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Treatment of printing wastewater by a combined process of coagulation and biosorption for a possible reuse in agriculture

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ABSTRACT

A coagulation–flocculation process was used to treat water-based printing ink wastewater in optimal conditions. A biological process treatment was combined to coagulation–flocculation process using fungal biomass biosorption capacity. Combined process has a significant effect on color removal and on COD removal (80%). The potential of reusing treated wastewater in agriculture was investigated. Germination tests of five species were carried out using treated and untreated wastewater and show that these effluents could be adequately recycled in culture irrigation.

Keywords: Printing ink wastewater; coagulation–flocculation; biosorption; germination test

1. Introduction

Water-based printing ink utilizes water as carrier to substitute a majority of organic solvent from solvent-based printing ink. Consequently, it produces less objectionable vapors in the workplace and does not contaminate packaged products [1]. Water-based printing ink has been widely used in packaging industry for the conditioning of cardboard boxes and the printing of advertisements, especially for printing the packaging of food, drug, toy, tobacco, and so on. In recent years, the annual increment of water-based printing ink consumption is 10–50%. During the production and consumption of water-based printing ink, equipment need to be cleaned frequently due to altering different colors of ink. Wastewater obtained from cleaning of the laboratory and industrial equipment is highly colored by pigments, which are invisible even at very low concentration, and is also highly contaminated by organic materials.

Typically, printing ink is a complex, multi-component compound composed essentially of dyes and pigments, resins, binders, solvents, and optional additives. Obviously, the wastewater generated from the printing process is highly colored and contaminated with organic minerals because of the aforementioned compounds. Hence, the wastewaters from such printing installation cannot be directly discharged into receiving streams without any treatment, not only due to its deleterious effect on human health and on the environment, but aesthetically due to the visibility of the color even at a low concentration [2].

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Wastewater quality varies with the different kinds of ink, which have different connected makings, pigments, and additives. The quality and quantity of wastewaters also varies with the different process section of the ink production [3]. Printing ink wastewater is usually difficult to treat biologically, but the possibility of utilizing bacteria to treat and degrade printing ink in wastewater was proposed [4]. Since coagulation–flocculation was shown to be a simple and efficient method for removing a substantial portion of the organic content and a very good method for the removal of color and turbidity [5–7].

Coagulation is mainly done with inorganic metal salts (aluminum and ferric sulphates and chlorides), polyelectrolytes of various structures (polyacrylamides, chitosan) [8]. According to Duran and Georgy [9], aluminum and iron salts are widely used as coagulants in water and wastewater treatment, and in some other applications. Their mode of action is generally explained in terms of two distinct mechanisms: Charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate so-called sweep flocculation. It was found that the praestol anionic flocculant used simultaneously with aluminum sulfate at the water-treatment plants provides efficient purification of water and wastewater [10].

In the coagulation–flocculation process, many factors can influence its efficiency, such as the type and dosage of coagulant/flocculant, pH [11], mixing speed and time [12], temperature and retention time [13], etc. Fendri et al. [14] have reported that coagulation–flocculation process used in optimal conditions can reduce turbidity and organic charge. However, the application of coagulation as a single process seems to be insufficient to remove total dark color from industrial wastewater. Henceforth, the combination of another process can reduce color. Ma and Xia [15] reported the efficiencies of Fenton process combined with coagulation to treat water-based printing ink wastewater. In another part, *Aspergillus niger* was known to be the micro-organism, which is the most efficient to remove color from wastewater by biosorption process [16]. It has been reported that *A. niger* biomass is able to remove completely black color in effluent generated from marine products processing factory [17].

The main objective of this work was to study the effect of the combination of a biological process using biosorption of fungal biomass to coagulation treatment on black color elimination. Finally, treated and untreated wastewaters were used on germination test of barley (*Hordeum vulgare*), feed barley (*Hordeum vulgare hexastichum*), wheat (*Triticum sativum*), fenugreek (*Trigonella foenum graecum*), and sorghum (*Sorghum bicolor*) to study their phytotoxicity effects.

2. Materials and methods

2.1. Wastewater

The wastewater used in the present study was collected from a card board packing industry located in Sfax, (South of Tunisia). This effluent presents a dark gray color mainly caused by the solid ink residue. Wastewater generated from printing process mainly is comprised of wiping solution cleaning along with excess ink including washings from printing section. Ink was present in colloidal form in the wastewater, and the quantity of wastewater generation from the printing section of the press was around 4.0 m^3/d. Sample collection and preservation were done in accordance with the Standard Methods for the Examination of Water and Wastewater [18]. Physicochemical analysis (pH, COD, TSS, …) of effluent was carried out immediately after samples arrived in the laboratory according to the standard methods [19]. The pH and temperature of the UNIPACK effluents were measured using a multifunction pH-meter Testo model (ECOMETP25, South Korea) was used to measure pH (precision 0.01) and temperature (precision 0.01). The color of the effluent was noted by visual observation. The remaining effluent characteristics parameters, i.e. total suspended solid (TSS), volatile solid (VS), total solid (TS), biological oxygen demand (BOD), and COD were analyzed by volumetrically/titrimetrically as per standard methods [19,20]. The characteristics of this wastewater are given in Table 1.

2.2. Coagulation–flocculation treatment

Industrial grade aluminum sulfate and praestol were used as the coagulant and as flocculant,

Table 1
Characteristics of industrial wastewaters

Industrial wastewaters	Average values	CV (%)
pH	7.79 ± 0.79	10.21
Color	Black	–
T (°C)	25.01 ± 0.10	–
COD_s (mg/l)	24,046 ± 13,306	55.33
COD_t (mg/l)	38,595 ± 20,926	54.21
BOD_5 (mg/l)	9,750 ± 3,126	32.06
TSS (mg/l)	4,228 ± 2,600	61.50
TS (mg/l)	27,555 ± 11,488	41.69
VS (mg/l)	16,840 ± 9,574	56.85
Salinity (g/l)	2.00 ± 0.10	
COD_t/BOD_5	3.74 ± 1.06	28.39

respectively. The chemical compounds were obtained from Fisher Scientific UK Ltd. They were prepared by dissolving powder with distilled water. The coagulation–flocculation experiments were conducted in bench scale using optimal doses previously described by Fendri et al. [14] (coagulant dose 8,250 mg/l; floculant dose 80 mg/l and pH 7.25). Treatment with the coagulation–flocculation process has been performed on the raw sewage without dilution.

2.3. Biosorption process

Biomass of *A. niger* was prepared according to Khannous and Gharsallah [17] and Naoyuki et al. [21], 1 ml aliquot of spore suspension (10^5 spore/ml) was used to inoculate 1 l Erlenmeyer conical flasks, each containing 0.1 l sterile GPY liquid medium (glucose–peptone-yeast extract) containing 10 g/L glucose; 3.0 g/L peptone; 2.0 g/L yeast extract; 1.0 g/L K_2HPO_4; and 0.5 g/L $MnSO_47H_2O$. pH was adjusted to 4.0 prior to autoclaving. Culture was incubated for 24 h at room temperature on a reciprocal shaker (150 rpm). This cultivation produced pellets of about 3 mm diameter. For the decolorization test by biosorption, the pellets were harvested after 24 h of growth by filtering. The harvested fungal pellicles were washed with generous amounts of deionized water. The biomass (85 g/l) was transferred into 100 ml of treated wastewater using coagulation process (in optimal conditions) for 24 h at room temperature.

2.4. Germination essays

Germination test was performed by using untreated and treated wastewaters (coagulation–flocculation in optimal conditions of treatment and combined process) according to Zucconi et al. [22]. Tap water was taken as a control (pH 6.5, turbidity: 25 NTU, conductivity: 400 μS/cm, chloride concentration: 0.1 mg/l). The germination indexes were determined for five vegetable species barley (*Hordeum vulgare*), feed barley (*Hordeum vulgare hexastichum*), wheat (*Triticum sativum*), fenugreek (*Trigonella foenum graecum*), and sorghum (*Sorghum bicolor*). The choice of these plant species is based on the results of previous works of Mekki et al. [23] and Arzu et al. [24]. Ten seeds of each vegetable were placed on Petri dishes containing a filter paper and were moistened with 10 ml of water. The Petri dishes were then placed for six days at 25 ± 1˚C in darkness.

Germination was recorded daily at a fixed hour, and a germination index percentage (GI) was calculated by counting the number of germinating seeds and the average sum of seed's root elongation in a sample as related to the control [25]. Results were finally expressed according to the following formula:

$$GI = \frac{GS}{GC} \times \frac{LS}{LC} \times 100 \quad (1)$$

where GS and GC are the number of seeds germinated in the sample and the control, and LS and LC are the root lengths in the sample and the control, respectively. The germination index is measured as % of control.

A seed was considered germinated when its root length exceeded 5 mm. For root length below 5 mm, it was considered equal to zero and the seed was not considered as germinated.

All experiments were carried out in triplicate and the results were averaged.

3. Results and discussion

3.1. Biosorption essay

Treatment of water-based printing ink wastewater using coagulation and flocculation process in optimal conditions can eliminate black color induced by ink. However, treated wastewater has a purple color. Indeed, the black color of wastewater is induced by ink used in printing process. Ink of the flexographic type contains pigments (organic or inorganic) dispersed in the varnish. The other compounds which are usually found in the ink, apart from about 60% water are: acrylic resins, waxes, anti foams additives, and various other additives. The organic pigments contain various metal oxides that give certain colors [26].

In order to further remove the color from wastewater, a biological process was combined to coagulation process. The objective of the first part of our work is to investigate the potential of *A. niger* as biosorbent for the color removal from wastewater treated preliminarily by coagulation–flocculation process in optimal condition. *A. niger* biomass collected after culture in GPY media at 30˚C was transferred (in sterile condition) to 250 ml of treated wastewater and incubated 48 h at 30˚C under shaking (150 rpm). To evaluate the effects of *A. niger* biosorption on color removal, the fungal biomass was removed from the treated solution by filtration and the supernatants were collected and analyzed for COD and Turbidity. Figs. 1 and 2 show the evolution of COD and turbidity at different treatment processes, respectively. It can be seen that the COD of treated wastewater using a single process (coagulation–flocculation) decreases from 656 to

388 mg/l when biosorption process is combined. Similarly, turbidity decreases significantly from untreated wastewater to treated wastewater using combined process. As shown in Fig. 3, combined process (coagulation–flocculation process flowed by biosorption process) can remove totally black color from wastewater. The biosorption capacity of *A. niger* biomass to remove color from wastewater has been extensively studied [27,28]. This study has reported the high capacity of *A. niger* biomass to remove reactive dye from textile wastewater and color removal reached 80% [29].

3.2. Germination essay

The GI for barley (*Hordeum vulgare*), feed barley (*Hordeum vulgare hexastichum*), wheat (*Triticum sativum*), fenugreek (*Trigonella foenum graecum*), and sorghum (*Sorghum bicolor*) are given in Fig. 4. GI was determined after two weeks of germination of each plant seeds placed in the presence of tap water as a control, untreated wastewater (E), treated wastewater using a coagulation/floculation process (C/F) and treated wastewater using a combined process TE (C/F/B). It has been observed that seed germination was strongly inhibited for barley, feed barley, sorghum, and fenugreek when untreated wastewater was applied. Printing wastewater seems to contain some toxic compounds which are responsible of this phytotoxicity and lethal for seeds. Therefore, the demonstrated toxicity means the release of this wastewater into environment without any treatment, which needs to be carefully monitored in order to prevent environmental degradation. However, seeds of wheat seems to be resistant against toxicity induced by wastewater, and index germination (IG) obtained was 34%. The response of germination seeds when treated

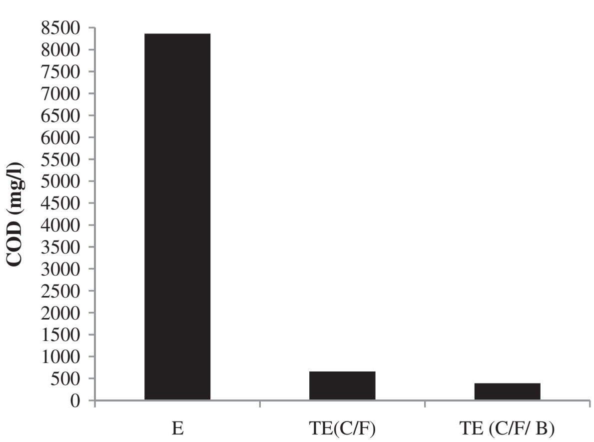

Fig. 1. COD evolution for the different treatment process of wastewater.

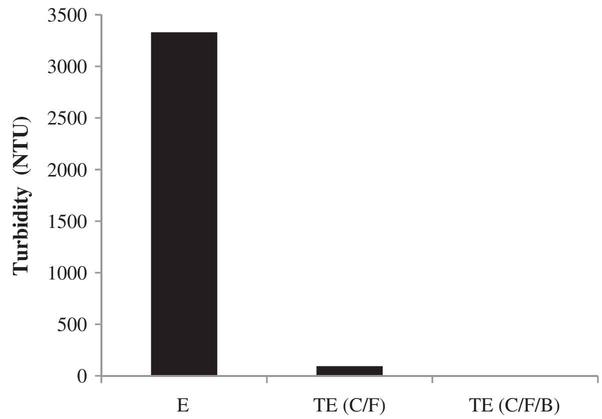

Fig. 2. Turbidity evolution for the different treatment process of wastewater.

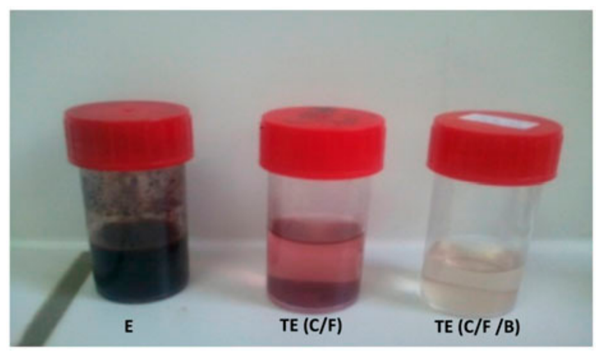

Fig. 3. Color evolution for the different treatment process of wastewater.

wastewater was applied depend on the treatment process used. The treatment of printing wastewater by a coagulation/flocculation process can reduce wastewater's toxicity of seed germination. IG decreases to 56% for wheat, 48% for sorghum, and to 30% for fenugreek. On the contrary, the GI calculated has not exceeded 10% for barley and feed barley. The application of a combined process (coagulation/flocculation and biosorption) to treat printing wastewater can significantly reduce their toxicity. Results are confirmed by the highest IG measured for fenugreek (114%) and barley (103%) seeds germination. The resistance of plant against wastewater toxicity was well described previously. Al-Dulaimi et al. [30] reported that fenugreek IG can reach 100% when sewage was applied. Singh et al. [31] showed that tannery effluent can stimulate germination of wheat seed. A positive effect of distillery on sorghum has also been reported by Kaushik et al. [32]. However, Mosse et al. [33] reported that the barley seed germination bioassays are highly relevant to plant growth, and therefore may be used as a

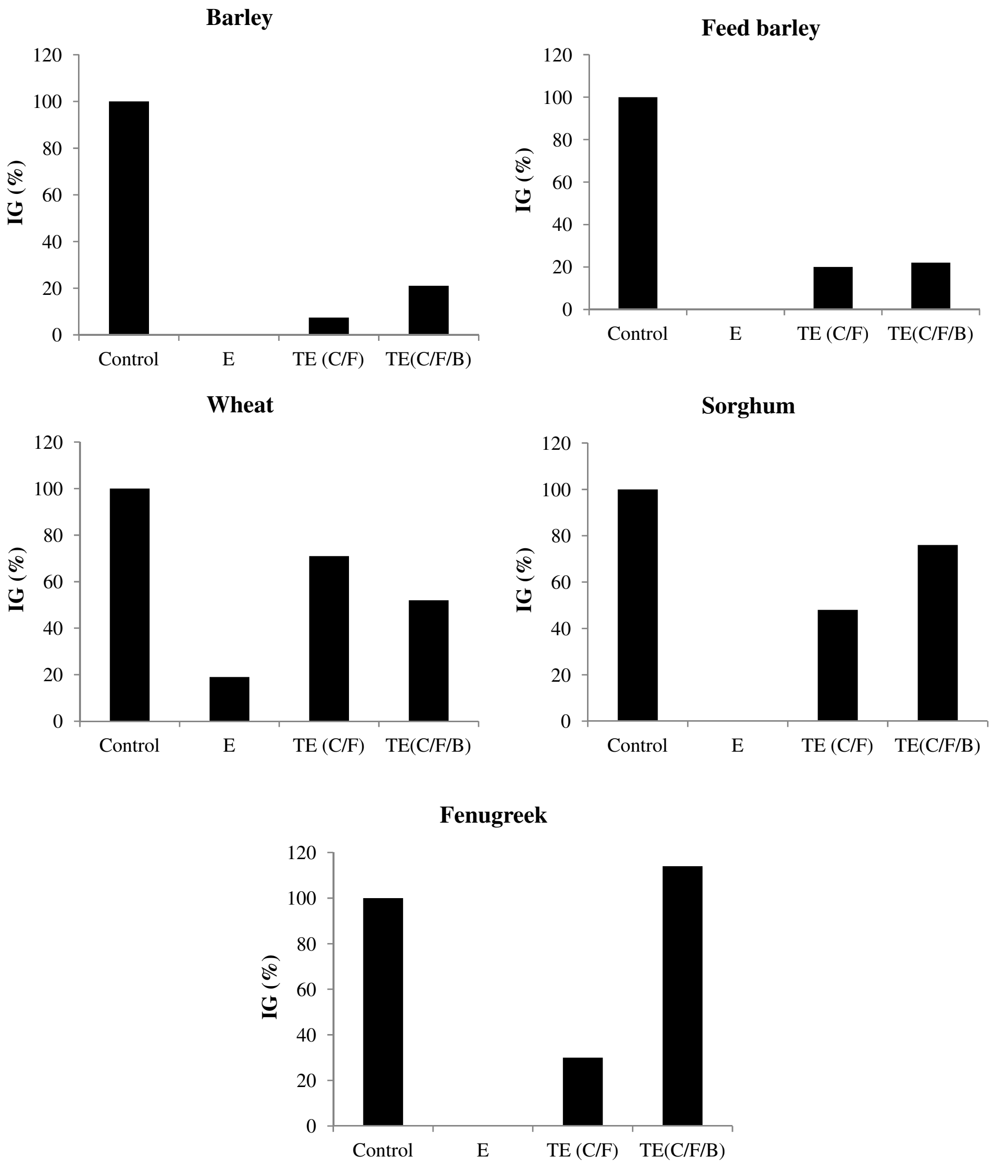

Fig. 4. Germination index of plant seeds determined on ink wastewater (E), Treated ink wastewater by coagulation/flocculation process: TE (C/F)) and Treated ink wastewater by combined process: TE (C/F/B).

potential useful tool for use in industry, to determine whether the wastewater is suitable to be used for irrigation at any time given. Treated wastewater can be used extensively for irrigation and other ecosystem services. Its reuse can deliver positive benefits to the farming community.

4. Conclusions

This study has demonstrated the efficient use of a combined process (coagulation/flocculation and biosorption) to treat wastewater from printing industry. Treatment process can reduce COD, turbidity, and completely remove the black color from wastewater. It has been shown that treated wastewater can be reused in the irrigation since it improves GI (%) of barley, feed barley, wheat, sorghum, and fenugreek. Results show the possibility to reuse wastewater in irrigation of ornamental plants after its treatment. Additionally, this treated wastewater can be reused for washing printing machines or alternatively for washing floors.

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Abbreviations

BOD	—	biological oxygen demand
COD_t	—	total chemical oxygen demand
COD_s	—	suspended chemical oxygen demand
E	—	untreated effluent
GPY medium	—	glucose–peptone–yeast extract medium
IG	—	index germination
TE (C/F)	—	treated effluent using coagulation/ flocculation process
TE (C/F/B)	—	treated effluent using combined process (coagulation/flocculation/ biosorption)

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