistical Yearbook (2015).

The Moroccan industrial sector is composed of 6070 units in which 31% are textile and leather industries. These industries consume significant quantities of dye and chemicals products in the various manufacturing synopsis (Khandegar and Saroha, 2013; Prigione et al., 2008). Those substances are known for their high toxicity rate (Jieying et al., 2017).

Enormous quantities of wastewater characterized by high concentrations of chemical oxygen demand (COD), suspended solids, heavy metals and salts are produced in the textile industries (Yurtsever et al., 2015). The highly variable nature of textile wastewater is due to the use of multiple processes such as dyeing, finishing, sizing, several washing, and rinsing cycles (Khandegar and Saroha, 2013; Prigione et al., 2008; Sahinkaya et al., 2008).

Due to their high fixation rate compared to other types of dyes, the annual worldwide use of reactive dyes reached an amount of 178,000 tons in 2004 (Philips, 1996). Reactive dyes are the most widely used with a market share of 60–70% (Çinar et al., 2008; Sen and Demirer, 2003a) and about 20–50% of the applied dyes remain in the aqueous phase during dyeing which eventually leads to the colorization of the flow. In addition to the dyes, several auxiliary chemicals are used in the maturation processes and the wastewater produced is quite complex and variable in characteristics (Sen, 2003b; Spagni et al., 2012). These reactive dye molecules, which are often highly water soluble, generally pass through the conventional system of activated sludge or municipal wastewater treatment systems, virtually unchanged (Willmot et al., 1998). The qualities of the products required by the textile industry and

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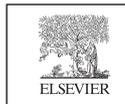
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consumers, namely high wash stability and wide range of colors, require the use of these reactive dyes even if they are not biodegradable (Cooper, 1998). In the textile industry, the dyeing processes is an essential link in the production chain. The effluents discharged by these processes contain products which give them a toxic character, notably dyes, detergents, insecticides, fats, oils, sulphates, solvents, and fibers (Gebrati et al., 2011; Balanosky et al., 2000).

According to Mountassir et al. (2013) and Kacha et al. (1997), this wastewater is also characterized by high pH, high temperature, and organic load as well as extreme colors. These carcinogenic and mutagenic pollutants (Sandra et al., 2000) are resistant to biodegradation and possess a potential for inhibiting microbial activity. This resistance is related to dyes, surfactants, and other additives used in large quantities by these industries (Sandra et al., 2000). The treatment of textile wastewater from these industries can be carried out either by physicochemical means or by a combination of a physicochemical and biological processes, most of these biological processes have often been recommended after a pre-treatment in order to reduce the polluting load of these effluents.

In the city of Marrakech, like other cities in the country, textile industries discharge their wastewater into the sewage network without any prior treatment. This wastewater is then conveyed to the activated sludge treatment plant. We therefore propose to study the ecotoxicological impact of dyestuffs and wastewater from these textile industries using the sludge of the activated sludge treatment plant by determining the inhibition conditions that corresponds to a decrease of 50% of bacterial activity.

Therefore, appropriate treatment is required before the discharge of textile wastewater due to their highly toxic nature (Sahinkaya et al., 2017).

2. Materiel and methods

The experiment was carried out in a PVC reactor, 8 cm in diameter and 30 cm in length, equipped with a pH electrode enabling the evolution of the pH to be monitored during the experiment. The pH was maintained at a value of 6.5 by the addition of the appropriate amounts of H_2SO_4. Aeration of the system was provided by an air pump, the concentration of oxygen was maintained at 8 mg/l. The sludge activity test was carried out by measuring the COD (Chemical Oxygen Demand) before and after the introduction of the sludge.

The physicochemical characteristics of the textile wastewater original from textile industrial "Tenmar" Located in the industrial zone of Marrakech City (Morocco) and sludge from the activated sludge treatment plant are respectively grouped in Tables 1 and 2.

The wastewater of textile brought to different percentages: 0; 20; 50; 80; 100% (V/V), was 100% supplemented with mineral water whose mineralogical composition is shown in Table 3. The sludge was added at a rate of 70 mg/l. All experimental tests were carried out at a temperature of 20 °C. The kinetics of removal of COD and color was followed after injection of the different doses of textile wastewater.

Over time, a volume of 50 ml was taken from inside the reactor and centrifuged for 10 min (5000 rpm) in order to eliminate turbidity which may cause interference when measuring the

Table 2
Physico-chemical characterization of the sludge from the activated sludge plant (city of Marrakech).

characteristics	Sludge
Moisture content %	81 ± 4
Volatile solids % DS	58 ± 2
pH	6.9 ± 0.2
Electrical conductivity mS/cm at 20 °C	667 ± 5
Total organic carbon μg/g	330 ± 25
Total nitrogen Kjeldahl μg/g DS	27 ± 4
Total phosphorus μg/g	1.2 ± 0.4
Chromium (Cr) mg/kg DS	2363 ± 43
Copper (Cu) mg/kg DS	147 ± 5
Arsenic (As) mg/kg DS	6 ± 1
Lead (Pb) mg/kg DS	99 ± 3
Zinc (Zn) mg/kg DS	796 ± 9
Iron (Fe) mg/kg DS	14,100 ± 110
Manganese (Mn) mg/kg DS	210 ± 24
Total coliform CFU/g DS	$1.32 \times 10^6 \pm 9.00 \times 10^4$
Fecal coliform CFU/g DS	$6.74 \times 10^5 \pm 2.43 \times 10^3$

Table 3
Mineralogical composition of dilution water.

Cations	Concentration (mg L^{-1})	Anions	Concentration (mg L^{-1})
Ca^{++}	12.02	HCO$_3^-$	103.70
Mg^{++}	8.70	CL$^-$	14.20
Na$^+$	25.50	NO$_3^-$	0.10
K$^+$	2.80	SO$_4^{2-}$	41.70

absorbance. The obtained supernatant made it possible to assay the COD by oxidation with potassium dichromate in acidic medium and by hot method according to the AFNOR method (AFNOR, 1983).

The volatile suspended solids (VSS) were determined on the mixed liquor respectively by evaporation at 110 °C. and then calcination at 550 °C.

Physico-chemical analyzes of waste water (Table 1) and sludge (Table 2) were carried out according to the methods recommended by Rodier (1984) and Aubert (1978) respectively.

3. Results and discussion

3.1. Inhibition of the initial rate of substrate elimination

The kinetics of elimination of the substrate as a function of time and of the concentration of the waste water are illustrated in Fig. 1.

The results obtained show that the removal of COD increases as the percentage of textile wastewater decreases. After 5 h of experimentation, the removal of the substrate is 51 and 9.1% respectively for a 20 and 80% of the input textile waste water.

The Initial COD/Initial SSV ratios are greater than 0.5; therefore, these ratios are sufficient for bacterial growth under the operating conditions of the bioreactor (Zhu et al., 2002; Benmoussa et al., 1986). Indeed, the speed of use of the substrate can be described by the Monod equation which is an approximation of Michaelis-Menten. This equation describes the relationship between the growth rate (μ), the maximum growth rate (μ$_{max}$), the substrate concentration and the K$_s$ constant.

Table 1
Physico-chemical characterization of textile wastewater original from textile industrial "Tenmar" Located in the industrial zone of Marrakech City (Morocco).

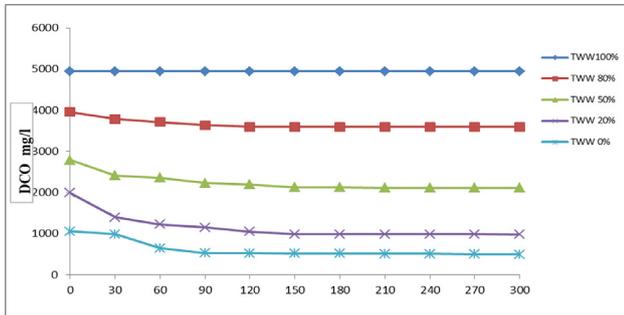| Parametre	pH	MES mg/l	T °C	CE ms/cm	DCO mg/l	DBO$_5$ mg/l	NTK mg/l	Pt mg/l	SO$_4^{2-}$ mg/l	NaCl mg/l
Average	8.6 ± 0.2	396 ± 15	57 ± 23	6.2 ± 1.8	2680 ± 797	240 ± 35	92 ± 19	36 ± 21	870 ± 113	714 ± 352

Fig. 1. Kinetics of substrate removal (COD) as a function of time and concentration of textile waste water (TWW).

Thus in equation $[dS]/Xdt_o = \mu_{max} \cdot S/(K_s + S)$, it would be appropriate to replace $[dS]/Xdt_o$ by μ.

The relationship would then become: $\mu = \mu_{max} \cdot S/(K_s + S)$.

with

$[dS]/Xdto$: Specific substrate utilization rate.
S: Substrate Concentration (mg l^{-1}).
K_s: saturation constant (mg l^{-1}).
X: biomass constant (mg l^{-1}).

The saturation constant and the maximum rate of bacterial growth are respectively evaluated at 881.67 mgDCOl^{-1} and 0.086 h^{-1}.

The graphical representation of $1/\mu$ as a function of $1/S$ makes it possible in determining Ks and μmax. Fig. 2 shows that this is a highly significant positive correlation. Indeed, the specific rate of use of the substrate decreases, as both the percentage of the substrate and inhibitor increase. The saturation constant and the maximum rate of bacterial growth were evaluated at 881.67 mgDCOl^{-1} and 0.086 h^{-1}, respectively.

3.2. Study of the distribution of the dye in the medium

Before studying the behavior of the biomass, it is necessary to study the adsorption of the dye (Co) on the sludge used. Indeed, by bringing the report (SSV/([Coi] − [Coeq])) as a function of the inverse of the concentration of dye remaining in solution at equilibrium (1/[Coeq]), we note that the adsorption of the dye is carried out in a significant way (0, 2%) (Fig. 3), and that the Langmuir relation applies well to the experimental points according to the following equation:

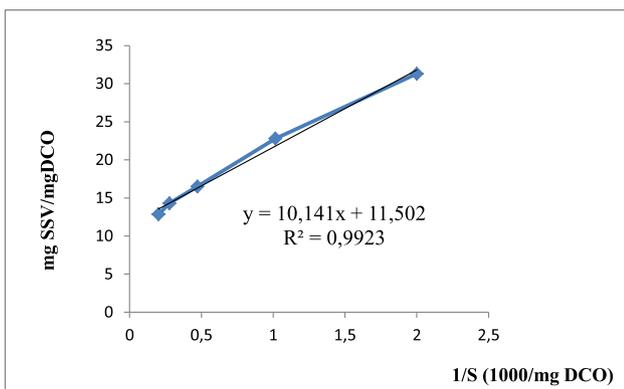$$([Coi] − [Coeq])/MVES = b \cdot C^* \cdot [Coeq]/(1 + b \cdot [Coeq])$$

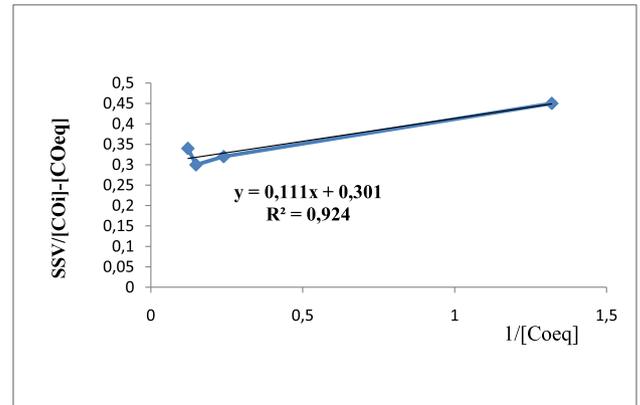**Fig. 2.** Evolution of the initial rate of substrate elimination as a function of $1/\mu$.

Fig. 3. The ratio (SSV/[Coi]-[Coeq] as a function of the reverse of the concentration of dye remaining in solution at equilibrium (1/[Coeq]) allowing the determination of b and C*.

With

C*: Maximum adsorption capacity of the dye by the sludge (mg of Co.gSSV^{-1}).
b: Coefficient related to the adsorption energy (l/mg).

The results recorded (Fig. 3) give values of mg Co/g SSV and 0, 0027 L/mg respectively for C* and b.

Indeed, the total theoretical inhibition of bacterial activity produced by the colored textile waste water in the biological reactor containing 2.6 g/l of SSV would be 8.58 mgCol^{-1}.

The study of the inhibition of activated sludge activity in the presence of dye (Co) reveals also that 1.09 mg/l of Co leads to a total inhibition of the bacterial activity in the biological reactor containing 0.76 g SSV/gCOD (Pala and Tokat, 2002).

3.3. Coefficient of degradation rate of substrate

The kinetics of substrate removal as a function of time (Fig. 1) shows that from one hour thirty to two hours of incubation, the degradation of the substrate is slowed down. This implies that the textile wastewater, at a certain dose given, inhibits the activity and the good functioning of the microorganisms. The substrate degradation rate constant (K′) can be deduced from the following equation (Benmoussa et al., 1986):

$$(S_o − S_t)/S_t = K.X.t,$$

with:

K′: substrate degradation rate constant (l/mg/h)
X: MVES concentration in the bioreactor (g/l)

The results shown in Fig. 4 confirm those obtained previously. Indeed, the degradation rate constant of the substrate decreases by about 65 times as a result of 80% (V/V) supply of textile waste water.

The values obtained from K′ are inversely proportional to those of [Co] and the relation linking these two parameters is:

$$K' = 0.5645e^{−0.255[Co]}$$

The relationship between K′ and [CO] (Fig. 4) shows that at low concentration of [CO] there is a steep increase in the rate of reaction with increasing [CO] concentration. However, at high concentration of |CO|, one of the approaches has been to slow down the rate of growth on a readily metabolizable substrate.
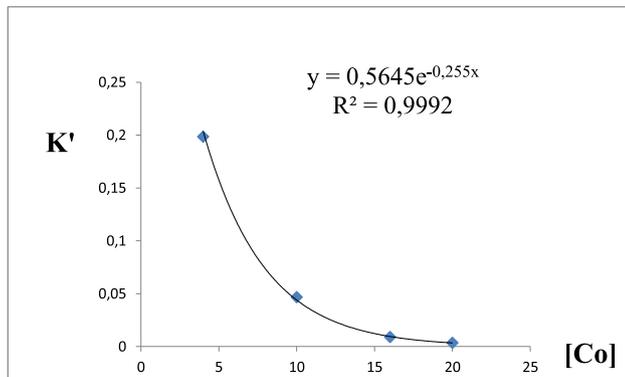
Fig. 4. Evolution of K′ as a function of the concentration of colorant [Co] provided by the textile effluents.

According to Eq. (K′ = 0.5645e−0.255[Co]), the low Ks for CO means that high rate of substrate utilization can be achieved at the low concentration, while the high Ks for CO means that much higher concentration of microorganisms would be needed to increase the utilization rate of CO. An increase in the k value would increase the rate of CO utilization. The kinetics of substrate utilization would be the critically important factors that can be influenced by CO concentrations (Helbling et al., 2014; Turkdogan-Aydinol et al., 2011).

3.4. Determination of the inhibition constant (Ki) of the dye provided by the textile wastewater

For each concentration of effluent, we determined mass speed of the substrate removal (r) measured by the slope of the COD experimental line as a function of time, in order in determining the inhibition rate (i), given by the following formula (Benmoussa et al., 1986):

$$i = (r_0 - r)/r_0$$

Hypothesis of a noncompetitive inhibition, if S and I are the respective concentrations of substrate and inhibitor, mass speed of the elimination is given by the following equation (Benmoussa et al., 1986):

$$r = r_0.S/(K_s + S)(1 + I/K_i)$$

Ks: Michaelis constant of the substrate S
Ki: inhibition constant which corresponds to the inhibitor concentration which causes 50% inhibition of bacterial activity

In our manipulations, we have S >> Ks because the substrate is used in sufficient quantity. Hence the following relation:

$$1/i = K_i/I + 1$$

Graphical representation of 1/i in function 1/I allow the determination of K_i. According to experience:

$$1/i = 0.65345(1/I) + 0.8654$$

The inhibition constant Ki corresponding to 50% inhibition of bacterial activity is evaluated at 0.65 mg/l. On the other hand, the ordinate at the origin is different from 1, this can be explained by the superposition of other phenomena (precipitation of the dye) or the existence of other inhibitors other than dyes, namely detergents.

The adsorption capacity C^* obtained is 5 times greater than the value of the inhibition constant K_i. Therefore, a high adsorption capacity does not mean that the bacterial activity will be all the more important.

4. Conclusion

This research is carried out with the aim of studying the impact of textile wastewater on the sludge bacterial activity from the activated sludge plant in the city of Marrakech (Morocco). The results obtained showed that the inhibition percentage of this activity depends closely on both the time and the effluent concentration till a limit value where the removal of the substrate is completely stopped. However, we noticed a 65 times decrease in the specific speed of use of the substrate due to an 80% (V/V) supply of textile wastewater. The correlation between the coefficient of degradation rate of the substrate and the concentration of dye is described by the following relationship:

$$K = 0.5645e^{-0.255[Co]}$$

The study of the distribution of dye in the medium reveals that the dye is adsorbed in a significant way and that the Langmuir law adjusts to the experimental points obtained during this study. The maximum adsorption capacity of the dye is 3.3 mg Co/g MVES, with an adsorption energy coefficient of 0.0027 L/mg.

The inhibition constant (Ki) which produces 50% of the inhibition of bacterial activity is evaluated at 0.65 mg/l, while the concentration of dye in the textile wastewater of the city of Marrakech is 20 mg/l, thus the inhibition of sludge from the activated sludge plant in the city of Marrakech may be due to other chemicals used in large quantities by the textile industries, in particular detergents. While the risks of inhibiting the activity of the sludge due to the textile wastewater in the city are conceivable, hence the need for treatment of these wastewater before any discharge into the receiving network.

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