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Regeneration and reuse of highly polluting textile dyeing effluents through catalytic ozonation with carbon aerogel catalysts

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Abstract

Reactive dyeing of cotton generates a great deal of coloring wastewater containing residual dyes, electrolyte, alkali, and other auxiliaries. Especially for the effluent from the first/initial spent dyeing bath, it may be comprised of as high as 60% of the initial dye dosed, 30-90 g/L of sodium chloride or sodium sulphate, and plenty of sodium carbonate, making it to be the most contaminative effluent among the entire reactive dyeing process. This paper presents a new alternative to regenerate the waste effluent from the first spent dyeing bath through catalytic ozonation with novel catalysts for reuse of the effluent in successive dyeing. Two novel ozonation catalysts, mesoporous carbon aerogel and its supported cobalt oxide nanoparticles, were successfully prepared and used in catalytic degradation of residual dyes in waste effluents with ozone. Degradation efficiency was determined by both decolorization and chemical oxygen demand removal. The result showed novel catalysts could improve both of these two targets. For chemical oxygen demand removal, carbon aerogel supported cobalt oxide strikingly enhanced the efficiency by 30% on the whole comparing to ozonation alone (approximately 50%) without the catalyst. Waste effluents after catalytic ozonation were thereafter reused in successive dyeing in the same process. It has been validated that the waste effluent was successfully regenerated and can be additionally reused twice without sacrificing fabric quality, which cannot be realized in ozonation alone. Color difference of the fabric dyed with the regenerated effluent was within the acceptable tolerance, and excellent levelness and equal colorfastness had also been achieved. This is probably the first study to investigate the feasibility of regenerating highly polluting dyeing effluents for reuse by catalytic ozonation with carbon aerogel materials. With novel catalysts, it could be speculated that catalytic ozonation is a promising technology for *in-situ* regeneration of waste effluents in textile dyeing plant for reuse.

Keywords: Textile dyeing wastewater; Effluent reuse; Catalytic ozonation; Carbon aerogel; Color quality; *In-situ* regeneration

1. Introduction

Wastewater treatment is a crucial issue in textile industry, which generates a great deal of polluting effluents containing significant residual dyes and dyeing auxiliaries. Considering both the great volume and effluent composition, textile dyeing plant is thought to be the most polluting one in all industry sectors (Alkaya and Demirer, 2014). Among all dyeing processes, cotton is the most commonly used materials (Rosa et al., 2015). As the most critical dye class for cotton, reactive dyes are developed dramatically to fulfill all around requirements, such as easy application, wide color range and good colorfastness. However, one of the biggest issues to tackle is the relative low fixation rate. It is estimated that dyes lost during dyeing could be as high as 60% of the initial dosage (Rosa et al., 2015) and in addition dyeing of 1 kg of cotton would consume around 70-150 L of fresh water totally to form the dyeing bath (Allegre et al., 2006). Consequently, at the end of dyeing procedure, significant reactive dyes that are not fixed onto the fabric are disposed with the substantial spent dyeing bath, generating enormous volume of extremely contaminative effluents. If the effluent is discharged without appropriate treatments, adverse influence would be given not only on the environment but also human health (Ozturk et al., 2015). As a consequence, removal of dyes, as well as other organic or inorganic contaminants, in textile dyeing effluent has been rated as the most important task in sustainable production of textile products (Wang et al., 2013b).

However significant challenges still exist in removal of dyes in dyeing effluents over the past years (Tian et al., 2013). Due to low biodegradability of synthetic dyes, conventional biological method, such as activated sludge, is ineffective to degrade dyes satisfactorily. It was underlined in many studies that removal of dyes by adsorption was efficient and economic (Abidi et al., 2015), but the heavy burden in replacement of adsorbents should not be ignored. Chemical oxidation, which involves dosing active oxidants onto wastewater, has been approved to be an effective approach. The reported oxidants or oxidation techniques include Fenton reagent (Yaman and Gunduz, 2015), Ultra Violet (UV) photolysis (Xing et al., 2015), ozone (Qu et al., 2015), and some combined techniques. Wherein, ozonation is thought to be a promising approach due to merits of ozone, such as high oxidation capacity, no by-products from self-decomposition and easy application without additional thermal or light energy.

Currently the environmental policy is increasingly more restricted than ever, thus more sustainable approaches are needed for cleaner production of textiles. Recent studies have been extended to carry out advanced treatments of dyeing effluents for reuse by suitable technologies, which demonstrate more significant and direct towards sustainability development. Previous research on applications of adsorption (Li and He, 2014), membrane filtration (Allegre et al., 2006), H202 oxidation (Li et al., 2013), UV photolysis (Kusic et al., 2013), radiation (Bhuiyan et al., 2016), and combining method of persulfate oxidation and lime-soda softening (Zheng et al., 2015) showed high feasibility in regeneration of dyeing effluents for successive reuse in coloration.

As growing investigations were made to utilize ozone in wastewater treatment, two pioneer studies have attempted to perform decolorization of spent effluents from bench-scale dyeing bath (Senthilkumar and Muthukumar, 2007) and industrial dyeing bath (Sundrarajan et al., 2007) by ozonation alone for reuse. However, since then few related studies are reported focusing on ozonation for reuse, especially on catalytic ozonation with catalysts. There is little available information on catalytic ozonation for regeneration of waste effluents for reuse. Comparing to ozonation alone, catalytic ozonation has great advantages. It has been Jong recognized during ozonation catalysts are capable to promote oxidative degradation of organic contaminants and thereby improve degradation efficiency. More important, they could yield mineralization, during which organics converts into inorganics completely. Consequently, over the past decades numerous attentions are paid to develop efficient catalysts to improve degradation efficiency and strengthen mineralization during ozonation. Materials which have been prepared as ozonation catalysts are mainly transition metaloxides (Zhao et al., 2014) or its hybrids (Li et al., 2015) in different forms, shapes or sizes. Unfortunately these significant outcomes have rarely been adopted in wastewater regeneration for reuse, almost all the attempts have overlooked the significance of catalytic ozonation in wastewater regeneration and reuse.

Recently a novel material, carbon aerogel (CA), has been developed for several applications due to its unique properties originating from excellent three-dimensional continuous porous structure (Yin et al., 2014). It has been used mostly for super capacitors (Liu et al., 2015) and biosensors (Peng et al., 2015), and also has also been adopted in wastewater treatment, such as catalysts for dye degradation via catalytic ozonation (Park et al., 2013) and photocatalysis (Lin and Chang, 2014), electrodes for dye electrolysis (Wu et al., 2008b), and absorbents for color removal (Wu et al., 2012). These attempts by other researchers encourage authors to pursue exploration of CA materials in wastewater regeneration by catalytic ozonation. With this in mind, the primary purpose of the present study is to evaluate the reusability of textile dyeing effluents which treated by catalytic ozonation in the presence of CA based catalysts. The catalysts used were mesoporous carbon aerogel (MCA) and MCA supported cobalt oxide nanoparticles (Co_3O_4/MCA) prepared in laboratory. Their catalytic performance was evaluated by decolorization and COD removal during catalytic ozonation. C.I. Reactive Blue 19 was selected as the target dye for degradation due to its frequent application in reactive dyeing. Dyeing effluents for catalytic ozonation were collected from the first/initial spent dyeing bath (known as the exhaustion & fixation bath), which is highly contaminated and full of residual hydrolyzed dyes, alkali and electrolyte. Fabrics from the dyeing with fresh water (fresh dyeing) and the treated/regenerated effluent (reuse dyeing) were compared, in terms of color difference, color fastness and color levelness, to assess the reusability of treated effluents.

On the basis of literature surveys, this is probably the first attempt to regenerate waste dyeing effluents by catalytic ozonation with MCA materials for effluents reuse. With the present study, it is expected to provide the feasibility assessment of reusing highly polluting dyeing effluents in successive dyeing, and simultaneously strengthen the understanding on MCA catalysts in catalytic ozonation for regeneration of waste effluents.

2. Experimental

2.1 Reagents and Materials

Cotton fabrics for dyeing (190 g/m^2) were purchased from Seven Seas Knitting & Dyeing Woks Ltd, China. Prior to dyeing, fabrics were firstly treated in a bath, containing 0.5 g/L sodium dodecyl sulfate (SDS) and 2.0 g/L Na_2CO_3, at 95 °C for 30 min, and then rinsed with cold water thoroughly. After naturally dried at ambient temperature, fabrics are ready for dyeing. C.I. Reactive Blue 19 (RB 19) was purchased from Zhejiang Longsheng Group Co., Ltd., China, and used without further purification. Its molecular structure and UV-vis adsorption spectra are illustrated in Fig. 1.

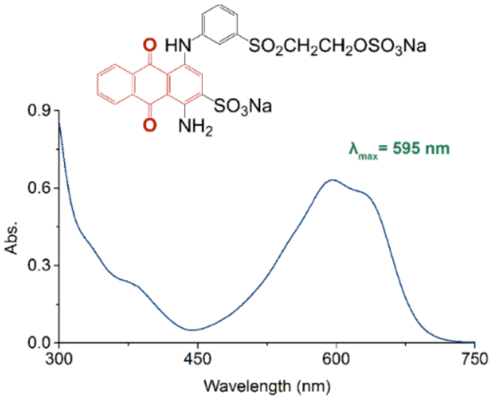


Fig. 1 Basic information of C.I. Reactive Blue 19

Other chemicals, such as formaldehyde, resorcinol, hexadecyl trimethyl ammonium bromide, cobalt (II) nitrate hexahydrate, are of analytical grades and commercially available.

2.2 Preparation of catalysts

The entire fabrication procedure has been described in our previous work (**Hu** et al., 2016). Specifically, MCA was synthesized via the sol-gel method and MCA supported cobalt oxide nanoparticles (CO_3O_4/MCA) was prepared by the impregnation approach. During impregnation, MCA granules was immersed into 0.2 mol/L $Co(NO_3)_2$ aqueous solution for loading with Co_3O_4 precursor. The loading percentage of Co_3O_4 was around 4.1% which was simply determined by thermal gravity analysis (TGA).

2.3 Experimental set-up and procedure

2.3.1 Dyeing procedure

Bench-scale dyeing was performed on a laboratory dyeing machine (Datacolor AHIBA IR™). At the beginning, at room temperature the fabric was gently immersed into the dyeing bath (fresh water) containing reactive dyes (2%, on the weight of fabric) and Na_2SO_4 (40 g/L) with a liquor ratio of 50:1. Subsequently temperature of the dyeing bath was gradually raised and later maintained at 60 °C for 30 min to fulfill dye exhaustion. The fabric was later on taken from the dyeing vessel which carefully added with Na_2CO_3 (10 g/L) soon (Shang, 2013). Afterwards, the fabric was re-immersed into the dyeing bath which was maintained at 60 °C for another 30 min for dye fixation. Towards the end, the fabric was gently transferred from the dyeing vessel and the fixation bath was carefully collected to form the highly contaminative dyeing effluent for eventually catalytic ozonation. The fate of dyeing effluents is illustrated in Fig. 2.

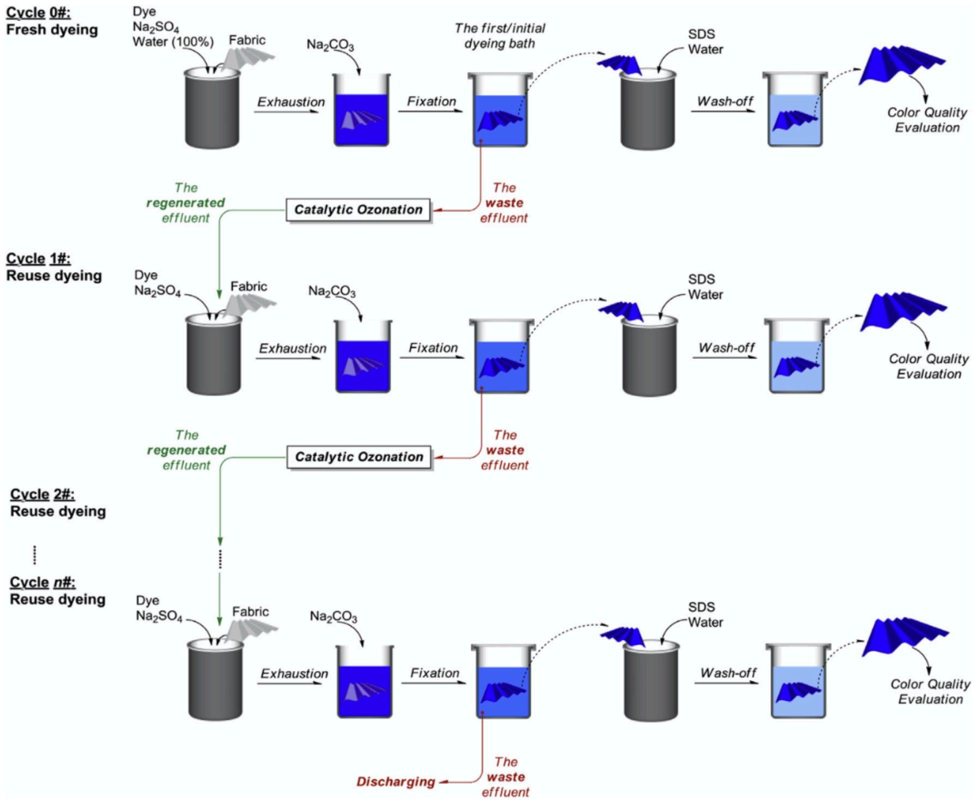


Fig. 2 Flow chart for treatment and reuse of dyeing effluents

The fabric from fixation bath was then rinsed for one warm bath (50 °C), followed by soaping with 0.5 g/L SDS at 95 °C for 15 min. One additional warm rinsing was conducted for thorough removal of the loose color on the fabric. All rinsing and soaping baths were prepared with a liquid ratio of 50:1. The fabric was finally air dried for later on evaluation of color quality. The entire dyeing process can be observed in Fig. 3.

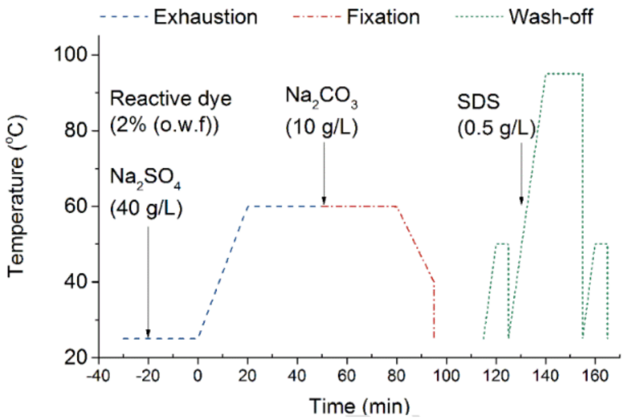


Fig. 3 Process curve for cotton dyeing with fresh water

2.3.2 Catalytic ozonation of dyeing effluents

Prior to ozonation, the effluent filtered through filtration paper (0.45 *μm)* to remove fiber tows for better utilization of ozone. Catalytic ozonation was performed in a 1000 mL glass reactor (Hu et al., 2016), in which the 750 mL dyeing effluent was continuously bubbled by an ozone and oxygen gas mixture through a gas diffuser which allocates at the reactor bottom. Ozone gas in the gas mixture is produced by a medical ozone generator (Medozons BM-02, Russia) which was fed with industrial oxygen with a purity of 99.9%. The off-gas containing residual ozone is washed by KI solution. After each predetermined time intervals in ozonation, 3 mL of effluent sample was carefully transferred out and slowly filtered through membrane filter (Millipore, 0.45 μm) to remove the trace catalyst from the liquid thoroughly. The filtrated liquid was then used for color and COD determination. To reduce experimental error, each independent measurement is performed triply, and the average value is adopted. At the end, the treated effluent in the reactor was completely transferred out and carefully filtrated again before reuse in dyeing afterwards.

2.3.3 Reuse of dyeing effluents in successive dyeing

Prior to carrying out successive dyeing, the effluent was first neutralized with 1 mol/L H_2SO_4 solution to avoid dye hydrolysis during reuse dyeing. The reuse dyeing procedure was principally in accordance with that in fresh dyeing as descript in section 2.3.1, except the dyeing medium was changed to treated effluents and the amount of Na_2SO_4 was re-calculated separately. Na_2SO_4 concentration in reuse dyeing was determined by effluent conductivity (Rosa et al., 2015), which should be equivalent to 40 g/L of Na_2SO_4 in fresh dyeing. The Na_2SO_4 concentration as a function of conductivity of its solution is shown in Fig. 4. According to the calibration equation from Fig. 4, the conductivity of treated effluents was therefore corrected to around 36.0 mS/cm to maintain the electrolyte effect in reuse dyeing.

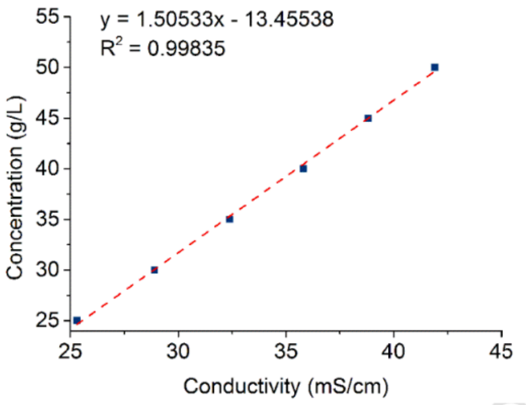


Fig. 4 Calibration curve of Na_2SO_4 solution (23.3 ℃)

2.4 Analytical methods

The structure and morphology of catalysts are investigated by SEM (Leica Stereoscan 440), TEM (JEOL Model JEM-2100F) and XRD (Rigaku, SmartLab) using Cu Ka radiation.

The efficiency of dye degradation was measured by both decolonization and COD removal. Decolonization is determined on a UV-vis spectrophotometer (Perkin-Elmer, Lambda 18) by evaluating the decrease of absorbance at the wavelength of 595nm. The decolorization percentage is calculated by using Eq. (1):

$$\text{Decolorization (\%)} = (A_o - A_t)/A_o \text{ x } 100 \tag{1}$$

Where A_o is the initial absorbance of the dyeing effluent; and

A_t is the absorbance of the dyeing effluent after a specific time of ozonation.

COD is determined in accordance with the Hach Method 8000: Oxygen Demand, Chemical (Zhao et al., 2015). COD removal is calculated by using Eq. (2).

$$\text{COD removal (\%)} = (COD_o - COD_t)/COD_o \text{ x } 100 \tag{2}$$

Where COD_o is the initial COD of the dyeing effluent; and

COD_t is COD of the dyeing effluent after a specific time of ozonation.

Color quality of fabrics dyed from reuse dyeing is compared with those from fresh dyeing. The CIELab color system (Gundogan and Eren, 2014) is adopted to evaluate lightness (L* chromaticity $(a*$ and $b*)$ and color difference ($\Delta E_{cmc(2:1)}$) on a spectrophotometer (Macbeth Color-Eye 7000A) in accordance with AATCC Test Method 173. AATCC Test Method 61 and AATCC Test Method 8 are used to determine colorfastness to laundering and crocking.

3 Results and Discussion

3.1 Characteristic of catalyst

XRD patterns of MCA and Co_3O_4/MCA are presented in Fig. 5. For both of curves, broad peaks at around 2θ=23° could be associated to the (0 0 2) plane of amorphous carbon materials (Han et al., 2015), which are similar to that of carbon nanofiber (Wang et al.,2013a). By comparing Co_3O_4/MCA to pure MCA, some new peaks were clearly observed. According to the JCPDS card no. 80-1541, characteristic peaks at 19.1°, 31.1°, 36.8°, 59.2° and 64.6° well matched up to the (1 1 1), (2 2 0), (3 1 1), (5 1 1) and (4 4 0) planes of Co_3O_4 in sequence (Guo et al., 2008), suggesting Co_3O_4 having a crystalline cubic structure (Lai et al.,2008).

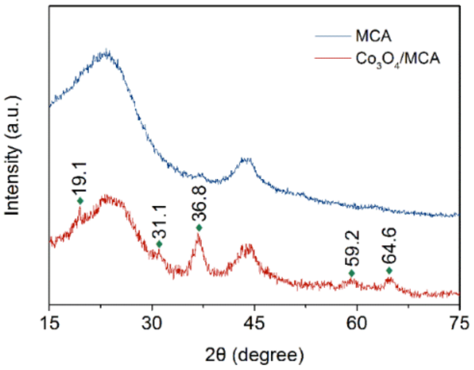


Fig. 5 XRD pattern of MCA and Co_3O_4/MCA

Fig. 6 shows TEM illustration of Co_3O_4/MCA. According to Fig. 6a and Fig. 6b, grey flakes and black spots were assigned to carbon particles and Co_3O_4 particles, which were main components of the composite. Carbon particles, ranging from 20 to 30 nm, interconnected to each other to form the three-dimensional structure, and meanwhile numerous mesopores were generated among the agglomerated carbon nanoparticles (Wu et al., 2012). In addition, the even distribution of nano-size black spots on grey flakes demonstrates that Co_3O_4 nanoparticles were well-dispersed and embedded in the amorphous MCA. According to high resolution images in Fig. 6c and d, evident spinel patterns were observed within the dark tone, suggesting Co_3O_4 existed as excellent nanocrystals, which was in a good agreement with the evidence from Fig. 5.

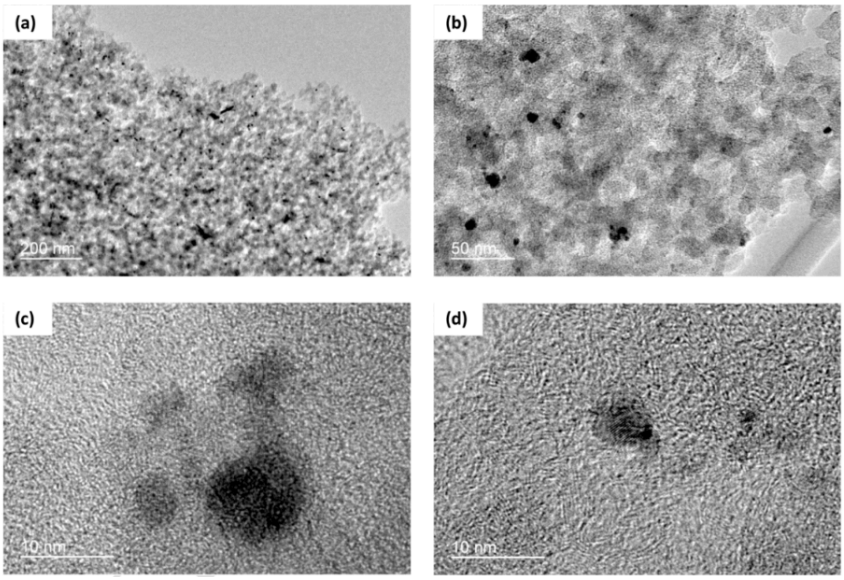


Fig. 6 TEM images of Co_3O_4/MCA

On the basis of Fig. 6a, the diameter distribution of total 323 Co_3O_4 nanoparticles was statically analyzed and the result can be found in Fig. 7. It is apparently nanoparticle diameter, which was 4.86 nm averagely, was mainly from 2 to 8 nm. The particle sizes of almost 50% of all nanoparticles were rather close to 4 nm, implying that the size distribution was of excellent monodispersity.

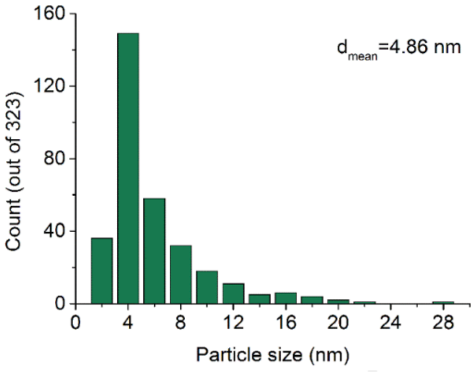


Fig. 7 Size distribution of Co_3O_4 over MCA

Fig. 8a and b show the SEM images of MCA in different scales. The rough surface was evidently observed, which predominantly stemmed from agglomerated carbon particles. This evidence was parallel to TEM patterns in Fig. 6a and b. The surface morphology of Co_3O_4/MCA is illustrated in Fig. 8c. It is hardly to observe clearly Co_3O_4 nanoparticles. This could be explained that the sizes of the nanoparticles were too small to be noticed in the current SEM resolution. This is thought to be an additional evidence to prove the particles were of nanoscale (Han et al., 2015). On the basis of characterization results mentioned above, the schematic representation of Co_3O_4/MCA surface/interface is inferred in Fig. 8d. Cubic Co_3O_4 nanoparticles are speculated to grow evenly on the surface/interface of MCA, which is consisted of agglomerated carbon particles.

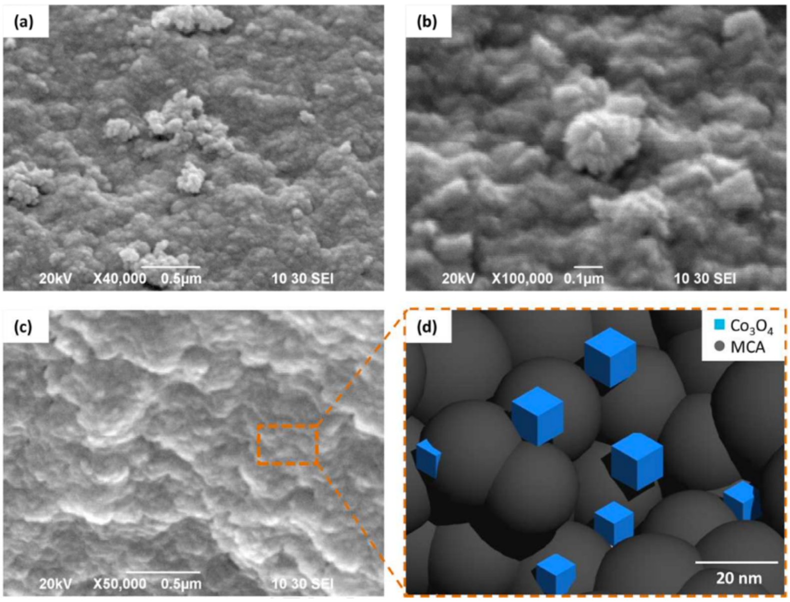


Fig. 8 SEM images of MCA (a & b) & Co_3O_4/MCA (c), and schematic representation of Co_3O_4/MCA (d)

3.2 Catalytic ozonation of dyeing effluents

In order to evaluate the potential of MCA materials in promoting ozonation of dyeing effluents, three ozonation essays, single ozonation and catalytic ozonation in the presence of MCA and Co_3O_4/MCA, were performed and compared with respect to decolorization, COD removal, pH and conductivity. Unless further stated, essays were performed under following conditions: T= 24°C; ozone dosage= 2.5 mg/min; catalyst amount= 3 g.

3.2.1. Decolorization of dyeing effluents

Decolorization is critical in reuse dyeing, as color quality could not be guaranteed if color removal was not implemented. Residual color in reused dyeing bath probably influences the followed dyeing, in terms of color tones, color depth and color fastness. In the current study the intention was to determine decolorization behavior of effluents by ozonation with or without catalysts, towards evaluation of catalytic performance in color removal. It is evident from the results that in cases involving ozonation, decolorization percentage was rapidly enhanced with time (see Fig. 9) on the whole. In addition, there was a sudden rise at the first beginning regardless of the presence of catalysts or not. Afterwards the increasing tendency leveled off at 5 min and no substantial improvements were observed.

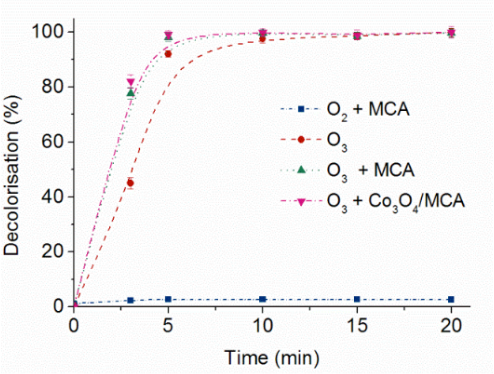


Fig. 9. Decolorization of dyeing effluent by catalytic ozonation.

However, exact situations in these cases were not fairly the same. For example, in two catalytic ozonation, before reaching to completed decolorization, color removal rates were substantially larger than that in ozonation alone. This could be inferred that the presence of catalysts, either MCA or Co_3O_4/MCA, could increase decolorization comparing to ozonation alone. Previously, it has been reported that in some circumstances the strengthened color removal stemmed from physical adoption of dyes by catalysts (Lin and Chang, 2014). Nevertheless, when considering the reference process which was only provided with oxygen, marginal decolorization percentage (as low as 3%, see Fig. 9) was observed. This goes against the evidence reported in a study (Wu et al., 2012), in which MCA displayed undeniable adsorption capacity to C.I. Basic Yellow 87. The contradictory could be interpreted as the target dye used in the previous study was much smaller (molecular weight: 337.4 g/ mol) than RB19 (molecular weight: 626.5 g/mol). Thus in the present study dye adsorption was not as noticeable as that for C.I. Basic Yellow 87. This implies that in this study color removal by physical adsorption was almost negligible according to Fig. 9. The improved efficiency presumably arised from chemical oxidation induced by catalytic ozonation.

It has been suggested that porous carbon materials could play important roles, besides adsorption, in catalytic ozonation in improving degradation efficiency (Wu et al., 2015). The most acceptable mechanism is porous carbon could enhance mass transfer of ozone into aqueous phase, and simultaneously promote decomposition of ozone to generate reactive species which may have even higher oxidation capacity than ozone itself (Liu et al., 2012). Because decolorization of dye is the consequence of oxidative cleavage of chromophoric group (mono azo group, -N=N-, in this case) within dye molecules (Wu et al., 2008a), the generated reactive species are likely to accelerate cleavage of -N=N- group and the relevant decolorization percentage is therefore higher. As total decolorization was almost achieved after the beginning 5 min, the advantage of catalysts in decolorization was believed to be fully shown only at the very short start.

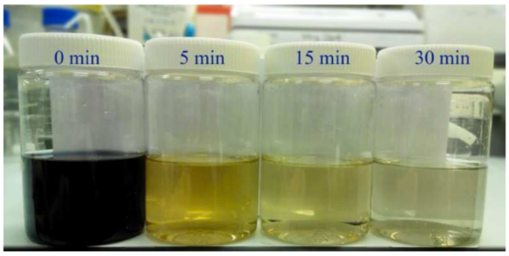


Fig. 10 Dyeing effluents after catalytic ozonation

As discussed previously decolorization almost reached 99% after the first 5 min, in the case of ozonation with MCA. Further supplying of ozone in the reactor was unlikely to account for additional color removal. Nevertheless, when carefully inspect the appearance of effluents during catalytic ozonation visually, shades of these treated effluents were considerably distinct. Fig. 10 corresponds to the visible image of waste effluents after catalytic ozonation with MCA for varied time. As can be observed in Fig. 10, the shade of color for the effluent without ozonation (0 min) was dark navy to black, being the deepest among four samples. After 5 min catalytic ozonation, the effluent was strikingly converted into transparent but with dark yellowish color. Continuously aeration of the effluent with ozone contributed to further reduction of color depth. After total 30-min catalytic ozonation, the yellowish color was appreciably lightened and was close to fresh water in appearance. These contradict evidences of color removal mainly originated from the instrumental method used in the color detection. In decolorization determination, the absorbance of the effluent obtained from the UV-vis spectrophotometer is accompanied with the concentration of dyes. In this case, absorbance used for calculation of decolorization is exclusively recorded at the wave length of 595 nm, where RB19 has the maximum absorbance (see Fig. 1). Thus 99% decolorization only suggests that almost all dyes having complete chromophoric group(s) were decomposed, rather than all coloring matters. For example, by-products from dye degradation may have no or little absorbance at the wave length, λ_{max}= 595 nm, but they possibly have absorbance elsewhere and may display certain color. It could be speculated by-products yielded the yellowish shade of the effluent which has been almost 100% decolorized according to UV-vis absorbance. The fact that increasingly paler shade of the effluent with ozonation time points to the likelihood that by-products were gradually degraded by catalytic ozonation as reaction proceeded. The inconsistent between observed yellowish shade and 100% decolorization of the effluent may imply that 5 min ozonation seemed not adequate to guarantee the treated effluent could be regenerated for reused.

3.2.2. COD removal in catalytic ozonation

Decolorization is only one of the objectives in catalytic ozonation for wastewater treatment. The more important aspect is to understand the capability of catalytic ozonation in degradation of organic pollutes towards total mineralization. For the sake of evaluation of catalysts in promoting mineralization, chemical oxygen demand (COD) was assessed to quantitatively describe the organic contaminants remaining in the solution, probably including residual dyes, dye intermediates from dye decomposition, and other by-products from advanced oxidation of dye/intermediates. This is because COD measures the overall organic substances that can be oxidized chemically in solution (Vittenet et al., 2015).

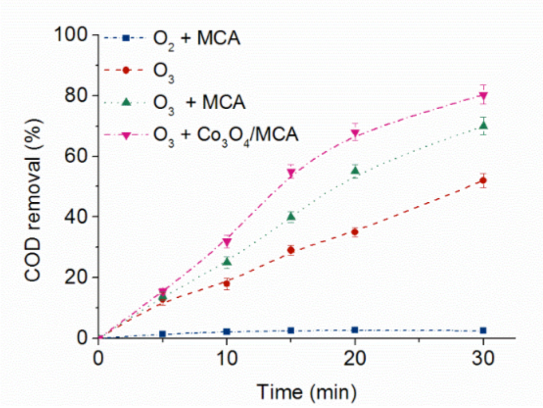


Fig. 11. COD removal of dyeing effluents by catalytic ozonation.

As shown in Fig. 11, unlike color removal, COD removal rose steadily rather than suddenly on each occasion, suggesting COD removal is much harder than decolorization. This could be attributed to the fact that decolorization only involves primary oxidation stage, corresponding to cleavage of azo group -N=N- in this study, which is much easier to implemented. 100% decolorization may only yield slight COD reduction especially when the dye molecule is large. Considerable COD reduction may require more complicated multistage oxidative reactions. Fig. 11 also demonstrates that the catalyst MCA strikingly enhanced the COD reduction efficiency by 20% on the whole, comparing to ozonation alone (approx. 50%). Besides the contribution from adsorption (approx. 2.6%), MCA could reasonably improve COD reduction, implying dye degradation was promoted via chemical oxidation by ozone in the aid of MCA. The most widely known reason for such improvement is the presence of carbon material imitates the decomposition of ozone into hydroxyl radicals (HO•) (Oulton et al., 2015), of which the oxidation capacity is even greater than ozone. It is also worth noting that process involving catalyst Co_3O_4/MCA could be ranked as the most efficient treatment, in which 30 min ozonation enabled around 80% of COD to be removed. This could be explained that both multivalence oxidation states of Co_3O_4 strengthened interfacial transfer of electrons, which plays critical roles in oxidation (Hu et al., 2008), resulting in improved catalytic activity of the catalyst.

3.2.3. pH and conductivity changes

pH control is important in textile dyeing, especially in reactive dyeing. Alkalinity should be maintained appropriately to certain extent to assist dye fixation onto fabric (Shang, 2013). Thus at the end of reactive dyeing, the first dyeing bath is generally alkaline. As it has been found that catalytic activity of MCA materials were greater in alkaline condition (Hu et al., 2016), the waste effluent was not neutralized or acidized before ozonation. It has been reported ozonation of organic compounds led to the generation of acidic by-products (Ikhlaq et al., 2014), causing pH fall in the solution. However, pH hardly varied through the entire treatment and little differences were noticed among the three essays according to Fig. 12.

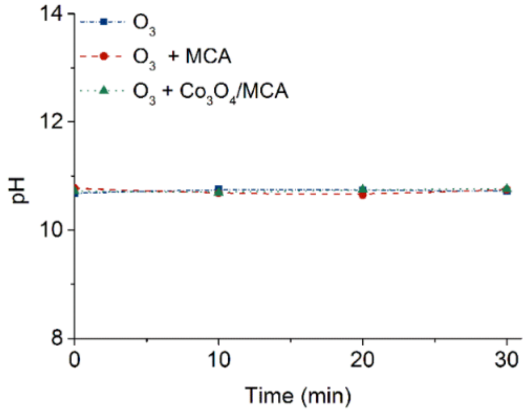


Fig. 12. pH evolution during catalytic ozonation.

In a similar study (Colindres et al., 2010), in which C.I. Reactive Black 5 was adopted as the target degradation dye by ozonation, pH declined radically to acidic range after ozonation. This dissimilar evolution trend of pH may attribute to the significantly excess amount of Na_2CO_3 (initial concentration was 10 g/L) presented in the effluent, which likely depleted newly generated acidic by- products and sustained the effluent being alkaline. To proof this conjecture, a parallel experiment, in which the effluents for ozonation were neutralized first, the results are shown in Fig. 13.

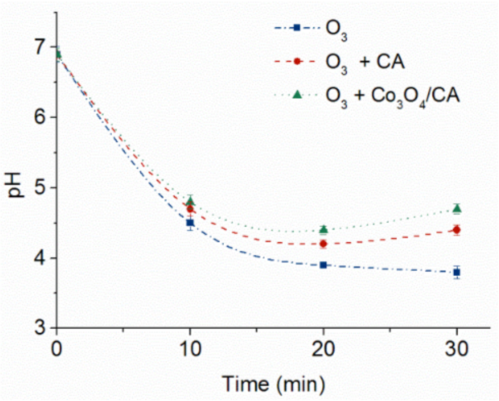


Fig. 13. pH evolution during catalytic ozonation (effluent after neutralization).

According to Fig. 13, pH declined with treatment time before the first 20 min, which could be attributed to the accumulation of acidic byproducts as mentioned earlier. However, the acidity of the effluent treated by ozonation alone was moderately lower than the two catalytic processes. This could be explained that in ozonation alone, molecular ozone which was oxidatively selective could not mineralize refractory acidic byproducts, such as oxalic acid and oxalic acid (Faria et al., 2008), to inorganics. In addition, although the hydroxyl radicals, which could be generated from spontaneous decomposition of molecular ozone, were oxidatively non-selective and therefore were capable to mineralize the refractory acids, acid removal in the effluent still hardly happened. This was because in the acidic condition, the spontaneous decomposition of molecular ozone was extraordinarily weak. Thus, these acids accumulated in the effluents gradually causing pH decline. While in catalytic ozonation, hydroxyl radicals could be produced from catalytic decomposition of molecular ozone in the presence of catalysts, in addition to spontaneous decomposition. Consequently the accumulation of refractory acids in the effluents subjected to catalytic ozonation was less severe than that in ozonation alone. As a result, the pH of effluents reclaimed by catalytic ozonation was higher than that of the effluent from ozonation alone.

After 30-min ozonation, the final pH was perceived to rise slightly comparing to the pH at 20 min in the two catalytic ozonation. This may be explained that when approaching the final mineralization of dye in catalytic ozonation. The degradation of refectory acids was strengthened, which led to the decreased solution acidity. By contrast in ozonation without catalyst, the degradation of refractory acid only depended on the hydroxyl radicals generated from the spontaneous decomposition of molecular ozone. Thus the final pH did not rise up as that in catalytic ozonation.

After the 30-min treatment for comparison, 100 mL of effluents from the three different ozonation processes were added with 1 g of Na_2CO_3, which was equivalent to the dosage in real dyeing process. It was observed the pH raised to around 10.7 no matter which process applied, suggesting the amount of Na_2CO_3 was substantially excess to acidic byproducts in effluents. Therefore regardless of the fact the amount of acidic byproducts generated during ozonation processes was slightly different, the overall pH of effluents was almost identical.

Conductivity is another essential target to monitor in addition to pH. As stated before, conductivity has been adopted to measure the electrolyte effect, which can be ranked as one of the most critical parameters in process control of reactive dyeing, of the effluent in this study. This is because the salt is usually added into reactive dyeing bath to overcome repulsive forces between the fabric and ionized dye molecules, so as to improve the substantivity of the fabric to dyes and eventually improve the dye uptake (Shang, 2013). In the fresh dyeing, electrolyte strength is generally sustained by dosing fixed amount of Na_2SO_4 or NaCl into dyeing bath. Nevertheless, in a reuse dyeing simple dosing of fixed salt amount is not ideal to process control, because the existence of significant amount of residual salt in the effluent has to be considered particularly. In modem wastewater reuse, electrolytes in aqueous solution are generally removed by reverse osmosis (Bunani et al., 2015). But in textile dyeing with reactive dye, salt presents in effluent can be recycled and the removal by reverse osmosis tends to be not extremely necessary. In a recently published research (Rosa et al., 2015), treated effluent was not desalinated but supplemented with additional salt to the required degree which was equivalent to that in fresh dyeing, on account of the dyeing effluent to be reused in that case had been diluted.

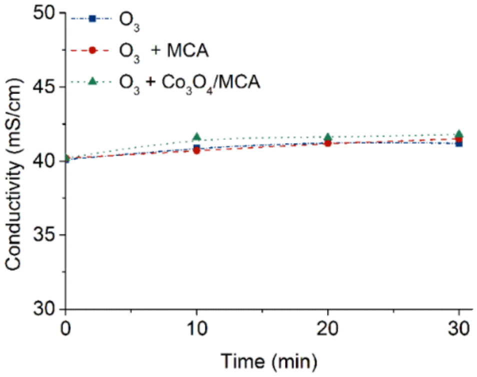


Fig. 14. Conductivity evolution during catalytic ozonation.

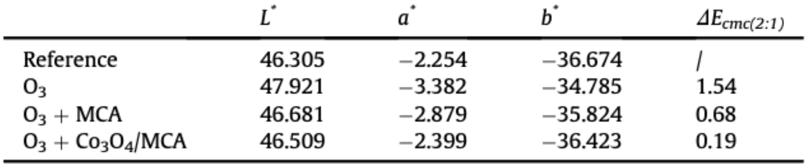
The objective on monitoring the conductivity was to add understanding on catalytic ozonation, and determine the concentration of salt in effluents as well. As displayed in Fig. 14, there were almost no differences observed from the beginning to the end for each process or among the distinct processes. This is not in agreement with the expectation that conductivity was likely to rise after ozonation (Colindres et al., 2010), due to the generation and accumulation of sulfate and nitrate ions from dye denitration and desulfuration (Tehrani-Bagha et al., 2010). The unexpected evidence may probably attribute to that the plenty Na_2SO_4 and Na_2CO_3 presented in the effluent. Under the same treatment conditions, the conductivity of the simulated waste effluents, which were in the absence of Na_2SO_4 and Na_2CO_3 but possessed equivalent dye amount, was increased from 193 μS/cm to 308 μS/cm, 395 μS/cm, 446 μS/cm, for ozonation alone, ozonation with MCA and ozonation with Co_3O_4/MCA. Despite the fact that the simulated effluents were not exactly as same as the real waste effluents from dyeing bath, it pointed to that the ions from dyes (completed dye molecules and byproducts from dye degradation) hardly contributed to the overall conductivity of effluents. Consequently, conductivity differences, which were no larger than 0.5 mS/cm, between the processes could be neglected if considering the overall conductivity of the effluents was as high as 41 mS/cm.

3.3. Color quality evaluation

3.3.1. Color reproducibility

As mentioned earlier, recent objective on chemical oxidation is not only limited to wastewater treatment. Attempts have been made towards reuse of the treated wastewater for certain purposes. Thus understanding removal of color and COD, as well as the evolution of pH and conductivity, are not the only intensions in the current study. More importantly it is necessary to ascertain the feasibility of catalytic ozonation in regeneration of waste dyeing effluents for reuse. Therefore, effluents after 30-min treatments were collected for dyeing of cotton to exam the reuse possibility. The other samples treated less than 30 min were not selected, as they still displayed substantial visible yellowish color (see Fig. 10) though 100% decolorization (see Fig. 9) has been achieved according to instrumental assessment by UV-vis spectrophotometer. CIELAB system is used to evaluate the color quality of fabrics dyed with treated effluents, including lightness value L^*, chromaticity a^* and b^*, and most importantly color difference $\Delta E_{cmc(2:1)}$.

Table 1 Color quality of fabrics dyed with fresh water and treated effluents.



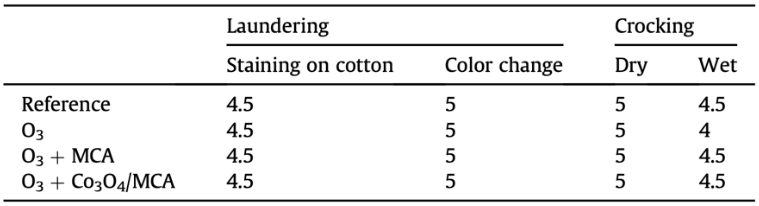
	L^*	a^*	b^*	$\Delta E_{cmc(2:1)}$
Reference	46.305	−2.254	−36.674	/
O_3	47.921	−3.382	−34.785	1.54
O_3 + MCA	46.681	−2.879	−35.824	0.68
O_3 + Co_3O_4/MCA	46.509	−2.399	−36.423	0.19

As summarized in Table 1, lightness of fabrics from reuse dyeing (fabric-$_R$) was relatively greater than the control fabric from fresh dyeing (fabric-$_F$), indicating that fabric-$_R$ was slightly lighter in shade than fabric-$_F$. The chromaticity a^* and b^* represent green-red axis value and yellow-blue axis value of the specific color located in the three-dimensional CIELAB color system (Rosa et al., 2014). The greater positive a^* of fabric-$_F$ listed in Table 1 implies that fabric-$_R$ was greener comparing to the reference fabric; by contrast the weaker positive b^* indicates that fabric-$_R$ was not as blue as fabric-$_F$. These variations of color parameters mentioned above were mainly affected by the accumulation of by-products from dye degradation, which tended to influence the dyeing procedure, in either exhaustion or fixation stages.

The color difference $\Delta E_{cmc(2:1)}$, which correlates well with visual assessment by human naked eyes (AATCC, 2009), is the most significant indicator to objectively evaluate color reproducibility in general. It can be seen in Table 1, the effluent treated with pure ozonation caused the fabric with the largest $\Delta E_{cmc(2:1)}$ corresponding to 1.54 against the control fabric-$_F$, conversely the effluent treated by catalytic ozonation with Co_3O_4/MCA showed the lowest $\Delta E_{cmc(2:1)}$, which was only 0.19. It has long been known that larger $\Delta E_{cmc(2:1)}$ means the color difference between two fabrics is easier to perceive by human naked eyes. Thereby the evidence from Table 1 points to the probability that effluents after catalytic ozonation could re-produce more similar color quality. Furthermore, by comparing effluents from catalytic ozonation processes with MCA and Co_3O_4/MCA, the later process could better regenerate effluents to obtain closer color performance than the former one. This could be associated with the result illustrated in Fig. 11, from which catalytic ozonation with Co_3O_4/MCA displayed the highest efficiency in contaminant removal. To sum up, it could be inferred that, in the aid of high efficient catalysts based on MCA, catalytic ozonation extensively eliminated by-products in effluent, which may affect dyeing procedure, by appreciable mineralization effect.

In general $\Delta E_{cmc(2:1)}$ no more than 1.0 is thought to be acceptable in evaluation of color reproducibility (Li and He, 2014), as human naked eyes could rarely detect the color variation within this limit. On this ground, it is conceivable that pure ozonation in the present conditions was not adequate to effectively regenerate the effluent to fulfill color reproduction in reuse dyeing. However, it can be validated that catalytic ozonation in same conditions offered waste effluents with reusability, without sacrificing color performance beyond acceptable level. Furthermore, colorfastness evaluation (see Table 2) also indicated that the fastness of fabric-$_R$ was almost identical to the control one fabric-$_F$.

Table 2 Colorfastness of fabric-$_R$ and fabric-$_F$.



	Laundering		Crocking	
	Staining on cotton	Color change	Dry	Wet
Reference	4.5	5	5	4.5
O_3	4.5	5	5	4
O_3 + MCA	4.5	5	5	4.5
O_3 + Co_3O_4/MCA	4.5	5	5	4.5

This practically valuable innovation demonstrates the feasibility of regeneration of highly contaminant effluent by simple catalytic ozonation for subsequent reuse in dyeing. Although some studies have been conducted on decolorization by ozonation alone (Colindres et al., 2010), or mineralization of textile dyeing effluents for reuse by Fenton reaction (Li et al., 2013) or H_2O_2 promoted photocatalysis (Rosa et al., 2015), the target effluents, which have been diluted by other colorless effluents, were of very low concentration of residual hydrolyzed dyes, electrolyte, and/or alkali, comparing to the effluent from the first spent dyeing bath. However, in this study the high contaminative effluent from the first spent dyeing bath was selected, rather than those diluted by rinsing or soaping bath from wastewater treatment plants. This is because regeneration of highly polluting effluents is much more significant. Firstly, there is no need to induce effluents to wastewater treatment plant for treatment and pump back for reuse after treatment. The effluents can be in-situ regenerated and renovated by ozonation devices in dyeing plant, which shortens recycling time and meanwhile downsize the scale of recycling system. In addition, the treatment of initial waste effluents could lead to saving of electrolyte. As stated earlier, reactive dyeing consumes a large quantity of salt to assist dyeing exhaustion. The effluent with high concentration of salt makes it unnecessary to add extra salt in successive reuse dyeing, provided that it has been successful regenerated. The salt can be recycled along with the reuse of regenerated effluents, until the effluent cannot be further used for the consideration of quality control. By contrast, once the initial dyeing effluent was induced to wastewater treatment plants, it is inevitably diluted by other effluents. Thus additional quantity of salt must be dosed into the regenerated dyeing effluents to compensate the decrease of electrolyte strength. It is believed that catalytic ozonation with MCA based catalysts could save both freshwater and salt by reuse of highly polluted waste effluents, so as to relief some burdens in wastewater treatment. Simultaneously the valuable innovation offers a new sight in in-situ regeneration of waste effluents to simplify the reuse process.

3.3.2. Effect of reuse cycles on color reproducibility

Though catalytic ozonation in the current study has demonstrated surprising potential in regeneration of waste effluents being of high pollution, the reused effluent has to be discharged and disposed eventually for consideration of quality control. Because persist by-products from catalytic degradation of dye would gradually accumulate in the effluent and may affect dyeing quality. For the purpose of knowing the repetitive utilization potential of effluents after catalytic ozonation, color differences $\Delta E_{cmc(2:1)}$ of fabric-$_{\mathrm{R}}$ against the number of reuse was examined. The result in Fig. 15 shows that $\Delta E_{cmc(2:1)}$ rose with the recycle number for both of the two catalytic ozonation and the increasing tendency accelerated as recycling proceeded forward. This phenomenon is parallel to findings from previous studies (Colindres et al., 2010; Li et al., 2013).

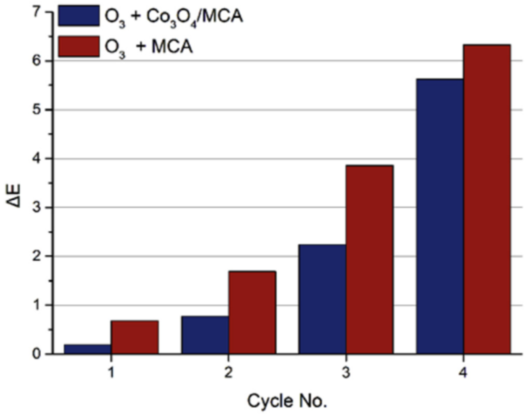


Fig. 15. CIELAB Color differences of fabric-$_{\mathrm{R}}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In addition, color similarity obtained from the effluent treated by catalytic ozonation with Co_3O_4/MCA was somewhat higher than that with pure MCA. The probably reason has been mentioned earlier, it corresponded to the likelihood that strengthened transfer of electrons on Co_3O_4 interface brought about improved mineralization of by-products. On account of the tolerance of color difference is 1.0, it can be speculated from Fig. 15 that the effluent could be reused twice after catalytic ozonation with Co_3O_4/MCA; however it could be only used one more time by catalytic ozonation with pure MCA. The reusability of effluents presented in the current study was relatively not as appreciable as those from similar studies regarding dyeing effluents reuse. There are several probabilities accounting for the difference. To begin with, effluents selected in the present study was highly contaminated from the first spent dyeing bath but others are not (Colindres et al., 2010; Li et al., 2013; Rosa et al., 2015), which makes effluents much more difficult to be regenerated through catalytic ozonation. In addition, the contaminant RB19 in effluent is a persist dye containing anthraquinone group (Tehrani-Bagha et al., 2010), leading to substantial difficulty in mineralization. Furthermore, one study employed extra means in reclamation of effluents such as adsorption (Li and He, 2014), producing effluents being of better quality.

3.3.3. Dyeing levelness of fabric-$_R$

Dyeing levelness of fabrics dyed in exhaustion process is generally seldom concerned in conventional reactive dyeing. Because the electronic repulsion between ionized fabric (Cell-O$^-$) and soluble dye (Dye-SO_3^{2-}) in dyeing bath is significant, dye absorption and de-absorption by fabrics dynamically occur in the dyeing bath at the same time, leading to good evenness of dye adsorption by fabrics. However, in reuse dyeing, the ingredients from dyeing bath were more complicated. Uncertain by-products from dye decomposition may influence the absorption and de-absorption procedures, contributing to affected distribution of dyes on fabric and inferior dyeing levelness in turn. Thus leveling property is essential to be considered in reuse of regenerated waste effluents.

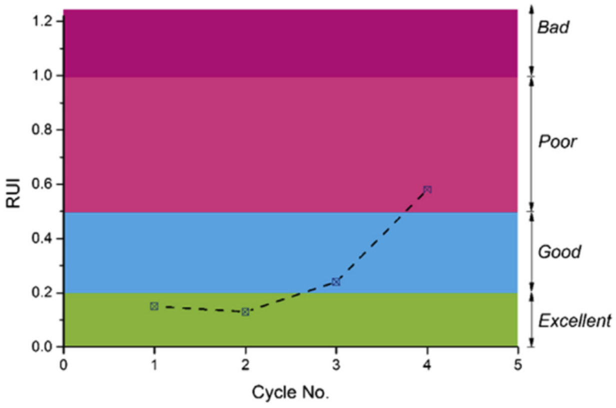


Fig. 16. Evolution of RUI during excessive reuse of dyeing effluents.

Relative unlevelness index (RUI), which has been proposed and used previously (Chong et al., 1992), was adopted as an objective method to quantify the evenness degree of colored fabrics. RUI of fabric dyed with the effluent treated by catalytic ozonation with Co_3O_4/MCA is illustrated in Fig. 16. The increasing number of reuse time gave rise to enlarged RUI, suggesting inferior evenness was achieved on the dyed fabric. This observed phenomenon may ascribe to gradual accumulation of retardant by-products in repeatedly reused effluents. The grades of RUI have also been illustrated in Fig. 16, from which RUI no more than 0.2 is associated with ‘excellent’ grade and by contrast RUI ranging from 0.2 to 0.5 is recognized as ‘good’ grade. Therefore, it is clear that the levelness of fabrics dyed from the first two cycles of reuse dyeing was both ‘excellent’ but it declined to ‘good’ in the followed third circle. This result could be related to the evolution of color difference $\Delta E_{cmc(2:1)}$ in successive reuse dyeing, which probably owning to the increasing accumulation of degradation by-products, from little to substantial, in regenerated effluents.

4. Conclusions

Reuse of wastewater is a new tide for environmental protection and sustainability development in textile industry. Very little research has been conducted concentrating on catalytic ozonation of highly polluting dyeing effluent towards reuse. Published reports predominantly focused on regeneration and reuse of dyeing effluent of much lower contaminative degree by photocatalysis, Fenton reaction or ozonation alone. In the present study, carbon aerogel materials were prepared and used as catalysts in regeneration of effluents pursuing successive reuse through catalytic ozonation. The results suggest that catalyst materials were well prepared and played important roles in promoting catalytic degradation of residual dyes in effluents. The addition of novel catalysts in catalytic ozonation enabled the waste effluent to be successfully regenerated and reused in successive dyeing without sacrificing color quality of the dyed fabrics, which could not be realized in ozonation alone without catalysts at same treatment conditions. This study is analogous to wastewater treatment & reuse, and textile coloration technology as well. It innovatively concentrates on regeneration of waste effluents from the first dyeing bath and extends treatment methods to catalytic ozonation with carbon aerogel materials. To the best of the authors' knowledge, this is the first attempt to apply MCA catalysts in waste effluents regeneration and reuse. The finding could offer an essential recognition of catalytic ozonation in reuse of waste effluents, and meanwhile provide a new insight into in-situ regeneration of waste dyeing effluents in textile dyeing plant rather than remote treatment in wastewater treatment plant. The research may help to develop a new alternative approach for both cleaner production of textile dyeing and sustainable development of textile industry, which benefits the whole industry and environment protections.

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