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Discoloration of industrial effluents by adsorption-based treatment onto coal fly ash activated with lime

Carmen Zaharia

Department of Environmental Engineering and Management, "Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, 73 Prof. Dr. Docent D. Mangeron Blvd, Iasi 700050, Romania, Tel. +40 232 278683 Ext: 2175; Fax: +40 232 271311; email: czah@ch.tuiasi.ro, czaharia2003@yahoo.com

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ABSTRACT

The paper presents the experimental discoloration data performed by adsorption-based treatment onto coal fly ash activated with lime (named as AX_i, $i = 1, \ldots, 4$) applied to a real industrial effluent (i.e., textile effluents from a few technological steps as chemical finishing, washing/rinsing of cotton fabrics), collected before entrance in the wastewater treatment plant. The main operating parameters tested for high efficiency of discoloration, chemical oxygen demand (COD), and phenol removals were pH, adsorbent concentration, temperature, and contact time. The results are encouraging (61%–98% removals, with 5–20 g of AX_i/L), helping the industrial operator to respect the requirements from the compliance plan imposed by the environmental regulator for legal and environment-friendly operating of textile manufacturing plant, and nonpolluting discharges in the natural aquatic receptor. Also, this one-single treatment step can be easily integrated in the existing wastewater treatment plant, and will help the industrial operator to recycle at least 50%–60% of its treated effluents in the textile technological manufacturing flux, or other reuse.

Keywords: Adsorption; Cleaning technology; Coal ash modified with lime; Discoloration; Textile effluent; AX_i Adsorbent regeneration

1. Introduction

Almost all industries in Europe are consuming significant volumes of relative fresh high quality water per kilogram of industrial product (2.2–630.7 L/kg of textile product) [1], generating wastewaters which are able to significantly contribute to pollution of the environment. Not only wastewater but also industrial products often contain chemicals that might pose a certain risk to the aquatic environment [2–5]. Some of these chemicals used in preparation of finite products are considered as residues, or wastes from production of colorants (dyes) and auxiliary chemicals, others are added to give certain characteristics to the industrial products (i.e., color, flame retardancy, antiwrinkling properties) [6,7].

Color is one of the easily recognized properties of final effluent discharged in the aquatic receptor because it is visible to human eye and is objectionable to the public for pollution and sanitation reason [8,9]. The industrial colored effluents, discharged into natural water bodies by a wide variety of industries, can generate important environmental impact and risk, caused not only of anaesthetic reason but also of impeding light penetration, and thus upsetting biological processes within streams [10,11]. Therefore, the dissolved organic and inorganic loads, degree of coloration, total solids content of final effluents are controlled by setting maximal admissible limits for the physical–chemical and biological quality indicators of industrial effluents produced.

In order to respect the setted admissible limits of color and organic load, but also to minimize the environmental impact of untreated, or noncorrespondingly treated effluent discharged in natural receptor nearby, or to reduce the hazardous toxic species in terms of cumulative effects when are mixed together with other wastewaters in sewage system [1], the industrial effluent must be treated before its final discharge, or inside reuse/recycling [5,9,10,12]. The effluent

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* Corresponding author.

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treatment must have a high performance referring to the partial, or even total removal of color, persistent organics and salts, involving treatment steps based on coagulation and precipitation, electrocoagulation, advanced oxidation/reduction, ionic exchange (with commercial exchangeable resins), or adsorption/sorption/biosorption with conventional (activated carbon, silica gel, alumina, and resins), or "low-cost" adsorbents/sorbents/biosorbents (natural and industrial/agricultural waste materials, or other by-products) [1,11,13–20], among others. For reason of costs and consumption minimization (e.g., adequate capital and operational costs with treatment equipments, chemical reagents and materials, energy, other facilities, space, and maintenance requirements), an industrial effluent treatment must be developed as simple as possible, consisting of at least one single step before entering in a local centralized wastewater treatment system, or a minimal number of treatment steps developed in a decentralized treatment system before inside reuse/recycling, or directly discharge in natural receptor nearby (e.g., "end of pipe" treatment systems of industrial wastewater) [10–12]. Adsorption/sorption, or biosorption, is one of the most used integrated treatment step for removal of polluting species from industrial effluents, mainly because of its numerous and well-known advantages such as increased processing sensibility and selectivity, reduced matrix effects, possibility of simultaneous preconcentration, possibility to use numerous categories of materials (i.e., materials with ionic exchange properties, activated charcoal, lignocellulosic materials, natural and synthetic zeolites, active, or inactive natural or industrial produced biomass) and to be properly assessed [10,13,17,18,20]. The conventional adsorbents such as activated carbon, alumina, and zeolite utilized especially in different treatments of the industrial process water are expensive materials, requiring also special treatment facilities for regeneration and action (under pressure), but the alternative of "low-cost" or cheap sorbent use is attractive, although high adsorbent amounts are required [21–24]. The "spent" adsorbent can be incinerated, valorized (e.g., synthesis of polypropylene fiber/high calcium fly ash geopolymers, or as binding agent in preparation of composite materials like different construction materials, i.e., manufacturing of bricks, derived sawdust, cement/consolidated concrete manufacturing used in eco-industrial parks), or regenerated with at least 8%–15% material loss, if necessary [25–33].

One of "low-cost" adsorbent that can be used into an industrial effluent treatment system is a production waste that can be usefully valorized for discoloration purpose of certain high loaded and colored industrial wastewaters, thus being solved simultaneously two concerns [1,10]: (1) efficient valorization of production waste as adsorbent/sorbent/biosorbent of polluting organic/inorganic species (for reduction and control of total waste volume, and also minimization of its polluting environmental impact onto storing emplacement) and (2) industrial effluent treatment for fulfillment of environmental requirements concerning the quality of final discharges in natural receptors, or maximal permissible limits for some specific quality indicators considering some polluting species needed to be partially or totally removed/eliminated for reuse/recycling facilities.

In the scientific literature, there were reported some interesting investigations of wastewater treatments, or treatment solutions for synthetic dye-containing effluents based on adsorption onto activated or modified fly and/or bottom coal ash, which were permitted the removal of a large variety of organic species and colors. This adsorbent type (activated or modified coal fly ash) has a few advantages of broad applications due to its characteristics, easy accessibility, low price, non- or low-polluting action, continuously processing possibilities/opportunities, and high hydrophilia, fact that determines rapid adsorption kinetics, possibility to be tolerated on biological molecules and also functionalized, possibility to be utilized in different sizes and shapes, but also relative good porosity and good mechanical resistance to diverse variations of wastewater loads and flow rate [10–12,20,21,25,27,34–37]. In this context, this adsorbent based on activated coal fly ash with lime is very easy to prepare, being necessary only the initial mixing of basic solid materials and calcination at low temperature. This preparation needs no chemicals addition, and its use as adsorbent needed no chemicals for adjustment of standard effluent pH when was discharged in natural aquatic receptor related to the use of only coal fly ash (without activation or activation with acids) which needed pH regulation, adsorption being efficient only at very low acidic pH ($pH < 2$) [10,21]. Of course, some contrasting results can be found when this type of adsorbent is used for discoloration purposes and/or different hazardous organics removals (e.g., phenols removal) from wastewaters caused of periodic variation of wastewater characteristics/different dyestuff bath formulations and dilution ratios, operating regime, and also adsorbent preparation conditions and its composition (ash/lime ratio and compositional origin and exploitation area). In addition, this adsorbent based on coal fly ash and lime had favorable action against aggressivity of textile effluent due to sulfates, or acidic species content, among others.

In brief, the principal aim of this paper is to perform a comparative evaluation of adsorptive potential of some "low-cost" adsorbents based on raw coal fly ash [21,38] activated with lime (named as AX_i, $i = 1, \ldots, 4$) in order to improve the treatment operating conditions (especially pH and adsorbent content requirements) [17,18,37–40] for discoloration of real Romanian textile effluents from a private textile company of cotton fabrics manufacturing [15,41,42]. In this context, some operating parameters of the adsorptive treatment process, such as initial effluent pH, adsorbent dose, adsorption time, and temperature, were studied for determination of the highest performance in color and COD removal. The good adsorptive performance of these adsorbents, the local coal ash availability, and the cheapness of adsorbent preparation, associated with no necessity of supplementary equipment, or building construction had recommended the feasible utilization of the proposed adsorbents (coal fly ash activated with lime) in textile effluent treatment at industrial setup scale for discoloration reason (especially by using "batch" adsorptive treatment technology). The results are encouraging and helping the industrial operator to respect the requirements from the compliance plan imposed by the local authorized environmental controller/regulator.

2. Materials and methods

2.1. Adsorbents

The adsorption experiments were carried out using adsorbent (named AX_i, $i = 1, \ldots, 4$) the coal fly ash activated with lime (6.25 ash: 3.75 lime, wt:wt) prepared by calcination/heating in oven at 70°C for 1 h (AX_1), 2 h (AX_2), 3 h (AX_3), and 4 h (AX_4) [10,27–30,37,40–43]. AX_1 has contained a higher amount of $Ca(OH)_2$, and AX_4 a higher amount of CaO [27,29]. The coal fly ash was the production waste of combustion installation of a Romanian thermal power plant (CET 2 Company, Holboca, Iasi), supplied with indigene huile containing 20%–40% slag and ash, 1%–2% S, having over 70% inorganic oxides (i.e., sum of SiO_2, Al_2O_3, and Fe_2O_3) in its chemical composition, corresponding to F class of coal fly ash [21]. It was characterized in other reports by advanced analysis techniques (thermogravimetry – TG, differential thermogravimetry, scanning electron microscopy, transmission electron microscopy, etc.), and it had around 1.3%–2.52% loss on ignition at 700°C, 0.446%–0.782% total humidity at 105°C, ash particle size in range of 0.04–0.125 mm, and Blaine specific surface in range of 4,126–5,631 cm^2/g [17–18,21,27–30,38,41,42].

The initial coal fly ash produced in the combustion process of the Romanian thermal power plant was separated from the combustion gases with help of an electrostatic separation installation (consisting in cyclones and electrofilter). Being permanently in contact with the hot combustion gases, onto coal fly ash surface promoted the formation of pores, and thus, the initial coal fly ash exhibited certain adsorption capacity, possessing potential adsorption capacity which can be valorized after its activation (thermic, or by contact with different acids, bases, salts, metal oxides, organic substances associated with calcination at different temperatures) [10,21]. In this study, it was performed calcination after treating of coal fly ash with lime in various mixing ratios. The advantage of lime utilization for preparation of this adsorbent is due to the fact that lime is not an expensive material and no special treatment is needed, only mixing of basic solids and after calcination at 70°C (no high energy consumption; no destroying of coal ash and lime structure).

A significant influence in preparation of this adsorbent category had the ash/lime ratio, calcination temperature and time, but no obvious influence was found in the preliminary laboratory tests in case of agitation, or mixing speed variation (a certain initial agitation was always required, stirring with 50–80 rpm-speed being preferred). In this context, the preliminary laboratory adsorption experiments indicated that it is recommendable to vary the ash/lime ratio in range (5–10)/(1–5) (wt/wt), good results being performed with the ash/lime ratio of 6.25/3.75, which was selected for this work. The calcination can enlarge the volume of coal fly ash pores, but very high temperature (>300°C) and time (>12 h) can cause the collapse of pores, resulting in decrease of specific surface area and implicitly adsorption capacity. That is why the calcination temperature was selected to be lower than 100°C, and calcination period no more than 5–6 h. For this study, the adsorbent was prepared considering the calcination temperature of 70°C ± 10°C and calcination times of 1, 2, 3, and 4 h corresponding to each studied AX_i absorbent ($i = 1, \ldots, 4$).

2.2. Industrial effluent characterization

The studied industrial wastewater is a real textile effluent from a private company (NE Romania) collected after the dyeing and rinsing stages (first and second rinsing) of cotton fabrics (flow of 18–20 m^3/d after a 80% twisting degree), with different compositions dependent on dyestuff bath formulation and dilution rates (dyestuff bath: process water, in range of 1:100 to 1:10,000). The Romanian textile operator had a production of around 4,615 kg cotton fabrics/d (i.e. 15,000 linear meters of cotton fabrics per day with specific weight of 410 g/mol) using a dyestuff bath of 3.70–4.00 m^3/d [1,5,10,11,21]. The dyestuff bath contained reactive azo dyes (Remazol arancio 3R and Remazol rose RB, commercial textile dyes) and auxiliary chemicals (tenside, pH buffer, binding agents between dyes and cotton fibers, electrolyte/salts, anticrust agent, reduction agent, acids) [10,11,21]. The conventional textile effluent treatment (mechanical–biological aerobic treatment) is not totally efficient, and significant amounts of textile dyes are present in the natural watercourse nearby in absence of an efficient tertiary treatment (e.g., adsorption-sedimentation, or advanced oxidation and/or filtration steps).

2.3. Analysis methods

Analysis methods of certain quality indicators of industrial effluents, that is, suspended solids, turbidity, chlorides, nitrates, nitrites, total hardness, fixed residues, phenol, and heavy metals, are using internationally approved standards and reference materials [1,10,21,41–43], being spectrophotometer-based analysis methods, adapted for specific test programs and reagent kits of DRELL 2000 spectrophotometer (HACH Company, USA). For the phenol analysis it was used the diazotated *p*-nitroaniline spectrophotometrical method [1,10,21,41–43].

The effluent pH was measured directly at HACH One Laboratory pH meter. The effluent color was expressed by the absorbance measurement at three wavelengths (436, 525, and 620 nm), obligatorily being the absorbance determination at 436 nm, but also at 456 nm for determination of Hazen color units ($A_{456} = 0.056$ corresponds to 50 Hazen color units, HU) [1,9,18,21]. The chemical oxygen demand (COD) was determined with the potassium dichromate spectrophotometer-based method (COD reactor method) consisting in absorbance measurement at 600 nm of the oxidized sample (i.e., catalytic oxidation of sample at 150°C for 2 h, in concentrated H_2SO_4 solution, with specific catalyst-$HgSO_4$ and chloride inhibitory agent-Ag_2SO_4) under a blank (distilled water treated in the same way as wastewater sample) and calculation with help of the calibration curve, $A_{600} = f(\mathrm{COD})$, where the potassium hydrogen phthalate was selected as reference model of organic compounds [1,5,9,10,12,18,21].

2.4. Adsorption experiments

All experiments were carried out as limited batchwise adsorption tests in static regime, applied mainly in laboratory setup investigations. Series of adsorption experiments were performed in duplicate by contacting 0.1–1 g of adsorbent with a known volume of textile effluent (usually 25 or 50 mL) into 50 or 100 mL conical shaking flask under intermittent stirring with 50–80 rpm speed [9,10]. The experiments were carried out for different temperatures of textile effluent varying in range of 5°C–45°C in the controlled thermostatic assembly. Solution of 0.1 N HCl, or 0.1 N NaOH was used to adjust the effluent pH to a certain value. After 24 h, or a specific adsorption time (t), the adsorbent was separated from treated textile effluent after sedimentation and/or filtration, and the supernatant was analyzed. The selected adsorption times in this research work were: 2 h (especially selected for comparison of adsorption treatment performance in color, COD, and phenol removals with that of other applied treatments, e.g., advanced oxidation treatment, electrochemical treatment, membrane processes, or rapid/lent filtration), 8 h (as corresponding adsorption time in a working shift in Romania), 5.5–6.8 h (as minimal recommended time for adsorption equilibrium establishment), and 24 h (as reference period when adsorption equilibrium is always attained and possible competitive stabilization or destabilization can appear, in static/dynamic regime).

The specific quality indicators, especially color, COD, phenols, and suspended solids concentrations, are quoted relative to values of untreated textile effluent. The adsorption efficiency is expressed by discoloration degree (%), that is, color removal (%), considered as the main goal of this research work, but also COD and phenol removals (%) using the well known relation (Eq. (1)) as follows [5,10,12,21,40]:

$$\text{Removal}\left(\%\right)=\frac{C_0-C_t}{C_0}\times 100 \tag{1}$$

where C_0 is the initial value of color, COD, or phenol concentration (HU, mg O_2/L, or mg/L) and C_t is the value of color, COD, or phenol concentration after t adsorption time (HU, mg O_2/L, or mg/L).

For determination of the most indicated value of studied operating parameters (i.e., pH, adsorbent dose, adsorption temperature, and time), there were performed series of experiments for describing the variation behavior of color, COD, and phenol removals by adsorptive treatment using the proposed AX_i adsorbents.

2.5. Regeneration of "spent" AX_i adsorbent

Regeneration of "spent" adsorbent is important caused of the possibility to recover useful compounds/species after the separation of polluting loads (detoxification of "spent" adsorbent), and also of adsorptive treatment cost effectiveness due to significant reduction of cost for "fresh" adsorbent and other facilities. It consists in removal of all, or majority of adsorbed molecular and ionic species from the "spent" adsorbent surface using regeneration solution (e.g., acid, alkaline solution, salts, organic solvents, or other desorbing agents), or specific regenerative treatment methodologies, that is, chemical and/or thermic desorption, sonication, advanced oxidative regeneration, reductive regeneration, or various combinations between them [7,10,44,45].

Desorption was selected for this study of "spent" adsorbent regeneration, being carried out in four successive cycles caused of significant decreasing of adsorption-based treatment efficiency in further runs (ith run, $i > 4$) associated with important adsorbent weight loss. There were tested for this study of desorption-based regeneration a few inorganic solutions (i.e., 0.1 N HCl, or 0.1 N NaOH), or organic solvents (i.e., chloroform, acetic acid solution (1:5), mixture of acetic acid and ethanol (1:5), or only ethanol), but also only distilled water by simple repetitive washings into separation funnels and the soft thermal desorption. After each desorption experiment, the regenerated adsorbent was separated at laboratory setup scale through a certain filtrating material support (45 mm filter paper or membrane), washed with distilled water for few times till the pH of filtrate remained constant, and further dried in air. The regenerated adsorbent was kept in closed recipient till utilization in new series of adsorption experiments.

3. Results and discussion

3.1. Textile manufacturing process and industrial wastewater production

The technological manufacturing process of textile fabrics consists in preparation, dyeing, and finishing steps, in each step being involved the conditioning, washing/rinsing operations, and also production of different finite products, or by-products together with individual effluents (Fig. 1), containing dissolved polluting species, solid wastes/particles (valorized in majority as supplementary, or additional agents/materials for composites, soil amendments/conditioning agent, self-consolidated concrete, different geopolymers), and/or gaseous emissions.

The collected textile wastewaters or raw reusable streams from cotton fabrics' manufacturing have characteristics expressed by general and specific quality indicators summarized in Table 1 [1,11,21].

The pollution profile of the manufacturing process of textile fabrics, especially of the fabrics dyeing and the next first and second rinsing operations, together with other chemical finishing processes, showed a continuous increase after dyeing followed by a rapid decrease in polluting species' concentration (especially COD and color) after the second rinsing operation. Therefore, depending on the applied dyeing technology, the second, third, or further ith rinsing wastewaters (i > 3), and also other next finishing process wastewaters (considered as relative "clean" wastewaters) were regarded as *reusable wastewater*. Contrarily, the dyestuff baths, the first and often second rinsing wastewaters were usually considered as *remaining composite wastewater*. The most commonly applied processes in a textile manufacturing

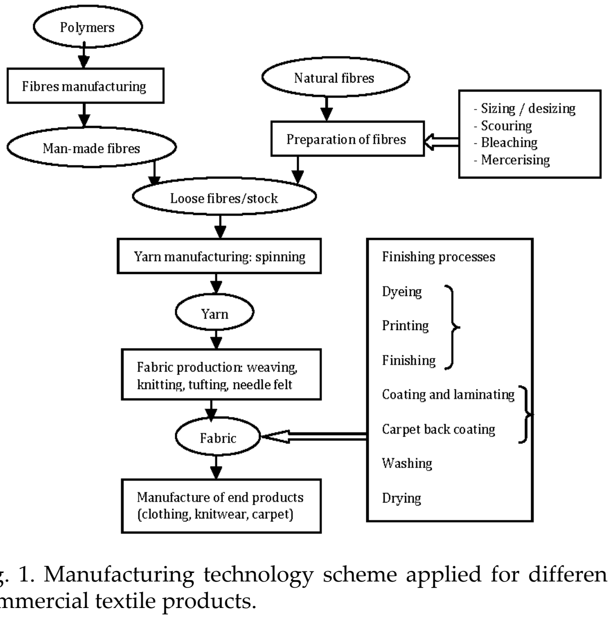

Fig. 1. Manufacturing technology scheme applied for different commercial textile products.

Table 1
Characteristics of textile wastewater and raw reusable streams

Quality indicators	Measurement units	Total value	Dyeing reusable stream	Finishing stream	Reusable composite stream
pH	–	7.1–7.8	7.6–7.8	8.0–8.1	7.8–8.0
Conductivity	μS/cm	1580 ± 126	542 ± 64	537 ± 55	540 ± 62
Total COD	mg O_2/L	600 ± 50	60 ± 10	150 ± 20	95 ± 18
Total alkalinity	mg $CaCO_3$/L	135 ± 15	130±12	320 ± 28	320 ± 34
Total hardness	mg $CaCO_3$/L	NA	30 ± 3	25 ± 2	27 ± 3.5
Total dissolved solids (TDS)	mg/L	850 ± 125	360 ± 32	335 ± 35	345 ± 36
Total suspended solids (TSS)	mg/L	15 ± 5	10 ± 2	31 ± 3	15 ± 2
Chlorides	mg/L	NA	49 ± 4	47 ± 4	48 ± 6
Detergents	mg/L	0.95 ± 0.78	0.03 ± 0.01	1.85 ± 0.89	1.30 ± 0.85
Total chrome ions	mg/L	NA	<0.04	<0.04	<0.04
Total manganese ions	mg/L	NA	<0.01	<0.01	<0.01
Total iron ions	mg/L	NA	<0.02	<0.02	<0.02
Absorbance at	$10^{-1} \times m^{-1}$				
620 nm		1.95 ± 0.9	1.28 ± 0.06	1.48 ± 0.08	2.14 ± 0.11
525 nm		3.2 ± 1.1	0.98 ± 0.05	1.08 ± 0.06	1.56 ± 0.08
436 nm		3.92 ± 1.2	1.08 ± 0.05	1.11 ± 0.05	1.21 ± 0.06

NA: not available data.

company, together with the associated phases of produced waste streams, considered as *reusable* and *remaining composite parts* of wastewater are summarized in Table 2.

For the investigated textile effluent produced in the private textile manufacturing company (NE Romania) of cotton fabrics after the first and second rinsing stages, the principal physical–chemical quality indicators are presented in Table 3. Majority of quality indicators exceeded the maximum admissible limits, and therefore textile effluent treatment was obviously necessary before final discharge (40%–50%), and even inside reuse (50%–60%) [1,12,21].

Table 2
Criteria selected for process wastewater management and water resource conservation

Manufacturing process of *i* (fabric)	Reusable wastewater	Remaining composite wastewater
Acidol (fabric)	Third rinsing	Dyeing First rinsing Second rinsing
Neolan (fabric)	Second rinsing Third rinsing	–[a]
Forosyn (fabric)	Third rinsing Fourth rinsing	Dyeing First rinsing Second rinsing
Cotton (fabric)	Third rinsing Fourth rinsing	Dyeing First rinsing Second rinsing

[a] Not in production program during sampling period.

The textile wastewater discharges carried usually risks in terms of environment pollution, and must be efficiently treated before discharge in natural receiving environment for causing no pollution, or aesthetic problems [11].

The corresponding *reusable wastewater* flow represents around 50%–60% of total overall waste stream flow, the *remaining composite wastewater* (not considered for reuse) was subject of the textile effluent treatment based on adsorption onto adsorbents prepared from coal fly ash and lime (AX_i, $i = 1, …, 4$) (*remaining composite wastewater* flow of 18–20 m^3/d).

The *remaining composite wastewater* for treatment, in case of direct discharge in natural receptor (40%–50%), or even inside reuse (50%–60%), had possessed values of COD almost 5–15 times higher than those of reusable streams (i.e., COD of 20–50 mg O_2/L). The overall industrial wastewater, consisting in collected and mixed wastewaters after the dyeing, finishing, and cleaning operations, had a COD concentration varying in range of 564.12–650.24 mg O_2/L, and a total rate of industrial treated wastewater discharge reduced to 18–20 m^3/d from 270–290 m^3/d by implementation of the reuse/recycling scenario (Fig. 2).

The implementation of reuse/recycling concept in the textile industry sector is beneficial alongside with optimization of wastewater treatment processes. The conventional wastewater treatment processes applied to the industrial remaining composite wastewater such as neutralization, biological treatment by activated sludge associated with nitrification and denitrification processes, supplemented with a tertiary step based on advanced oxidative process (e.g., ozonation), or adsorption followed by sedimentation/filtration were designed to attain the reusable wastewater characteristics (e.g., COD concentration as low as 20–25 mg O_2/L, color as low as 50–100 HU), meaning color removal of 90%–97%, and phenol or COD removal efficiency of 75%–90%, even 100% if possible, related to the original raw composite wastewater.

Table 3
The principal physical–chemical quality indicators of the studied textile effluent (cotton fabrics manufacturing)

Quality indicators	Measured value (mg/L)	MAC[a] (mg/L)	Quality indicators	Measured value (mg/L)	MAC[a] (mg/L)
pH	7.49–7.75	6.50–8.50	Total P	5.72–6.39	1
Color, HU (A_{436})	181–436 (0.203–0.388)	50 0.056	Extractible substances	45–62	20
Suspended solids	386–400	35 (60)	Total N	8.34–9.80	10
Turbidity, FTU	85–108	–	Ammonia	2.10–2.45	2
Fixed residues	3,600–4,000	1,000	Sulfates	782–810	600
COD (mg O_2/L)	564–650	125	Chlorides	99–108	70
BOD_5 (mg O_2/L)	322	25	Phenol index	2.63–3.26	0.30
Synthetic detergents	1.78–2.10	0.50	Total heavy metal ions	<4	<2 (max 5)

[a] MAC – maximum admissible concentration, according with Romanian Government Decision No. 352/2005-Technical Norms for Treated Wastewater Discharged in Natural Water Resources (NTPA 001) [10,21].

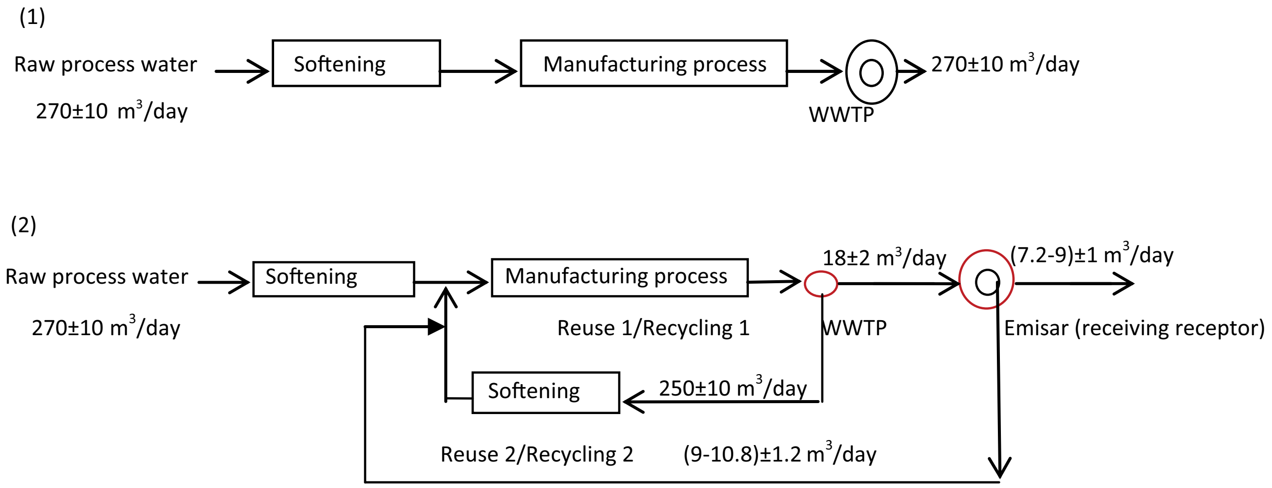

Fig. 2. Graphical scheme of two treatment scenarios applied in case of studied textile wastewater management system.

A schematic illustration of the two principal scenarios considered for the studied textile private company is presented in Fig. 2 as: (1) "end of pipe" treatment approach of total waste streams and (2) cleaner production approach with consideration of reuse/recycling concept after wastewater treatment (in wastewater treatment plant (WWTP), decentralized system).

In terms of costs analysis and fulfillment of minimal environmental requirements, the second scenario is considered beneficial for the textile company.

3.2. Effect of initial pH

For all tested adsorbents (AX_i, $i = 1, \ldots, 4$), the dependence of adsorption process toward effluent pH for discoloration purpose was studied by varying the pH from 2.1 till 11.2, at room temperature (22°C±3°C), working with 12 g/L of AX_i-based adsorbent in static adsorption regime (Fig. 3).

The discoloration degree increases in all cases with pH increase in acidic range (from pH 2.1 up to 4.1, or 6.2), and decreases significantly in neutral and alkaline range. As seen in Fig. 3, the discoloration degrees are no higher than 50% after 2 h of adsorption, except for AX_1 at pH 6.3, caused it was not established the adsorption equilibrium as in case of 24 h of adsorption. Most appreciable effluent discoloration was registered in the pH range of 4.1–6.2, maximum being of around 96% reported at pH 6.2 for AX_1 after 24 h of adsorption, and also 67.5% for the same AX_1 at pH 6.2 but after only 2 h of adsorption. In case of AX_4-based adsorbent – textile effluent system at pH 4.1, around 91% of color was adsorbed after 24 h of adsorption, while only ca. 38%–50% color removal was achieved after 2 h of adsorption in pH range of 4.1–6.2. On the other hand, AX_1 adsorbent showed the highest removal at pH 6.2, and about 92% at pH 4.1 were reported the highest discoloration using AX_4 adsorbent. The lowest effluent discoloration degree (ca. 15%) was performed using AX_4 at pH 11.2, where the maximal discoloration was of around 24% using AX_1 adsorbent. Hence, for three adsorbents (AX_1, AX_2, and AX_3), pH 6.2 was considered the adequate pH for effluent discoloration and COD removal, but for phenol removal is recommended AX_2 as shown in Fig. 4, the majority of adsorption experiments being carried out in pH range of 6.2–6.8, excepting for AX_4 adsorbent.

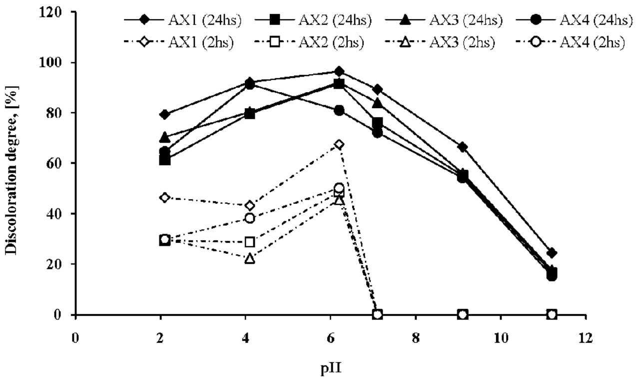

Fig. 3. Effect of initial pH onto effluent discoloration by adsorption onto AX_i (i = 1–4) (12 g/L, room temperature, 2 h or 24 h of adsorption, static regime).

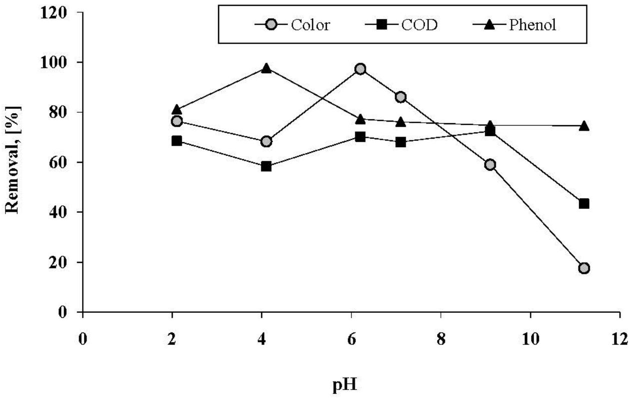

Fig. 4. Effect of initial pH onto color, COD, and phenol removals by adsorption onto AX_2 (12 g/L, room temperature, 24 h of sorption, static regime).

3.3. *Effect of adsorbent dose*

Adsorption investigations were also performed by varying the adsorbent amount from 0.1 to 1 g per 25 mL of effluent sample (i.e., 4–40 g/L of adsorbent) at fixed pH 6.2–6.8, room temperature, and 24 h of adsorption. The effluent discoloration degree by adsorption onto AX_i (i = 1, …, 4) is increasing with the increase of adsorbent concentration, as clearly shown in Fig. 5.

The results also indicate an increase in adsorption efficiency for effluent discoloration with increasing of adsorbent concentration from around 51% (AX_1), 46.5% (AX_2), 45% (AX_3), 44% (AX_4) at 4 g/L to approx. 98% (AX_1), 92% (AX_2), 81% (AX_3), or 63% (AX_4) at 40 g/L (or, at 12 g/L, to 93% for AX_1, 87% for AX_2, 76% for AX_3, or 60% for AX_4). Whereas, for all adsorbents AX_i (i = 1, …, 4) the color removal increased from 44% to 89% when the adsorbent concentration was increased from 2 to 10–12 g/L or even 20 g/L, in almost the same operating conditions. Also, considering the adsorption efficiency – overall treatment cost criteria dependence – it is indicated the utilization of adsorbent concentration no higher than 12–20 g/L for high effluent discoloration, and also COD and phenol removals as shown in Fig. 6 for AX_3 adsorbent.

The efficiency was the highest in case of AX_1, that is, around 92% for color, 69% for COD, and 72% for phenol (12 g/L), and in the case of AX_3 adsorbent the highest efficiency was of 88.12% for color (20 g/L), 66.13% for COD (20 g/L), and 97.5% for phenols (6 g/L) as shown in Fig. 6.

3.4. *Effect of temperature*

The sensibility of adsorption process toward temperature is illustrated in Fig. 7, the results being performed working with series of 8 and 24 h adsorption experiments at 5°C, 25°C, and 45°C, with an adsorbent concentration of 8 g/L, at pH 6.2–6.8, and static regime. The adsorbent concentration and adsorption time were selected considering the minimization reason of materials/reagents consumption in a working shift of 8 h.

The maximal discoloration degree after 24 h of effluent adsorption was performed at 5°C, being between around 43% (AX_4) to 61% (AX_1) (or 58% for AX_2 and 52% for AX_3), referring with the minimal discoloration degree resulted at

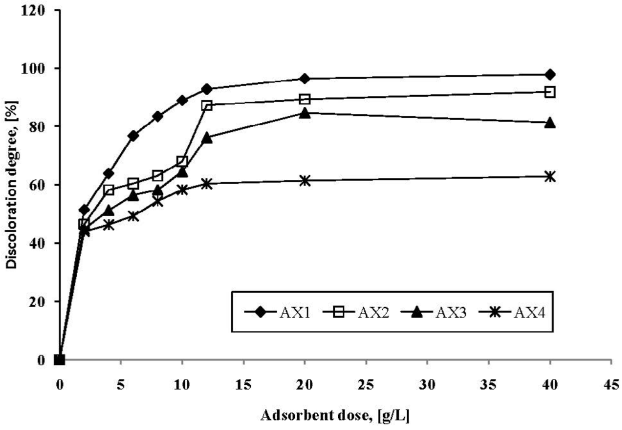

Fig. 5. Effect of adsorbent dose onto effluent discoloration by adsorption onto AX_i (i = 1–4) (pH 6.2–6.8, room temperature, 24 h of sorption, static regime).

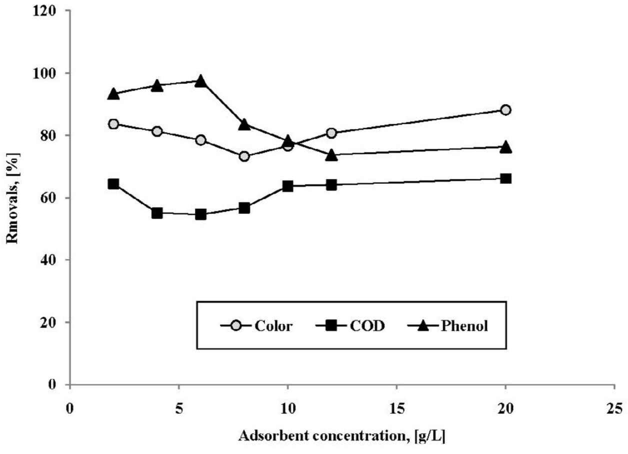

Fig. 6. Effect of adsorbent concentration onto color, COD, and phenol removals by adsorption onto AX_3 (pH 6.2–6.8, room temperature, 24 h of sorption, static regime).

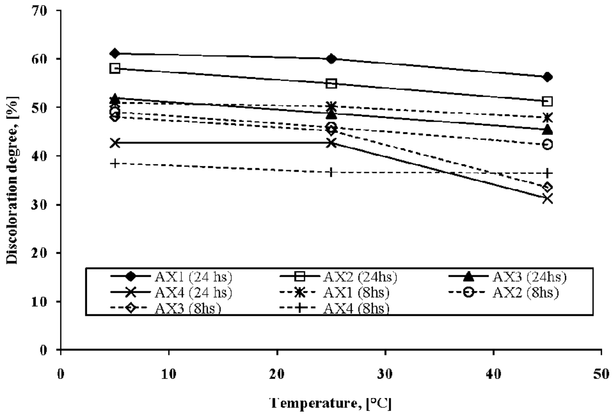

Fig. 7. Effect of temperature onto effluent discoloration by adsorption onto AX$_i$ (i = 1–4) (pH 6.2–6.8, 8 g/L of adsorbent, 8 h or 24 h of sorption, static regime).

45°C which was varied between around 41% (AX$_4$) to 56% (AX$_1$) (ca. 51% for AX$_2$ and 45% for AX$_3$).

It was observed that in all adsorption experiments the discoloration degree decreases with increasing temperature, indicating thereby a possible exothermic nature of adsorption process. Moreover, the most cost-efficient adsorption experiments are recommended to be performed at room temperature for high effluent discoloration degrees (>81%) and organics removal (>45% COD and ca. 92% phenol, as shown in Fig. 8, working with 14 g/L AX$_3$ adsorbent). Therefore, the further adsorption experiments were practiced at room temperature (22°C±3°C).

3.5. Effect of adsorption time

An important operating parameter for getting high removals of color and organics is the contact time period of adsorbent with the textile effluent, having also beneficial significance for elucidation of adsorption mechanism, and also chosen of practice operating conditions. The discoloration of industrial effluent by adsorption onto studied AX$_i$ adsorbents (i = 1, … ,4) depicts that adsorption is initially quite rapid (no more than 300–360 min, or 5–6 h), gradually slows down, and finally reaches the equilibrium (until 1,000–1,200 min, or 18–20 h) as shown in Fig. 9.

In all studied industrial systems (textile effluent – AX$_i$ adsorbent) nearly 36% (for AX$_4$ or AX$_3$) to 60% (for AX$_1$ or AX$_2$) of effluent discoloration by ultimate adsorption occurred within minimal 5.5–6.8 h of solid/wastewater contact, while minimal 14–18 h were taken for attaining adsorption equilibrium. Therefore, it is recommended for good adsorption efficiency, especially in terms of high effluent discoloration, at least 5.5–6.8 h of contact between the adsorbent and industrial effluent in static regime (or 8 h as for a working shift in Romania), at room temperature, and pH 6.2–6.8, close to pH value of initial untreated industrial effluent (minimal, or no requirement/necessity of reagents for pH adjustment).

After 24 h of effluent treatment by adsorption in static regime, there were obtained the highest discoloration degrees working with relative low concentration of adsorbent (10 g/L), that is, around 98% for AX$_1$, 92% for AX$_2$, 82% for AX$_3$, and 61% for AX$_4$ adsorbent, in all systems being also established the adsorption equilibrium.

The effluent discoloration onto coal ash activated with lime is explainable by the occupation of large number of vacant available surface sites of adsorbent by molecules of dyes or other organics and ionic species, and also interparticle diffusion during all steps of adsorption (*physical* – dye, or other competitive organics accumulation at external surface of adsorbent by hydrogen, van der Waals bonds, or hydrophobic interactions, and *chemical* – electrostatic attraction, ionic exchange, formation of covalent bonds dependent of adsorbent surface charges at different pH variations). In high loaded or concentrated textile effluents (i.e., remaining composite wastewaters), the adsorption process operates mainly by polluting species diffusion within adsorbent particles, whereas in dilute industrial effluents the diffusion takes place through a solution film at the external adsorbent particle surface.

A neutralization step is sometimes necessary before final discharge of treated effluent in natural receptor, or sewer system (admissible pH limits of 6.5–8.5 for discharging of

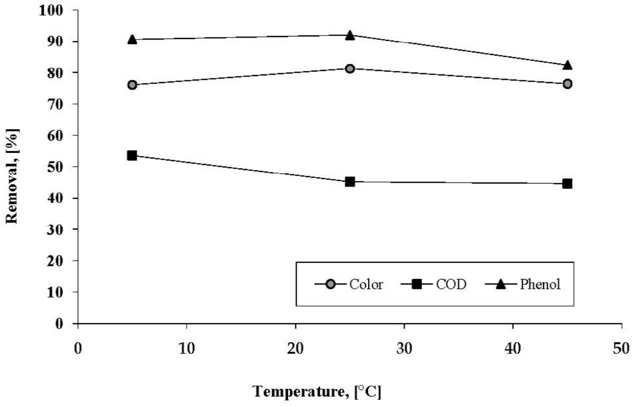

Fig. 8. Effect of temperature onto color, COD, and phenol removals by adsorption onto AX$_3$ (pH 6.2–6.8, 14 g/L of adsorbent, 24 h of sorption, static regime).

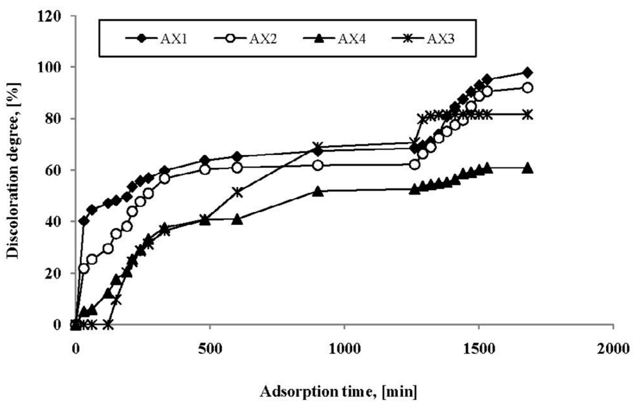

Fig. 9. Effect of contact time onto effluent discoloration by adsorption onto AX$_i$ (i = 1–4) (10 g/L, room temperature, pH 6.2, static regime).

treated effluent), or inside reuse/recycling (treated effluent after adsorption–sedimentation/filtration treatment can have an alkaline character, being recommended a neutralization step with CO_2, or specific acidic solution). Usually, using these AX_i adsorbents in specific operating conditions, it was no necessary the final regulation of pH before discharging in natural aquatic receptor, or inside reuse/recycling. In addition, some supplementary treatment steps may be introduced to improve the treated effluent quality (e.g., advanced oxidation, membrane processes), or 100% removal of polluting species, and also the "spent" adsorbent separation (e.g., by sedimentation/filtration and sediment/sludge pumping), valorization (mainly for processing of some composite materials such as construction/building materials after its inertization by cementation in the composite structure, e.g., bricks, or consolidated concrete, or geopolymers manufacturing), or regeneration by nondestructive treatments (e.g., desorption with diluted acids or solvents, thermal treatment, and also sonication) [8], if necessary. Appreciation on a few "spent" adsorbent regeneration results were discussed below considering as main regeneration process – the *desorption* by using some inorganic solutions, organic solvents and also the conventional thermic desorption.

3.6. Regeneration study of "spent" AX_i adsorbents

Regeneration of AX_i adsorbents is important caused of the possibility to recover some useful substances (dyes, low organic and/or macromolecular compounds, ionic species such as heavy metals), to minimize, or even eliminate pollution extending to other environmental components, or geographical areas (from water environment to soil, air, or waste management system, or from a region to an other one) and also due to cost effectiveness.

Regeneration of AX_i adsorbents based on activated coal fly ash with lime was achieved by *desorption*-based regenerative treatment using different regeneration solutions (chloroform, acetic acid solution (1:5), mixture of acetic acid and ethanol (1:5), ethanol, 0.1 N HCl, 0.1 N NaOH, distilled water) to remove the adsorbed molecular or ionic species, and also to activate the reactive sites by thermic treatment (thermic desorption, temperature <100°C ± 5°C). The best adsorption removal results by using certain AX_i regenerated adsorbent after a few desorption treatments applied for the real studied textile effluents (no adjustment of effluent pH, meaning initial pH = 7.49 ± 0.26) were summarized in Fig. 10, working with an adsorbent concentration of 20 g/L at room temperature and intermittent stirring (around 50–80 rpm-speed, for no more than 1–3 min, after each hour of adsorption experiment).

From Fig. 10, it can be noticed that the best removals of color and COD were performed with ethanol (AE) for AX_4 adsorbent, followed by mixture of (1:5) acetic acid (AAc) and ethanol (AE) for COD removal with AX_3, and chloroform (CF) for color removal with AX_1. Further, the variation of color removal (discoloration degree (%)) in textile effluent treatment by adsorption (real effluent pH = 7.49 ± 0.26) is illustrated in Fig. 11, considering four successive regeneration cycles of AX_i adsorbents by using the selected organic solvents and working with 20 g/L of adsorbent at room temperature and intermittent agitation regime (stirring for no more than 1–3 min after each hour of adsorption treatment).

The plots indicate the highest color removals, that is, 84.54% and 78.02% (maximal effluent discoloration), performed by working with regenerated adsorbents after the first adsorbent regeneration cycle (run 1) in case of desorptive regeneration with ethanol (AX_4) and chloroform (AX_1), respectively. After the first regeneration cycle, the

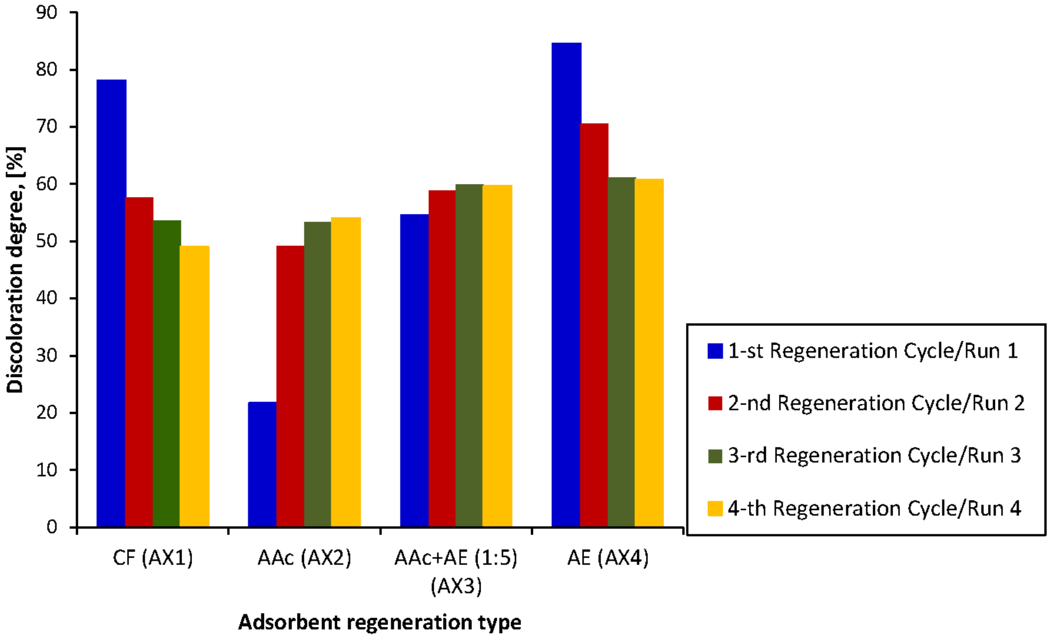

Fig. 10. Color and COD removals by adsorption treatment of textile effluent working with the first regenerated AX_i adsorbent (pH = 7.49 ± 0.26, 20 g/L of adsorbent; room temperature; initial 50–80 rpm-agitation).

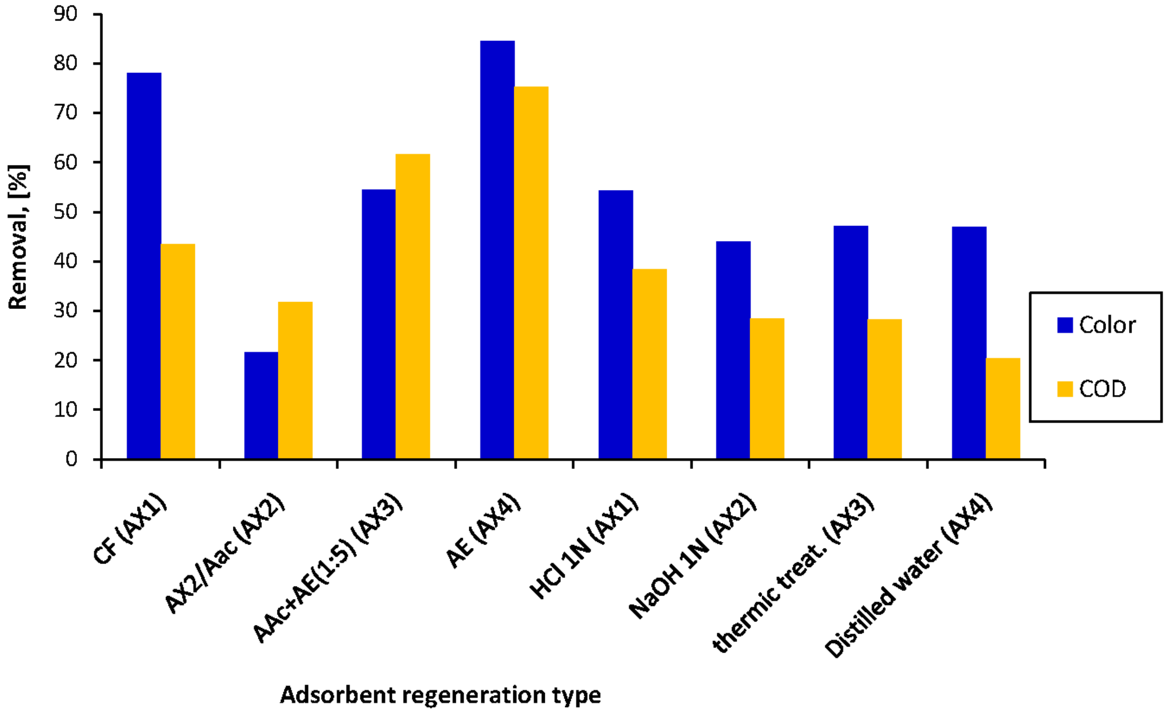

Fig. 11. Adsorption efficiency in textile effluent discoloration working with *i*th regenerated AX_i adsorbent ($i < 5$) with organic solvents ($pH = 7.49 \pm 0.26$, 20 g/L of adsorbent, room temperature, slow intermittent agitation).

textile effluent discoloration decreased gradually till the fifth adsorption run, that is, 60.67% and 49.04%, working with the fourth successively regenerated AX_i adsorbent in case of desorptive regeneration with ethanol and chloroform. After that the (*i*th) regenerated adsorbent ($i > 4$) had a continuous decreasing performance in color removal, meaning values lower than <50%. The discoloration efficiency of the (*i*th) regenerated adsorbent ($i > 4$) was technically too small for strict treatment requirements, therefore the desorptive regeneration became not feasible due to cost effectiveness versus discoloration performance. Color and also COD removals decreased simultaneously with increasing of successive regeneration cycles working with regenerated AX_i adsorbents and using of ethanol and chloroform solvents.

Contrarily, in case of acid acetic solution (1:5) (AX_2) and mixture (1:5) of acetic acid and ethanol (AX_3), the color removal of real textile effluents increased simultaneously with increasing of successive adsorption cycles until a constant value (i.e., 54.04% and 59.61%) after the fifth adsorption run with the fourth successively regenerated AX_i adsorbent.

The high discoloration and COD removals by adsorptive treatment of textile effluents working with regenerated AX_i adsorbents using organic solvents (polar solvents) related to inorganic regeneration solutions (acid, base, or only distilled water, generally ionic solvents) are indicated that the higher part of retained/adsorbed species onto AX_i adsorbents are nonionic in nature and are dissolved in a polar solvent caused of dissolution, prevailing over delicate physical interaction between AX_i adsorbent and adsorbed species. Same similar interpretations had been reported by Güzel et al. [46], Wang et al. [44], and Hunter and Sanders [47] researchers in their reported works.

After each regeneration cycle, it was noticed a certain adsorbent weight loss, which varied in range of 8.81% (for regeneration with acetic acid, AAc) to 20.93% (for regeneration with ethanol, AE) depending on regeneration solution and adopted desorption working methodology. The variation of adsorbent weight loss after each regeneration cycle is presented in Fig. 12, being in range of 11.32%–12.36% for desorptive regeneration with chloroform, 8.81%–18.13% for acetic acid, 14.07%–18.70% for mixture AAc and AE, and 14.12%–20.93% for ethanol (AE).

The performance and interpretation of adsorption treatment applied to the studied textile effluent must also consider the variation of final treated effluent pH related to the initial nontreated industrial effluent pH. The illustration of the pH variation working in adsorption treatments of real textile effluent with fresh and regenerated AX_i adsorbents based on coal fly ash activated with lime (20 g/L) is presented in Fig. 13 working at the room temperature.

As it is observed in Fig. 13, the adsorption onto AX_i adsorbent applied in the case of studied real textile effluent is beneficial in terms of a few polluting species (color, COD, and phenol) removals, and a few significant pH variations were found depending on the initial real textile effluent pH, or adjusted pH value applied in adsorption treatment system. For the studied textile effluent without any pH correction ($pH = 7.49 \pm 0.26$), the adsorption onto regenerated AX_i adsorbents changed the effluent pH to neutral (6.8–8.0), or low (9.4), or high alkaline values (10.5–11.2), being sometimes necessary a final neutralization step, usually performed by

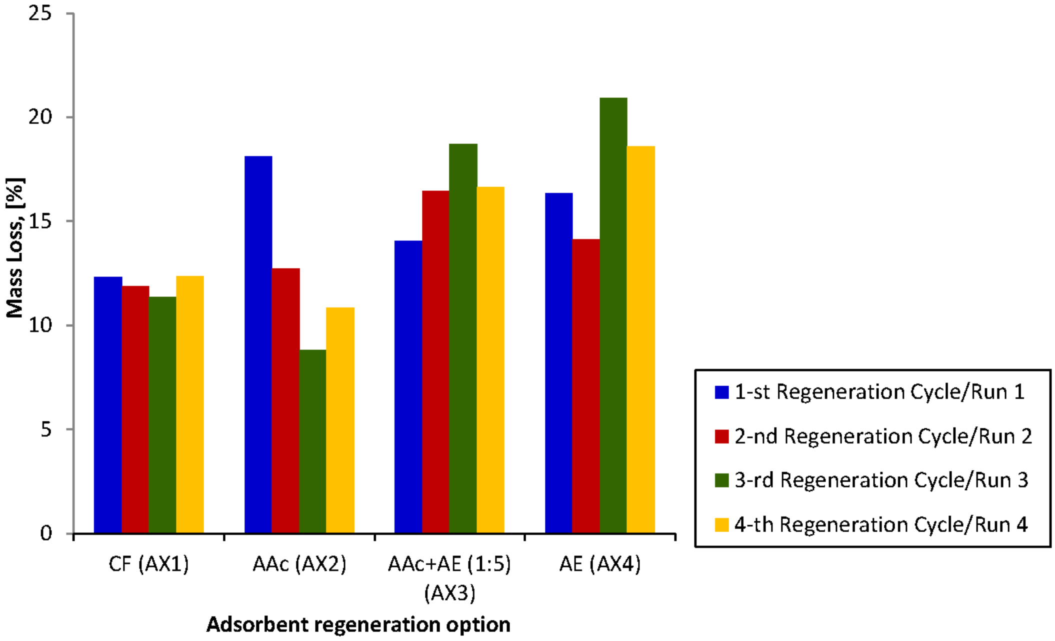

Fig. 12. Variation of weight loss after successive regeneration cycles of AX_i adsorbents applied for textile effluent adsorptive treatments (pH = 7.49 ± 0.26, 20 g/L of adsorbent, room temperature, intermittent 50–80 rpm-based stirring).

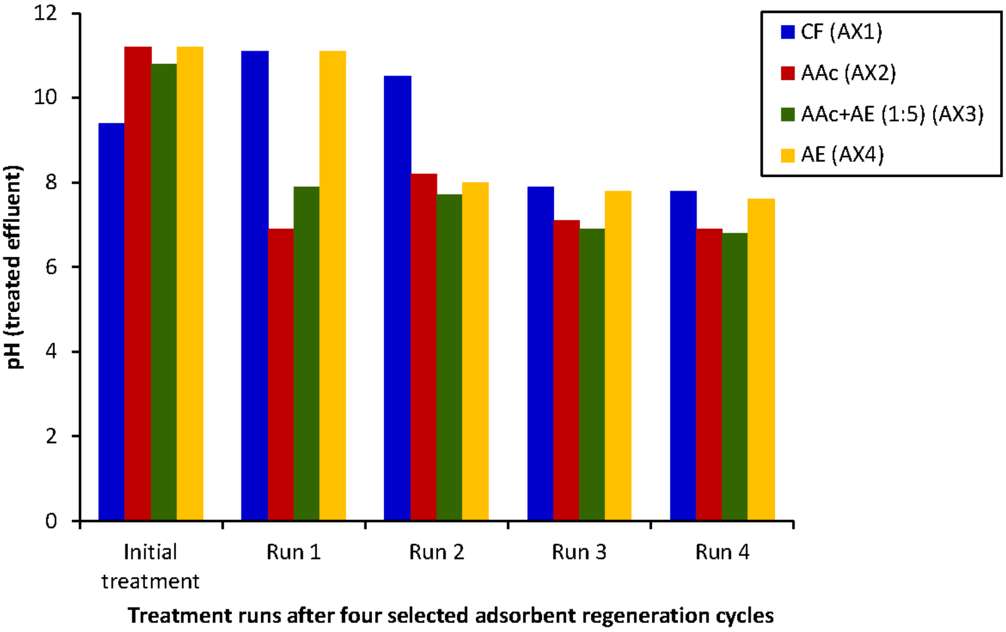

Fig. 13. Variation of treated textile effluent pH after successive adsorption experiments working with fresh and *i*th regenerated AX_i adsorbent ($i < 5$).

using direct CO_2 injection or nonaggresive acidic solution addition. Majority of adsorption experiments with regenerated AX_i adsorbents needed no supplementary neutralization step after the second regeneration cycle in both cases of direct discharge in receiving receptor nearby (watercourse), or even inside reuse/recycling.

For the real textile effluent with initial pH adjusted till the adequate acidic range (6.4–6.8), it was not necessary a supplementary neutralization step, the final treated effluent pH being in the corresponding admissible range of 6.5–8.5.

Other regeneration treatments of "spent" AX_i adsorbents can also be applied such as a few *destructive treatments* of adsorbed species with or without significant modification of AX_i adsorbent structure and composition (e.g., advanced oxidative or reductive regeneration methods), and some *nondestructive treatments*, offering the possibility to recover useful species adsorbed onto AX_i adsorbents without significant changing of adsorbent structure and composition (e.g., sonication, soft thermic, and chemical desorptions with diluted solutions of certain chemicals).

4. Conclusions

New "low-cost" materials based on mixture of coal fly ash activated with lime (AX_i, i = 1, …, 4) prepared in different calcination conditions (e.g., temperature, heating time, ratio ash: lime) were tested for evaluation of its adsorption potential to discolorize specific high loaded and colored industrial effluents (produced in a private textile company of cotton fabrics manufacturing), and also to significantly remove the content of COD and phenolic derivates.

The adequate operating parameters were found after a few series of adsorption experiments in static regime corresponding to pH range 6.2–6.8 (AX_i, i = 1–3) or 4.1–4.8 (AX_4), adsorbent dose no higher than 12–20 g/L, room temperature (22°C ± 3°C), and minimum 5.5–6.8 h of adsorption time (for adsorption equilibrium attaining), or 8 h (as a working shift), or 24 h (reference for period after adsorption equilibrium establishment with possible destabilization or stabilization action when variation of operating regime conditions appears, i.e., after min 14–18 h).

AX_1 (6.25 ash:3.75 lime, calcination/heating at 70°C, 1 h) presented highest adsorptive performance at pH 6.2–6.8 in terms of discoloration and organics removal, reported to lowest discoloration performance of AX_4, the adsorptive mechanism being probably exothermic, physical–chemical in nature (chemisorption), acting mainly by interparticles diffusion, covalent bonding, and ionic exchange. With no pH adjustment of real textile effluent, fresh and regenerated AX_4 adsorbent had higher discoloration performance related to the other AX_i adsorbents. Efficient adsorption treatments were possible by working with ith successively regenerated AX_i adsorbent (i < 5) at concentration of 20 g/L, but the "spent" adsorbent regeneration is feasible only till the fourth regeneration cycle. In this context, the results are good, offering new attractive possibilities of selective adsorption of polluting species for textile effluent discoloration purpose, and specific organics removal for recovery proposes.

This single-adsorptive treatment step can be easily integrated in the existing WWTP, helping the textile operator to recycle at least 50%–60% of its treating wastewaters in the technological manufacturing flux, being overall beneficial for process water management in the textile company.

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