

Clinoptilolite Assisted Persulfate Decolorization of a Raw Textile Wastewater

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Authors' contributions

This work was carried out in collaboration between both authors. Author HAA designed the study and wrote the experimental protocol. Author FOK conducted the experiment, managed the analyses of the study and wrote the first draft of the manuscript. Both authors read and approved the final manuscript.

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ABSTRACT

Textile wastewater is strong colored and contributes immensely to water pollution if not appropriately treated. However, it is hard to treat by the conventional biological methods if applied singly, hence, the application of a physicochemical technique for the treatment was proposed in this study. Clinoptilolite (CPL) was used in combination with persulfate (PS) as an activator, to catalyze and improve the persulfate oxidation of raw textile wastewater in the process of decolorization. The influence of variation of CPL dosages, initial pH and contact times were investigated when a predetermined persulfate dosage of 4/1(g/g) was used. The system investigated was effective in reducing the residual color concentration by 96% when the initial pH of 4 was applied over a 420 minutes contact time and the CPL and PS dosages of 6/1 and 4/1 were used respectively.

Keywords: Clinoptilolite; persulfate; color; dyes; textile wastewater.

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1. INTRODUCTION

Water pollution is detrimental to health and the wellbeing in the environment. Hence, legislations are instituted to prevent the occurrence at best, or to reduce the incidences. It is therefore very important that very decisive steps be taking to treat source polluted water, to the required standard before an eventual discharge into either sewers or surface waters. The commonest source of water pollution is the industrial wastewaters while the most prominent characteristic of any polluted water is the color. By and large, the textile industries generate large quantities of wastewater as it also uses large volumes of water in the various stages of a wet process of production [1]. Wastewater from the textile manufacturing processes is not unlike many industrial wastewaters and therefore characteristically colored, even strongly so, due to the use of dyes. Dyes are used in the printing and finishing of textiles to make colorful and attractive. Very often, these dyes are not all fixed to the textiles, and the excess remain in the wastewaters [2,3], making the latter darkly colored and unappealing to the sense of sight.

Although the traditional biological, physical, and chemical methods are used in the treatment of wastewaters; textile wastewaters are rather recalcitrant and non-biodegradable due to the complex nature of its chemical constituents which makes them difficult to treat by the conventional treatment methods, if applied singly, especially the more economical biological process, [4,5]. Therefore, the treatment of industrial and textile wastewater are often based on a combination of methods. In this regard, the advanced oxidative processes (AOPs) have shown to be highly effective either applied singly or in combination with other processes [6,7]. They have attracted more research interest with a view to improve on the treatability of wastewaters and the hope to use the method for the complete mineralization of recalcitrant pollutants such as dyes to produce carbon dioxide (CO₂), water, and inorganic compounds. Although effective, AOPs may be very expensive if applied solely for treatment [8-10].

Other combination of methods and techniques previously applied in wastewater treatment include: Fenton and biological processes [11]; integration of ozone biological aerated filters and membrane filtration [12]; electrochemical-electrocoagulation [13]. In particular, techniques used in the decolorization of textile wastewater

includes; photo-Fenton like process [14]; dual-stage membrane bioreactors (MBR) and reverse osmosis (RO) systems [15]; biological followed by photo-Fenton oxidation [16]; photo-catalytic [17]; electro-coagulation and chemical-coagulation [18].

Besides the advanced oxidative related processes that were integrated into biological processes amongst others, adsorption and its integration with other methods have also shown to be successful for the decolorization and removal of dyes from textile wastewater. Such techniques specified by the materials includes; FeOOH-GAC nanocomposites [14]; Fe³⁺ doped TiO₂ nanotubes [19]; organoclay [20]; milled sugar cane bagasse [21].

Clinoptilolite is the most common, abundant and widely used member of the zeolites family whose ion exchange behavior varies with the environment of formation [22]. Zeolites are a family of crystalline hydrated aluminosilicate minerals with a porous structure and valuable physicochemical properties viz., sorption, molecular sieving, catalysis and ion-exchanging. Acting either singly or supported, zeolites have been previously used in water and wastewater treatments for the removal of heavy metals [23,24] and ammonia (NH₃) [25,26].

Persulfate is relatively new in in-situ chemical oxidation [27,28] and also applied in wastewater remediation. The reaction of PS in the degradation of organics at the room temperature is generally slow [29,30]; hence various means are applied to improve it [31-34]. The study, therefore, aims at investigating the feasibility of decolorizing real textile wastewater by the novel catalyzation of persulfate using clinoptilolite.

2. MATERIALS AND METHODS

2.1 Materials

Raw textile wastewater samples were collected straight from the discharge point of a textile manufacturing industry in Prai, Malaysia. 5 kg of clinoptilolite (CPL) produced by BIO Organic were supplied in granules and prepared into appropriate particle sizes prior to use. 1 M aqueous solution of persulfate was prepared from the analytical grade sodium persulfate of Hamburg Chemicals, without any further purification. Deionized water was used in the preparation of aqueous solutions, and double-

distilled water was used for other cleaning processes.

2.2 Batch Experiments

Dosages of both persulfate and clinoptilolite were based on a ratio to the initial concentration of chemical oxygen demand (COD) of the wastewater (i.e. COD/PS and COD/CPL respectively), in grams/grams, [35]. The wastewater sample volume was kept at 200 mL for all experiments. This volume of wastewater was put into 500 mL Erlenmeyer flask reactors each, and a pre-determined dosage of persulfate was added to each reactor, to which clinoptilolite had also been added. The batch studies were in three categories; determination of the effect of dosage; initial pH of reaction and contact time. In the first category, the persulfate dose was standardized based on previous experiments but the dosage of clinoptilolite was varied from 1/1-10/1, as a ratio of wastewater COD to CPL. The experiments were conducted at room temperature, without the adjustment of pH (unadjusted pH, only for the determination of the influence of dosage) and the reaction was agitated by the laboratory orbital shaker for 30 minutes contact time each. The procedure was repeated for the second category, which considered the effect of initial pH of the reaction but dose of clinoptilolite was standardized based on the optimum dosage from category one and pH was adjusted between 2 and 11. Dosage and pH from categories one and two were used in the third category, while contact times were varied from 30 to 420 minutes. Aliquots were collected from each reactor after allowing settling for 30 minutes, and after that, analyzed for residual color concentrations. The raw textile wastewater was also analyzed for the initial color concentration.

3. RESULTS AND DISCUSSION

3.1 Influence of Dosage

Dosage was determined as a ratio of treatment media to the initial concentration of wastewater [35,36] i.e. the initial concentration of chemical oxygen demand (COD) measured from analysis of the raw sample wastewater as 1800 mg/L and the initial color concentration was 2870Pt.Co. A pre-determined persulfate dosage (4/1) was used for all the experiments. The predetermined range of 75 μ m - 250 μ m clinoptilolite particle sizes was used for all the experiments. At a contact time of

30 minutes and unadjusted pH of raw wastewater, an increase in color removal with increased dosage observed is as shown in Fig. 1, until an optimum of 56.8% at 6/1. The addition of clinoptilolite was to catalyze the persulfate oxidation by the enhanced release of sulfate radicals. Fig. 1 also shows a 48.3% removal of color by the application of PS only, as against the 56.8% decolorization when CPL of 6/1(g/g) dosage was added. The reaction was enhanced until the 6/1 dosage of CPL after which a scavenging effect is observed as in the Figure. The CPL dosage of 6/1 is thus considered as the optimum in this set of experiments. Various means have been used to activate persulfate and enhance the oxidation of pollutants; a similar effect was observed with an increase in persulfate dosage when it was activated carbon catalyzed [37]. Furthermore, the increase in decolorization with the dosage of CPL could be attributed to the increase in the available active sites with CPL loading and the radical formation when PS is activated and catalyzed [38,39].

3.2 Influence of Initial pH

Solution pH has often shown to be a very important factor that affects the rate of reactions either positively or negatively. The result of this study, in the investigation over a pH range of 2-11 is shown in Fig. 2. By using an optimum dosage of 6/1 for clinoptilolite, combined with 4/1 persulfate dosage, the pattern of decolorization of the wastewater was monitored over the different adjustment of pH. Adjustment of initial pH of the reaction resulted in a fluctuating amount of decolorization of the wastewater, but a significant increase was observed at pH 4, which was the optimum (79%), followed by 75.5% at pH 6, and over the range of pH investigated. The effect of pH of reaction medium was shown in the results from the use of clinoptilolite as a carrier for immobilized biocatalyst systems which had pH 4.7 as the optimum immobilization medium over the pH range investigated [40]. Also, in the degradation of phenol using Fe/c clinoptilolite as heterogeneous Fenton reaction, pH 3.5 was the optimum initial pH where the shortest induction period was observed [41].

3.3 Influence of Contact Time

The influence of contact time on the reaction was investigated for between 30-420 minutes. In Fig. 3, decolorization is observed to increase

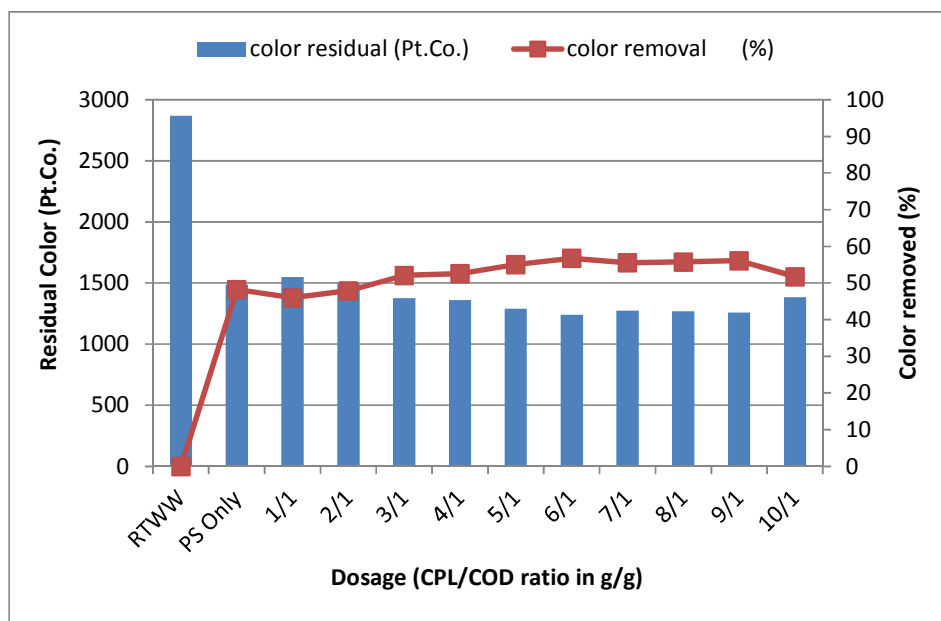


Fig. 1. Influence of dosage, (PS dose: 4/1, Initial colour: 2870Pt.Co, agitation speed: 150rpm, contact time: 30minutes, initial pH not adjusted)

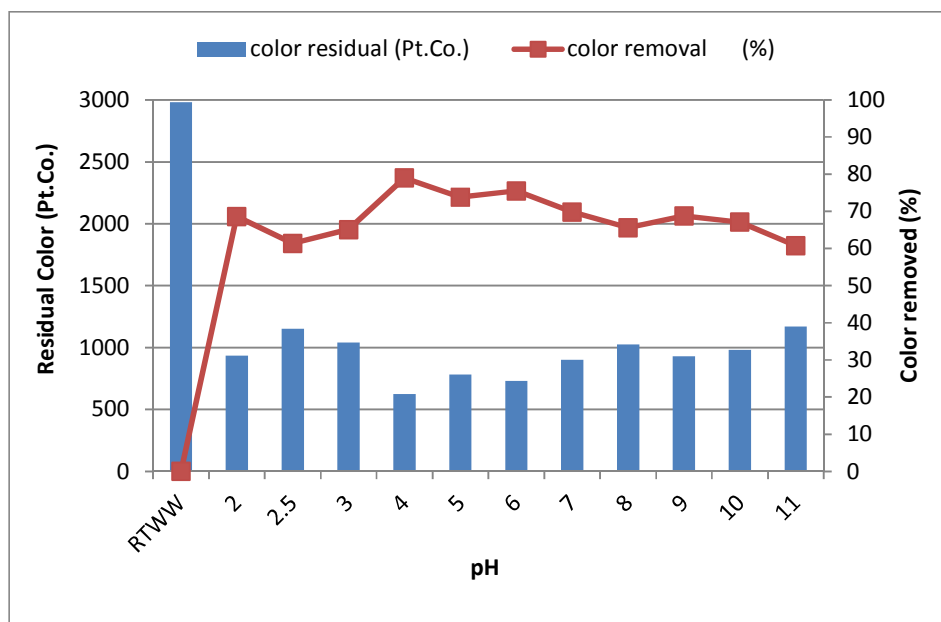


Fig. 2. Influence of pH, (PS: 4/1, CPL: 6/1, Initial colour: : 2870Pt.Co, agitation speed: 150 rpm, contact time: 30 minutes, initial pH: 4)

generally with contact time from 74% at 30 minutes to 90% at 240 minutes 96% optimal at 420 minutes. The significant increase in decolorization in the first 30 minutes of the reaction indicate a rapid reaction taking off with most of the color (74%) being removed at the

contact time. Decolorization thereafter increased but at a decreased rate. The initial increased decolorization with contact time may be due to the oxidation of the dissolved organics in the textile wastewater [42].

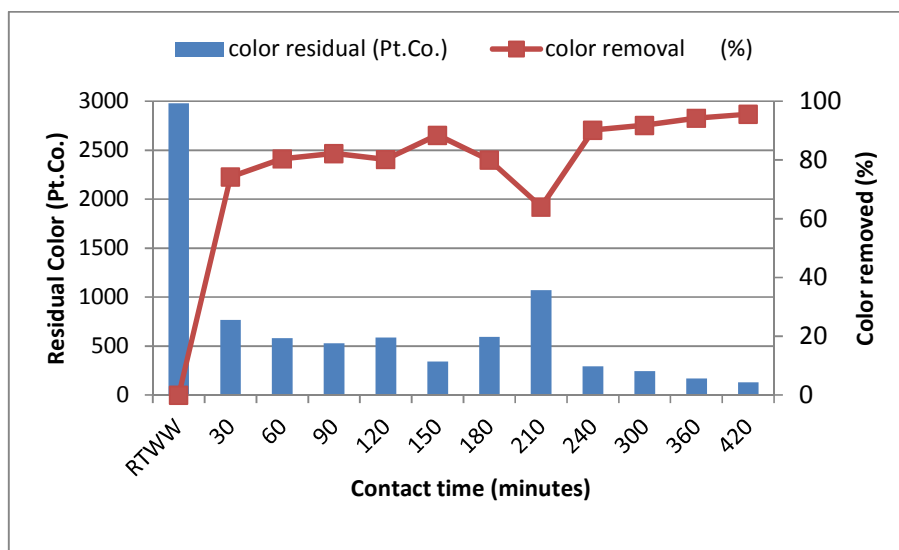


Fig. 3. Influence of contact time, (PS: 4/1, CPL: 6/1, Initial colour: 2870Pt.Co, agitation speed: 150 rpm, pH:4)

PS: Persulfate; CPL: Clinoptilolite; COD: Chemical oxygen demand; RTWW: Raw textile wastewater

4. CONCLUSIONS

Results from the present study have shown that the use of clinoptilolite as a catalyst in persulfate oxidation is feasible and positive, to decolorize raw textile wastewater. Also, the investigation of the influence of operating conditions showed optimum clinoptilolite dosage of 6/1 and initial pH of 4. Although a higher removal of color (96%) was achieved at 420 minutes, the 240 minutes contact time with a 90% decolorization is considered optimum, due to an increase at a decreasing rate of decolorization beyond that point. The combination of clinoptilolite and persulfate has shown a better performance at decolorization of the wastewater than the lone application of persulfate, hence the catalyzation of the reaction by clinoptilolite.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Robinson T, et al. Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*. 2001; 77(3):247-255.
2. Nguyen TA, Juang RS. Treatment of waters and wastewaters containing sulfur dyes: A review. *Chemical Engineering Journal*. 2013;219:109-117.
3. Miah L, Ferdous N, Azad MM. Textiles material dyeing with supercritical carbon dioxide (CO₂) without using water. *Chemistry and Materials Research*. 2013; 3(5):38-40.
4. Kalra SS, et al. Advanced oxidation processes for treatment of textile and dye wastewater: A review. in 2nd International Conference on Environmental Science and Development. IACSIT Press Singapore. 2011.
5. Nidheesh P, Gandhimathi R. Textile wastewater treatment by electro-fenton process in batch and continuous modes. *Journal of Hazardous, Toxic, and Radioactive Waste*. 2014; 04014038.

6. Punzi M, et al. Combined anaerobic–ozonation process for treatment of textile wastewater: Removal of acute toxicity and mutagenicity. *Journal of Hazardous Materials*. 2015;292:52-60.
7. Jamal MA, Muneer M, Iqbal M. Photodegradation of monoazo dye blue 13 using advanced oxidation process. *Chemistry International*. 2015;1(1):12-16.
8. Verma AK, Dash RR, Bhunia P. A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. *Journal of Environmental Management*. 2012;93(1): 154-168.
9. Oller I, Malato S, Sánchez-Pérez J. Combination of advanced oxidation processes and biological treatments for wastewater decontamination-a review. *Science of the Total Environment*. 2011; 409(20): 4141-4166.
10. Poyatos J, et al. Advanced oxidation processes for wastewater treatment: State of the art. *Water, Air, and Soil Pollution*. 2010;205(1-4):187-204.
11. Blanco J, et al. Fenton and biological-fenton coupled processes for textile wastewater treatment and reuse. *Desalination*. 2012; 286:394-399.
12. He Y, et al. Application of integrated ozone biological aerated filters and membrane filtration in water reuse of textile effluents. *Bioresource Technology*. 2013;133:150-157.
13. Eyvaz M, et al. Preventing of cathode passivation/deposition in electrochemical treatment methods—A case study on winery wastewater with electrocoagulation. 2014.
14. Sheydaei M, Aber S, Khataee A. Preparation of a novel γ -FeOOH-GAC nano composite for decolorization of textile wastewater by photo fenton-like process in a continuous reactor. *Journal of Molecular Catalysis A: Chemical*. 2014;392:229-234.
15. De Jager D, Sheldon M, Edwards W. Colour removal from textile wastewater using a pilot-scale dual-stage MBR and subsequent RO system. *Separation and Purification Technology*. 2014;135:135-144.
16. Punzi M, et al. Degradation of a textile azo dye using biological treatment followed by photo-fenton oxidation: Evaluation of toxicity and microbial community structure. *Chemical Engineering Journal*. 2015;270: 290-299.
17. Gümüş D, Akbal F. Photocatalytic degradation of textile dye and wastewater. *Water, Air, & Soil Pollution*. 2011;216(1-4): 117-124.
18. Yuksel E, Gurbulak E, Eyvaz M. Decolorization of a reactive dye solution and treatment of a textile wastewater by electrocoagulation and chemical coagulation: Techno-economic comparison. *Environmental Progress & Sustainable Energy*. 2012;31(4):524-535.
19. Pang YL, Abdullah AZ. Fe 3+ doped TiO 2 nanotubes for combined adsorption–sonocatalytic degradation of real textile wastewater. *Applied Catalysis B: Environmental*. 2013;129: 473-481.
20. Elemen S, Kumbasar EPA, Yapar S. Modeling the adsorption of textile dye on organoclay using an artificial neural network. *Dyes and Pigments*. 2012;95(1): 102-111.
21. Kadam AA, et al. Exploiting the potential of plant growth promoting bacteria in decolorization of dye disperse red 73 adsorbed on milled sugarcane bagasse under solid state fermentation. *International Biodeterioration & Biodegradation*. 2014;86:364-371.
22. Popov N, et al. Use of natural and modified zeolites from Bulgarian and Chilean deposits to improve adsorption of heavy metals from aqueous solutions. 2012.
23. Syafalni RA, Nair PU. New approach of heavy metal (chromium, iron, copper and nickel) removal using surfactant modified zeolite for tin mining wastewater. *World Applied Sciences Journal*. 2013;27(5): 614-620.
24. Rondón W, et al. Application of 3A zeolite prepared from venezuelan kaolin for removal of Pb (II) from wastewater and its determination by flame atomic absorption spectrometry. *American Journal of Analytical Chemistry*. 2013.
25. Ho L, Ho G. Mitigating ammonia inhibition of thermophilic anaerobic treatment of digested piggery wastewater: use of pH reduction, zeolite, biomass and humic acid. *Water Research*. 2012;46(14): 4339-4350.
26. Zhou L, Boyd CE. Total ammonia nitrogen removal from aqueous solutions by the natural zeolite, mordenite: A laboratory test and experimental study. *Aquaculture*. 2014;432:252-257.
27. Kaur K, Crimi M. Cadmium mobility with persulfate chemical oxidation: Effects of soil properties and activation methods.

- Journal of Environmental Engineering. 2014.
28. Wu X, et al. Degradation of trichloroethylene in aqueous solution by persulfate activated with citric acid chelated ferrous ion. Chemical Engineering Journal. 2014;255:585-592.
 29. Liu H, et al. In situ chemical oxidation of contaminated groundwater by persulfate: Decomposition by Fe (III)-and Mn (IV)-containing oxides and aquifer materials. Environmental Science & Technology. 2014;48(17):10330-10336.
 30. Pu M, et al. Fe/S doped granular activated carbon as a highly active heterogeneous persulfate catalyst toward the degradation of orange G and diethyl phthalate. Journal of Colloid and Interface Science. 2014; 418:330-337.
 31. Chen WS, Huang CP. Mineralization of aniline in aqueous solution by electrochemical activation of persulfate. Chemosphere. 2015.
 32. Yan J, et al. Biochar supported nanoscale zerovalent iron composite used as persulfate activator for removing trichloroethylene. Bioresource Technology. 2015;175:269-274.
 33. Deng D, et al. Efficient chemical oxidation of high levels of soil-sorbed phenanthrene by ultrasound induced, thermally activated persulfate. Chemical Engineering Journal. 2015;265:176-183.
 34. An D, et al. UV-activated persulfate oxidation and regeneration of NOM-saturated granular activated carbon. Water Research. 2015;73:304-310.
 35. Amr SSA, et al. Pretreatment of stabilized leachate using ozone/persulfate oxidation process. Chemical Engineering Journal. 2013;221:492-499.
 36. Liang C, Wang ZS, Bruell CJ. Influence of pH on persulfate oxidation of TCE at ambient temperatures. Chemosphere. 2007;66(1):106-113.
 37. Yang S, et al. Activated carbon catalyzed persulfate oxidation of Azo dye acid orange 7 at ambient temperature. Journal of Hazardous Materials. 2011;186(1):659-666.
 38. Gupta VK, et al. Photo-catalytic degradation of toxic dye amaranth on TiO₂/UV in aqueous suspensions. Materials Science and Engineering: C. 2012;32(1): 12-17.
 39. Shahrezaei F, et al. Process modeling and kinetic evaluation of petroleum refinery wastewater treatment in a photocatalytic reactor using TiO₂ nanoparticles. Powder Technology. 2012;221:203-212.
 40. Bahar T. Clinoptilolite particles as a carrier for biocatalysts immobilization: Invertase immobilization and characterization. Asia-Pacific Journal of Chemical Engineering. 2014;9(1):31-38.
 41. Bayat M, Sohrabi M, Royaei SJ. Degradation of phenol by heterogeneous fenton reaction using Fe/c clinoptilolite. Journal of Industrial and Engineering Chemistry. 2012;18(3):957-962.
 42. Karthikeyan S, et al. Treatment of textile wastewater by homogeneous and heterogeneous Fenton oxidation processes. Desalination. 2011;281:438-445.

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