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Remediation of metal containing dye solutions by combined ozonation-adsorption process

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ABSTRACT

Many dyes applied for textile colouration contain heavy metal ions posing double complexity in possible recycling of such wastewater. The metal containing dyes, color index (C.I.) Acid Red 362 [containing Cr (III)] and Reactive Blue 71 [containing Cu (II)] were first decolourised/degraded by ozonation followed by batch adsorption on activated carbon (AC), synthesized from wild almond shells. This process enhanced the adsorption efficiency of the AC. Thirty sec pre-ozonation of 500 mg/L dye concentration, carried out at pH 7.4 with ozone flow rate 2 L/min and48 mg/L ozone concentration led to partial decolourisation. The increase in dye adsorption was 25.5 and 64.1%, respectively after 8 h adsorption at initial pH 2.0 and a carbon dosage of 0.2 g/L, due to pre-ozonation. Prolonged ozonation followed by adsorption removed 73.3 and 98.9% of Cr (III) and Cu (II) released from these dye solutions respectively, with no residual colour at 0.5 g/L carbon dosage. Maximum metal ion adsorption was 45.5 and 54.8 mg/g from dye solutions comparing to synthetic metal solutions (80.16 and 79 mg/g) confirmed the adsorption of metabolites formed due to pre-ozonation. Toxicity of the treated solutions to green gram and common wheat revealed germination of seeds, thus confirmed that it can be safely recycled for irrigation purposes.

Keywords: Chromium (III); Copper (II); Phytotoxicity; Pre-ozonation; Wastewater

1. Introduction

Synthetic dyes find extensive use in textile, paper, rubber, plastic and cosmetic industries for imparting colour. Among these, textile ranks the highest in usage. Due to the heterogeneous interactions in dyeing of the textile substrates, at least 10–15% of the dye is lost in the effluent [1]. The presence of dyes in waterbodies make it aesthetically displeasing, hinders the photosynthesis and harms the aquatic life due to their toxicity [2,3]. Many of the dyes contain heavy metal ions such as Cr, Cd, Co, Cu, etc. as a part of their chemical structure and they are commercially important. These dyes belong to various application classes such as, direct, reactive and acid, used for dyeing of cotton, wool and polyamides due to their excellent light fastness properties. However, these metal ions are harmful to living beings as they are not biodegradable and potentially accumulate in the food chain causing acute toxicity [4]. Consequently, the presence of such dyes in wastewater poses dual problem of presence of colour as well as that of heavy metals [5,6].

Various techniques have been used for the treatment of dye wastewater like adsorption [7,8], membrane filtration [9], coagulation/flocculation [10], bioremediation [11], advanced oxidation [12,13], etc. These treatments can be broadly classified as dye removal and dye degradation techniques. The advantages and disadvantages of every technique have been extensively reviewed [14,15]. One major limitation of any dye degradation technique is that it will only degrade a dye molecule leaving behind the other inor-

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ganic impurities like heavy metals, if present in it. Bioremediation technique is the exception, wherein the adsorption of such metal ion impurities can occur onto a biomass [5]. Chromium (III), although an essential nutrient in humans, can cause respiratory and skin problems at high concentrations. Copper is an irritant and allergic to humans and can affect kidneys and liver. There is evidence that exposure to phthalocyanines can cause serious birth defects by copper depletion in developing embryos [16,17].

Activated carbon (AC) is an extensively used adsorbent having highly developed porosity and large surface area. Various toxic pollutants like dyes, heavy metals, phenols and their derivatives, pesticides, etc. are removed from the wastewater using AC. In recent years, synthesis of AC from cheaper biomass materials such as palm shell [18], sawdust and rice husk [19], jute fiber [20], mango nuts [21], pumpkin seed shell [22], etc. instead of coal has been promoted. The adsorption capacity of AC is governed by its surface area and porosity, which depends on the type of precursor as well as the method of activation [23].

Ozonation is very effective in decolourising coloured effluents. It is often used to bring down the colour concentration and COD level of highly concentrated wastewater. Depending upon the solution pH, ozone reacts with various organic compounds either by a direct reaction or through formation of hydroxyl radicals [24]. Ozone and hydroxyl radicals generated in the aqueous solution are able to break the aromatic rings by attacking conjugated double bonds associated with colour [25].

Since each individual wastewater treatment possesses one or the other drawback, some efforts have been made to integrate two different treatments together. These include ozonation coupled with techniques like granular AC/sandfiltration [26], adsorption [27], coagulation [28], UV/H_2O_2 process [29], etc. As far as the treatment of dye containing wastewater is concerned, there are few reports on integrated systems, viz. adsorption and ozonation [30,31], adsorption and ultrafiltration [32], electrocoagulation and ozonation[33], adsorption and photocatalysis [34], etc. However, there is no literature reporting such treatment for the remediation of metal containing dye wastewater.

In the work reported here, batch adsorption of C.I. Acid Red 362 (AR 362), an azo dye containing 3.6% Cr (III) and C.I. Reactive Blue 71 (RB 71), a phthalocyanine dye containing 3.4% Cu (II)was carried out using AC synthesized from wild almond shells. Sequential ozonation and adsorption was done to enhance the overall dye removal efficiency and to remove the residual metal ion released after the ozonation of these dyes so that the treated water can be safely recycled.

2. Materials and methods

Wild almond shells, collected from the surrounding area of ICT campus, were washed thoroughly with water to remove the dirt and dust present and then oven dried at 105°C overnight. They were then cut into small pieces and ground into fine powder. The dyes AR 362 and RB 71 were procured from Dy Star India Pvt. Ltd. The chemicals, phosphoric acid, hydrochloric acid and sodium hydroxide were of laboratory reagent grade and were purchased from SDFine-Chem limited, India.

AC was synthesized and characterized according to the procedure reported in our previous work [35]. The BET surface area and the total pore volume of the produced AC was 1133.25 m^2/g and 1.41 cm^3/g, respectively. The value of average pore size (4.99 nm) showed that the AC was mesoporous in nature, suitable for the liquid phase adsorption.

Ozonation experiments on 100 mL dye solutions of 500 mg/L concentration were carried out at their original pH (7.4) in a gas washing bottle of 250 mL capacity. Ozone was generated by ozone generator unit (A. M. Ozonics Pvt. Ltd., India) from pure oxygen at an input current of 0.15A with a flow rate of 2 L/min; ozone concentration being 48 mg/L in the dye solution. The excess ozone gas coming out from the bottle outlet was destroyed by passing it through thermal destructor.

In order to evaluate the effectiveness of adsorption of dyes as well as metal ions on synthesized AC, the original dye solution, the partially decolourised dye solution after 30 s ozonation and the fully decolourised dye solution after prolonged ozonation were subjected to adsorption in a batch mode. For pH optimization study, 50 mL dye solutions (100 mg/L) of varying pH (2–10) were agitated with 0.02 g of AC at 60 rpm for 2 h in a thermostatic shaker. The initial pH of the solutions was adjusted using H_2SO_4 (1 N) or NaOH (1 N). To study the pH effect on metal adsorption, initial metal ion concentrations were selected equivalent to those present in the respective dye solutions of 500 mg/L concentration. This was performed for comparing the adsorption of metal ions from the synthetic pure metal ion solutions and from the metal containing dye solutions. For equilibrium adsorption studies, stoppered flasks containing 100 mL dye solutions (500 mg/L) were agitated at 60 rpm for 8 h. Samples (1 mL) were withdrawn at predetermined time intervals and analyzed for the residual dye and its corresponding metal ion concentration after filtration. The dosage of AC was 0.02 g for these studies.

Residual dye concentration was estimated using UV-Visible spectrophotometer (8500 TECHCOMP, Hong Kong). The absorbance was read at 505.5 and 667.5 nm for AR 362 and RB 71, respectively. Heavy metal concentration was measured using flame Atomic Absorption Spectrometer (932 Plus, GBC, Australia). Solutions of chromium nitrate and copper nitrate were used to prepare standards of Cr (III) and Cu (II). The adsorption (%) and the amount of dye / metal adsorbed was obtained using the equations

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

$$\text{Dye/metal uptake}(q_t,\ \text{mg/g}) = \frac{(C_0 - C_t)V}{W} \tag{2}$$

where C_0 is the initial dye/metal ion concentration (mg/L), C_t is the residual dye/metal ion concentration at time 't' (mg/L), V is the volume of solution (L) and W is the mass of AC(g). All the experiments (ozonation and adsorption) were carried out at the room temperature (28°C) in triplicate and the average values have been reported.

Phytotoxicity study was done using two crops, green gram (*Vignaradiata*, dicot) and common wheat (*Triticumaestivum*, monocot).Solutions of AR 362 and RB 71 (500 mg/L) as well as their treated solutions were adjusted to pH 7.0.

Ten healthy seeds of each crop were separately sowed into pots containing soil. The study was carried out at room temperature (28°C) by daily watering 5 mL for each using distilled water (as control)/treated wastewater [36,37]. Germination (%) and the lengths of shoot and root were recorded after 8 d of growth. The mean values of these parameters obtained for different test solutions were compared with that of control sample using student's '*t*' test analysis at 95% confidence level.

3. Results and discussion

3.1. Effect of initial pH on dye and metal ion adsorption

Fig. 1 shows that at the lowest studied pH of 2.0, the adsorption values for the dyes AR 362 and RB 71 having initial concentration of 100 mg/L were maximum as 244.6 and 218.9 mg/g, respectively. At this pH, the AC is positively charged since its pH of zero point charge is 6.5, as reported in our previous study [38]. The higher adsorption of dyes at lower pH is attributed to the electrostatic attractions between AC and the sulphonic acid groups of adsorbate. With rise in pH, excess hydroxyl groups compete with dye anions causing a decrease in adsorption. Similar results are reported for the adsorption of anionic dyes [39–41].

The concentrations of Cr (III) and Cu (II) in the dye solutions (500 mg/L) of AR 362 and RB 71, as determined by AAS, were 16.2 and 15.6 mg/L, respectively. The optimum pH values for the adsorption of Cr (III) and Cu (II) were found to be 8.0 and 10.0 (Fig. 2). The speciation of Cr (III) shows that the dominant species at pH 8.0 are Cr (OH)$_2^+$ and Cr (OH)$_3$ [42]. At acidic pH, there is electrostatic repulsion between positively charged AC and Cr (III) cation. Beyond pH 8.0, Cr (OH)$_4^-$ forms and repels negatively charged AC. Similar is the case with Cu (II), which is adsorbed as Cu (OH)$_2^+$. The adsorption values for Cr (III) and Cu (II) were 80.16 and 79 mg/g, respectively. Similar results have been reported in the literature for the adsorption of these metal ions onto various ACs [43–45].

3.2. Effect of pre-ozonation on adsorption

When pre-ozonation of dye solutions was carried out for 30 s, the decolourisation was found to be 47.4 and 42.7% for the dyes AR 362 and RB 71, respectively. Fig. 3 shows the effect of pre-ozonation on the adsorption of these dyes as well as that of the metal ions present therein. Upon carrying out the adsorption on the AC thereafter, an increase from 66.1, for original,to 82.9%, for pre-ozonated dye solution, was observed for the dye AR 362 (Fig. 3). Similarly, in the case of the dye RB 71, the adsorption increased from 46.2 to 75.6% (Fig. 3).This amounts to an increase of 25.5 and 63.6% in the adsorption of AR 362 and RB 71 dyes, respectively, due to pre-ozonation. Greater increase in the latter case is attributed to higher initial concentration after pre-ozonation [46].

The metal adsorption showed little increase in the adsorption, 8.4% for Cr (III) and 22.5% for Cu (II), in comparison with the original dye solution without pre-ozonation. This is due to the fact that metal adsorption is dependent on the dye adsorption when it is in the complex form. This is clear from Fig. 3, which shows equivalent adsorption of dyes and corresponding metals through the complex form. When a dye is degraded, metal is released as free ion. However, after pre-ozonation of dye solutions, AC preferentially adsorbs dye and its metabolites than metal ions, since it is organophilic [47]. Moreover, solution pH is favorable for the adsorption of dyes than metals as seen from Figs. 1 and 2.

3.3. Prolonged ozonation and adsorption of metal ions

Prolonged ozonation was conducted to achieve complete decolourisation of AR 362 and RB 71 solutions. Almost complete decolourisation of AR 362 (99.3%) occurred within 10 min and that of RB 71 (99.7%) in 15 min. The metal ion concentrations did not change after ozonation.

Fig. 4 shows the adsorption of Cr (III) and Cu (II) released after the prolonged ozonation of respective dye solutions. The adsorption after 2 h of contact time was 34.7 and 58%, respectively for Cr (III) and Cu (II) at 0.2 g/L

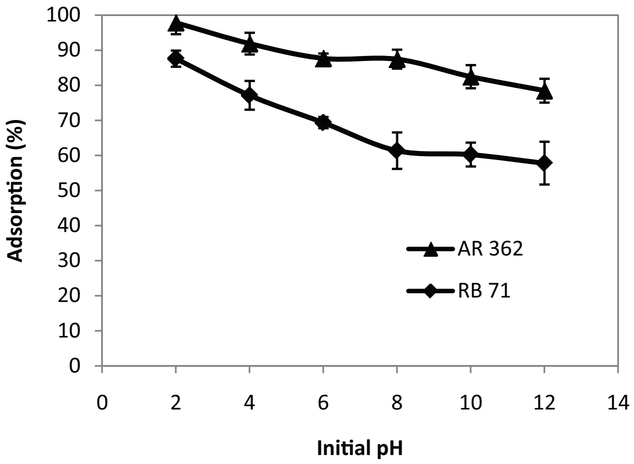

Fig. 1. Effect of initial pH on the adsorption of AR 362 and RB 71 onto AC (C_0: 100 mg/L, AC: 0.4 g/L, time: 2 h, agitation rate: 60 rpm).

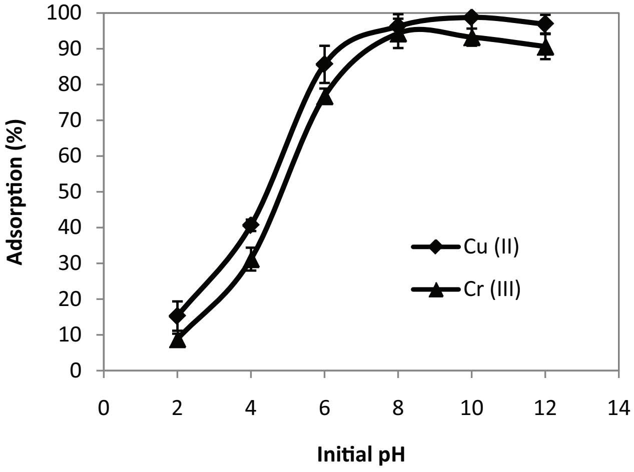

Fig. 2. Effect of initial pH on the adsorption of Cr (III) and Cu (II) onto AC (C_0: 17 and 16 mg/L for Cr (III) and Cu (II) respectively, AC: 0.2 g/L, time: 2 h, agitation rate: 60 rpm).

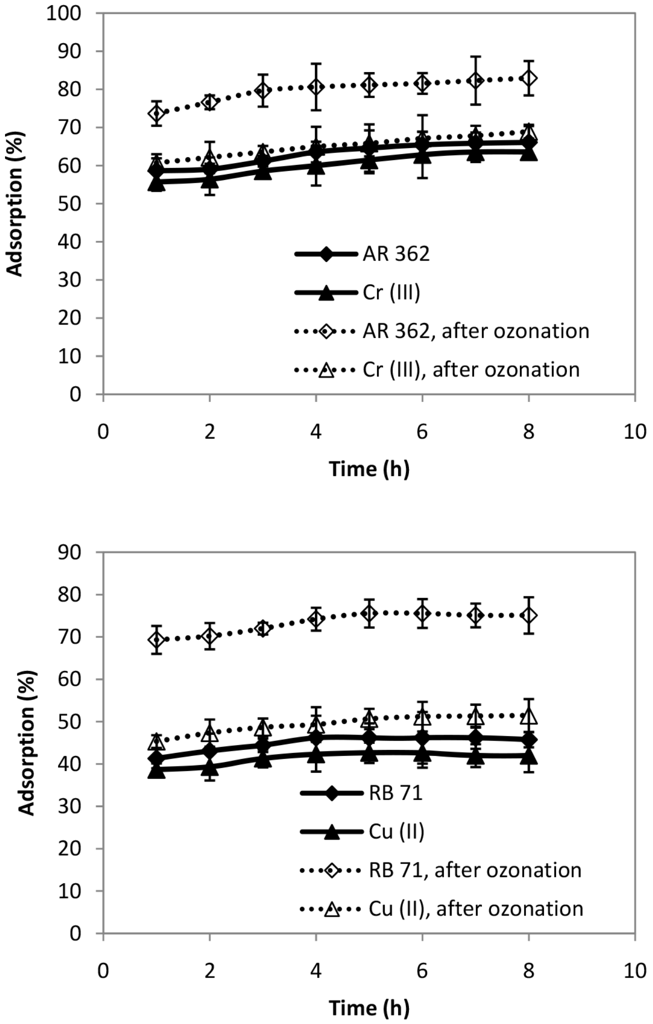

Fig. 3. Effect of pre-ozonation (30 s) on the adsorption of dyes (AR 362 and RB 71) and corresponding heavy metals [Cr (III) and Cu (II)] onto AC (C_0: 500 mg/L, initial pH: 2.0, AC: 0.2 g/L, time: 8 h, agitation rate: 60 rpm).

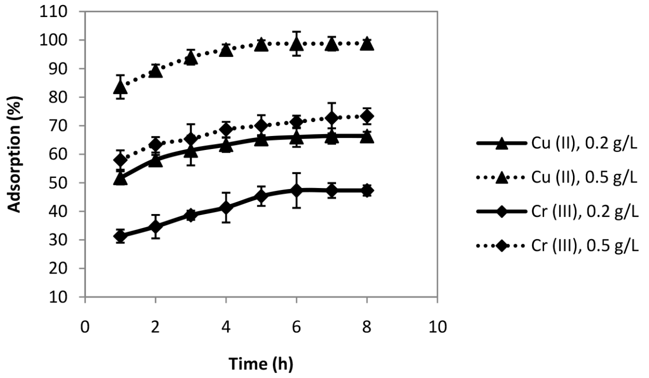

Fig. 4. Adsorption of residual Cr (III) and Cu (II) released after complete decolourisation of AR 362 and RB 71 solutions by ozonation at different AC dosages (C_0: 17 and 16 mg/L for Cr (III) and Cu (II) respectively, time: 8 h, agitation rate: 60 rpm).

AC dosage. This can be compared with the adsorption of these metal ions from synthetic solutions as 94.3 and 98.8%, respectively (Fig. 2). This indicates that the presence of dye metabolites compete with the metal ions during the adsorption. The maximum metal uptake was 45.5 and 54.8 mg/g for Cr (III) and Cu (II), respectively. In order to recycle the treated dye solutions, adsorption of metal ions was also carried out by increasing the AC dosage to 0.5 g/L. With this, the adsorption of Cu (II) increased to 98.9 and that of Cr (III) increased to 73.3%. This was due to the increased number of sites available on AC for the adsorption [48,49].

3.4. Phytotoxicity study

Toxicity of dye, as well as that of treated and synthetic metal ion solutions to green gram and common wheat was studied and results are presented in Table 1. It is clear that the presence of dyes inhibited the germination and also adversely affected the plant growth. RB 71, a phthalocyanine dye, was found to be more phytotoxic than the azo dye AR 362. Solution of Cr (III) gave fair germination of both seeds as compared to Cu (II) but lengths of shoot and root

Table 1
Toxicity of dye, metal ion and treated solutions to green gram and common wheat

Test solution	Green gram (Dicot)			Common wheat (Monocot)		
	Germination (%)	Shoot length (cm)	Root length (cm)	Germination (%)	Shoot length (cm)	Root length (cm)
Control	100	15.8 ± 0.8[a]	8.6 ± 0.6[a]	100	14.7 ± 0.7[a]	8.4 ± 0.5[a]
AR 362 (500 mg/L)	50	11.4 ± 0.9[b]	7.2 ± 0.7[a]	70	9.5 ± 0.6[b]	5.2 ± 0.7[b]
RB 71 (500 mg/L)	40	9.8 ± 0.2[b]	4.6 ± 1.1[b]	50	8.8 ± 0.5[b]	4.9 ± 0.9[b]
Cr (III), 17 mg/L	70	12.5 ± 0.6[b]	5.1 ± 0.4[b]	80	8.9± 0.8[b]	4.2 ± 0.6[b]
Cu (II), 16 mg/L	60	10.1 ± 0.4[b]	4.4 ± 0.7[b]	60	7.5± 0.5[b]	3.4 ± 0.6[b]
AR 362 (Treated)	80	14.6 ± 0.5[a]	8.1 ± 0.3[a]	90	13.8 ± 0.8[a]	8.1 ± 0.2[a]
RB 71 (Treated)	90	15.1 ± 0.8[a]	8.4 ± 0.7[a]	90	14.2 ± 0.9[a]	8.2 ± 0.4[a]

Standard difference values (*t*) between control and sample at 95% confidence level are: a ≤ 1.812 and b ≥ 1.812.

were significantly lower than the control for both metal ion solutions (Table 1). Kalpana et al. [5] and Ghosh et al. [50] reported similar results for chromium metal complex dyes, while Silva et al. [51] obtained increased toxicity after degradation of a copper phthalocyanine dye C. I. RB 21, due to the release of Cu (II).Treated solutions of both the dyes gave results comparable with the control showing that the treated water can be used for irrigation purposes.

4. Conclusion

In the present study, a cheaper adsorbent with large surface area, derived from the waste biomass material. An integrated process of adsorption coupled with ozonation is found very effective in decolourising the metal containing dye solutions. The adsorption efficiency of AC for AR 362 and RB 71 increased by 1.3 and 1.6 folds, respectively due to pre-ozonation. Moreover, the drawback of dye degradation technique of releasing metal ions from pre-metalized dye after degradation has been overcome. In addition to metal adsorption, any toxic metabolites, if formed after dye degradation can also be removed by adsorption and thus the treated wastewater can be safely recycled for irrigation purposes. Based on this batch adsorption study, a continuous column adsorption system for the treatment of pre-metalized dye wastewater can be proposed.

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