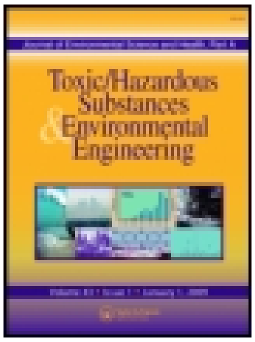
Article:

Tony, Maha A., Parker, Helen L. orcid.org/0000-0001-7576-2470 and Clark, James H. orcid.org/0000-0002-5860-2480 (2016) Treatment of laundrette wastewater using Starbon and Fenton's reagent. Journal of environmental science and health part a-Toxic/hazardous substances & environmental engineering. pp. 974-979. ISSN 1093-4529

https://doi.org/10.1080/10934529.2016.1191817



Journal of Environmental Science and Health, Part A

Toxic/Hazardous Substances and Environmental Engineering

ISSN: 1093-4529 (Print) 1532-4117 (Online) Journal homepage: http://www.tandfonline.com/loi/lesa20

Treatment of laundrette wastewater using Starbon and Fenton's reagent

Maha A. Tony, Helen L. Parker & James H. Clark

JOURNAL OF ENVIRONMENTAL SCIENCE AND HEALTH, PART A
2016, VOL. 0, NO. 0, 1–6
http://dx.doi.org/10.1080/10934529.2016.1191817

Taylor & Francis
Taylor & Francis Group

Treatment of laundrette wastewater using Starbon and Fenton's reagent

Maha A. Tony[a,b], Helen L. Parker[a], and James H. Clark[a]

[a]Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, UK; [b]Basic Engineering Science Department, Faculty of Engineering, Minoufiya University, Shbin El-Koum, Egypt

ABSTRACT

The use of grey water for a variety of purposes is gaining increased popularity as a means of preserving scarce freshwater resources. In this work, catalytic oxidation over Fenton's reagent and adsorption techniques using Starbon (mesoporous material derived from polysaccharides) has been applied. These novel techniques are used as an alternative to already studied treatments of grey water such as filtration and/or biological processes. In this study, grey water, collected from a commercial laundrette, has been used. Treatment efficiency was determined by changes in the chemical oxygen demand (COD) of the grey water. Experiments using Fenton's reagent at optimum conditions of $Fe^{3+} = 40$ mg L^{-1}; $H_2O_2 = 400$ mg L^{-1} and pH 3 were very successful, resulting in a 95% COD removal after 15 min. Treatment with Starbon adsorption was also effective, reaching up to 81% COD removal at pH 3 within 1 h. The combined treatment with Fenton's reagent and Starbon resulted in a 93% COD removal at a significantly reduced concentration of Fenton's reagent compared to the treatment with solo Fenton's reagent. This lower chemical dose has the advantage of reducing costs and lowering sludge generation.

ARTICLE HISTORY
Received 24 January 2016

KEYWORDS
Chemical oxygen demand; Fenton's reagent; laundrette wastewater; Starbon

Introduction

Today many large urban areas across the globe suffer from water scarcity. It is, therefore, necessary that action be taken to guarantee a supply of freshwater for all people in the present and future. The reuse and recycling of domestic wastewater are emerging in many countries as a sustainable concept to reduce overall urban water demand.[1,2]

In developed countries, the indoor domestic water demand usually reaches between 36 and 66 m^3/y per capita (100–180 L/d per capita), comprising 30–70% of the total urban water demand.[2] Most consumed water is transformed into wastewater, which can be classified into two major categories: "grey water" and "black water." Grey water is untreated wastewater which has not been exposed to toilet waste; its name is derived from its cloudy appearance and from its status is between freshwater (known as "white water") and sewage water ("black water"). Leftover water from bathtubs, showers, sinks, floor drains and washing machines are all classified as grey water and comprises 60–70% of in-house water demand. Black water originating from toilets comprises the remaining 30–40%. In the United Kingdom, an average of 150 L of water is used per person in a day, of which about a third is used for toilet flushing, which could potentially be replaced by treated grey water.[3–5]

Laundry wastewater is defined as "grey water." Detergents are the main contaminants resulting in high phosphate and sodium levels. If untreated, these compounds pose a health risk and serious environmental damage. Collection and treatment of waste laundry water would overcome this problem and also supply an alternative water source for toilet flushing or other applications where fresh/drinking quality water is not necessary.[6]

In the literature, a range of treatment systems are suggested with varying complexity and degree of effectiveness.[2,7] Many conventional treatment systems are based on physical separation, e.g., nanofiltration and reverse osmosis. However, the major shortcoming of these techniques is the production of large quantities of secondary pollutants in the form of concentrated sludge, which requires further processing and disposal. These methods also require high initial investment and maintenance costs.[5,8]

Conversely, adsorption processes are superior to other techniques for wastewater treatment in terms of simplicity of design/operation and insensitivity to toxic substances.[9,10] Among several materials used as adsorbents, activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment throughout the world.[11] Unfortunately, activated carbon also presents disadvantages, i.e., it is highly microporous and these small pores create limited diffusion by slowing pollutant uptake and reducing material efficiency.[12] This led many workers to search for better adsorbent alternatives.[9]

Recently, innovative porous materials derived from polysaccharides, such as starch, have been developed by the Green Chemistry Centre of Excellence based at the University of York. This material, named Starbon, offers a greener alternative to conventional adsorbent materials. Polysaccharides are relatively inexpensive, naturally abundant and

CONTACT Maha A. Tony maha_tony1@yahoo.com Basic Engineering Science Department, Faculty of Engineering, Minoufiya University, Shbin El-Koum, Minoufiya, Egypt.

biodegradable; they also possess a range of surface functionalities that are maintained in the final Starbon material.[12–14] Starbon offers the significant advantage, over activated carbon, of being highly mesoporous. Previous work carried out by Parker et al. investigating adsorption of dye molecules by Starbon and activated carbon has shown that this mesoporosity increases adsorption rate and capacity compared to the activated carbon Norit®.[12] Based on these results, Starbon is considered appropriate as a potential material for laundry grey water treatment.

Several advanced oxidation processes (AOPs) for wastewater treatment have also been given considerable attention in recent years as an alternative to conventional treatment techniques. AOPs are characterised by the use of highly reactive intermediates, hydroxyl radicals (·OH), which attack the organic pollutants in the wastewater and mineralise them.[10,15] Such processes include UV, O_3/H_2O_2,[1] O_3/UV,[16] TiO_2 photocatalysis, and Fenton and photo-Fenton processes.[17,18]

Among those AOPs, the Fenton's reagent, a homogeneous catalytic system comprising hydrogen peroxide and a ferrous salt, is an interesting solution because it allows high mineralisation levels at room temperature and pressure conditions. The high efficiency of this technique relies on the formation of strong hydroxyl radical (·OH) and oxidation of Fe^{2+} to Fe^{3+}. Both Fe^{2+} and Fe^{3+} ions are coagulants; therefore, the Fenton process can have a dual function, namely oxidation and coagulation of pollutants during the treatment process.[18,19]

In spite of the volume of work published on Fenton processes and adsorption techniques for wastewater treatment, there appears to be a lack of information regarding the combination of these two systems. The work presented here not only focusses on the treatment of laundry wastewater with Starbon and Fenton's reagent separately but also goes further to present, for the first time, the combination of these two techniques to treat laundry wastewater and determine if any advantages can be gained.

Materials and methods

Grey water

Grey water effluent used in this study was collected from a commercial laundry facility in the city of York, United Kingdom. This laundry system is operated with a standard washing machine programme using a powder detergent, which includes three main ingredients: pH control/salts, water softeners and surfactant cleansers (chemical composition is illustrated in Table 1). Two types of grey water from the laundry system were studied depending on the initial organic matter content. Samples were collected and analysed before treatment.

Grey water with low organic matter content obtained from the last rinse was called "low load"; this is carried out for the purpose of removing residual laundry agents and suspended dirt at the end of the wash. The main characteristics of low-load wastewater are pH 7.2, suspended solids 23 mg L^{-1} and COD 96 mg L^{-1}.

Grey water with high organic matter content obtained from the first wash cycle was called "high load." The main characteristics of high-load wastewater are pH 7.4, suspended solids 34 mg L^{-1} and COD 704 mg L^{-1}.

Table 1. Composition of detergent used in this study.

Common name	Concentration (%)
Alcohol ethoxylates AE7	1–5
Citric acid	1–5
Disodium disilicate	1–5
Salt of LAS	5–10
Sodium carbonate	20–30
Sodium carbonate peroxide	5–10
2-Propenoic acid/2,5-furandione polymer	1–5

LAS, linear alkyl benzene sulphonates.

Catalyst and reagents

Starbon materials

Starbon carbonaceous materials were previously prepared at the Green Chemistry Centre of Excellence, University of York. This material is prepared by heating 1.6 g corn starch in 8 L of deionised water at 120°C and 80 kPa for 45 min, and then subsequently cooling for 48 h to yield a porous gel block. The water in the block then undergoes five stages of solvent exchanges with increasing concentrations of ethanol. The mesoporous starch is then doped with *p*-toluene sulphonic acid (5% w/w) and refluxed for 6 h. The resulting material was heated under vacuum to 180°C to ensure drying and begin the carbonisation process. It was then further heated to 300°C at 1°C min^{-1} under nitrogen. The resulting material is referred to as S300. Full characterisation of S300 can be found in the work of Parker et al.[12]

Fenton's reagent

Fenton's reagent, which is a solution of Fe^{3+} (prepared from ferric chloride) and hydrogen peroxide (30%, by weight), was used in the experiments for hydroxyl radical generation. Sulphuric acid and sodium hydroxide were used to adjust the pH to the desired values. All chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Analytical determinations

The wastewater substrate concentration was measured by its chemical oxygen demand (COD) using the standard methods.[20] Jenway pH meter (3505) from Japan was used for pH measurements of the wastewater. Suspended solid is determined according to the standard methods.[20]

Experimental methods

The experiments were performed in a batch mode test by pouring 20 mL of the grey water into a 100-mL glass vessel. The Fenton reagent was then introduced to the solution by adding the required amounts of ferrous solution and hydrogen peroxide. For the experiments in which S300 was used, it was added to the grey water instead of Fenton's reagent. In the case of the experiments where the effect of the pH was examined, a mass of 20 mg of S300 was added to a 100-mL glass bottle containing 20 mL of grey water, pH was adjusted using H_2SO_4 or NaOH. The bottles were then sealed and stirred for 1 h. For the effect of temperature changes, a range of (room temperature)

22–60°C was used. Samples of grey water were taken at regular time intervals during experiments to determine their COD removal efficiency.

Results and discussion

Fenton's reagent treatment

Effect of Fenton's reagent concentrations

In order to determine the optimum concentration of Fenton's reagent necessary for maximum efficacy, a range of experiments were carried out with varying reagent concentrations. Figure 1 shows the decrease of COD over time for each concentration of Fe^{3+} or H_2O_2. In general, COD removal increased with the increasing concentration of Fe^{3+} up to the optimal concentration of 40 mg L^{-1}, which gave a 63% COD reduction after 15 min. Iron concentrations above 40 mg L^{-1} resulted in reduced process performance, because Fe ions were produced instead of the more useful ·OH radicals. This finding is in agreement with the previous observations.[10,21]

The results, illustrated in Figure 2b, show a significant enhancement of the degradation process when the H_2O_2 concentration was increased from 100 to 400 mg L^{-1}. Increasing H_2O_2 concentration results in the generation of additional reaction intermediates, ·OH radicals, that enhance the degradation process. However, at higher peroxide concentrations, the excess hydrogen peroxide can act as a ·OH scavenger, forming HO_2, a less reactive oxidising agent that has a longer lifetime than the ·OH, resulting in decreased COD removal.[22–24]

The reaction kinetics show that COD reduction was most significant within the first 15 min of the reaction after which COD levels reached a plateau. This behaviour has previously been reported in the literature and could be attributed to the consumption of all the hydrogen peroxide in the first 15 min, and thus, no reaction can take place after this.[9]

Effect of the initial pH

The pH significantly affects the Fenton process, as it affects the activity of the speciation of both iron and hydrogen peroxide decomposition. To determine this effect, the initial pH of the high-load grey wastewater was varied from pH 3.0 to 8.0 (Fig. 2). In accordance with the literature, results show that the removal efficiency increases with a decrease in the pH, with the optimal performance found at pH 3.0.[17,25] It is thought that pH is the controlling parameter in the hydrogen peroxide decomposition to produce ·OH radicals, which is maximised at pH 3.0 for the laundry wastewater resulting in COD reduction up to 95%.

Organic matter removal by Starbon adsorption

Effect of contact time

Figure 3a shows the effect of contact time on COD removal of both high- and low-load laundry wastewater. The results show that rapid COD removal occurred within 60 min of adsorbent addition. COD removal remained constant after 60 min, and it was considered that equilibrium had been reached. As may be expected, the removal of COD was dependent on the concentration of organics in the wastewater. For high-load wastewater (initial COD of 704 $mg_{\text{-COD}}$/L), COD removal was found to be 63%; for low-load wastewater (initial COD of 96 $mg_{\text{-COD}}$/L), COD removal was 70% at 60 min of reaction.

Effect of solution pH on adsorption

The influence of pH value (range of 2–8) on the process of adsorption was investigated. As with Fenton's reagent, it was determined that acidic pH 2–3 was preferred for COD removal from water (Fig. 3b). The lower removal level at basic pH is believed to be due to repulsion between the adsorbent surface and the wastewater.[26,27]

Effect of reaction temperature

The influence of temperature was also investigated; a temperature range of room temperature (22), 30, 40, 50, and 60°C was used. Results show that a temperature increase of 20–40°C leads to a small decrease in COD removal from 63% to 54%, but at an increase of 40–60°C, there is a dramatic decrease in COD removal from 54% to 9% (Fig. 3c). This would suggest that the adsorption process is exothermic,[28] and this decrease in adsorption with temperature increase may be attributed to the weakening of adsorptive forces between the adsorbate and the adsorbent, and also between the adjacent sites of the adsorbed phase.[26,29] As the majority of laundry washes are carried out at ≤40°C, Starbon should

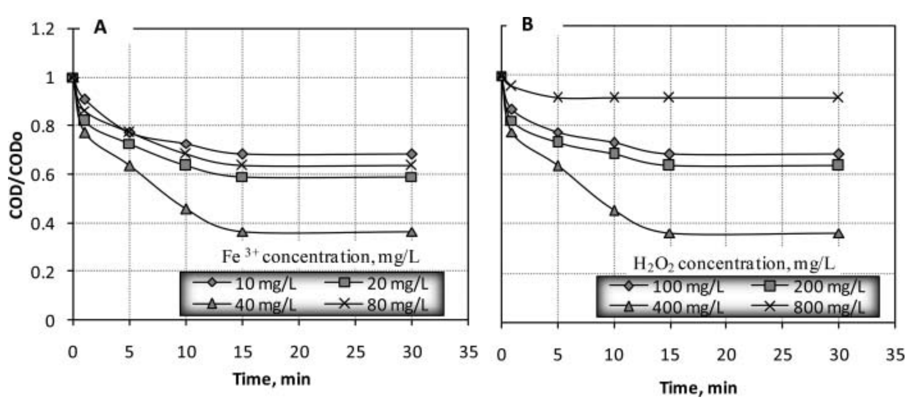


Figure 1. Effect of the Fenton's reagent concentration on low-load grey water treatment. (a) Effect of iron concentration (operating parameters: $[H_2O_2] = 400$ mg L^{-1}; pH 7.4). (b) Effect of hydrogen peroxide concentration (operating parameters: $[Fe^{3+}] = 40$ mg L^{-1}; pH 7.4).

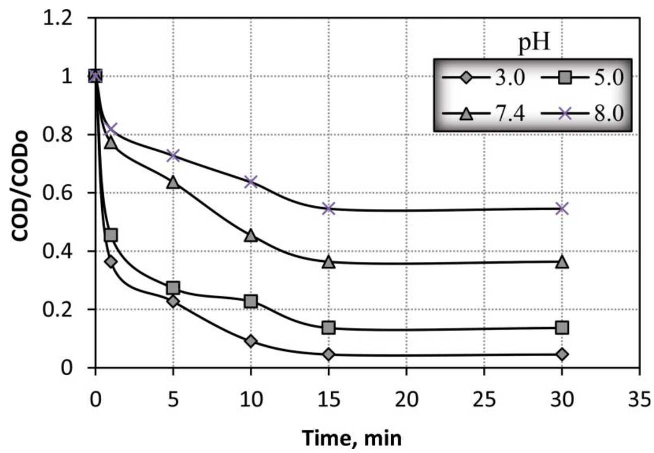


Figure 2. Effect of pH on the Fenton's reagent treatment ($[Fe^{3+}] = 40$ mg L^{-1}; $[H_2O_2] = 400$ mg L^{-1}).

perform well if added directly to the waste as it is expelled from the washing machine.

Effect of different S300 dose

The effect of adsorbent dosage on COD removal in high-load wastewater is shown in Figure 3d. It is observed that the COD removal increases with an increase in adsorbent dose up to 20 mg/20 mL wastewater; a further increase up to 25 mg/20 mL did not provide further improvement in COD removal. Therefore, 20 mg/20 mL dose of the adsorbent was used in further studies. The increase in the COD removal with an increase in the adsorbent dose is likely due to the larger surface area that will be present in solution. The decrease observed for the adsorbent dose of 25 mg/20 mL suggests that after a certain dose of adsorbent an overlapping of the adsorption sites due to overcrowding of adsorbent particles may be taking place, reducing the available surface area. This is similar to studies reported by Abdel-Ghani et al.[30]

Dual adsorption/Fenton oxidation techniques

Finally, dual adsorption/Fenton's reagent experiments were carried out (Fig. 4). The major purpose of this integrated process was to reduce the treatment costs, by reducing the amount of Fenton's reagents required.

Results showed that the optimum level of the Fenton's reagent, when used in combination with S300 (20 mg/20 mL), was 20 mg L^{-1} Fe^{3+} and 200 mg L^{-1} H_2O_2 at pH 7.4. This gave a COD removal of 93%. If this result is compared with the results of solo Fenton's reagent use (Fig. 1), in order to obtain a similar COD reduction 40 mg L^{-1} Fe^{3+} and 400 mg L^{-1} H_2O_2 are required. Therefore, the Fenton's reagents required are halved when using a combined process.

It has been suggested that this treatment process could be further improved by the adsorption of iron onto the Starbon prior to the use in wastewater treatment, thus creating a semi-heterogeneous process. As a result, the Starbon adsorbent could act to immobilise and concentrate the contaminants. Hydrogen peroxide would then react with the iron contained within the adsorbent, initiating the Fenton reaction and generating the hydroxyl radicals required. Subsequently, the radicals would oxidise the adsorbed contaminants. Thus, the COD is decreased and the Starbon + Fe material is regenerated.[31]

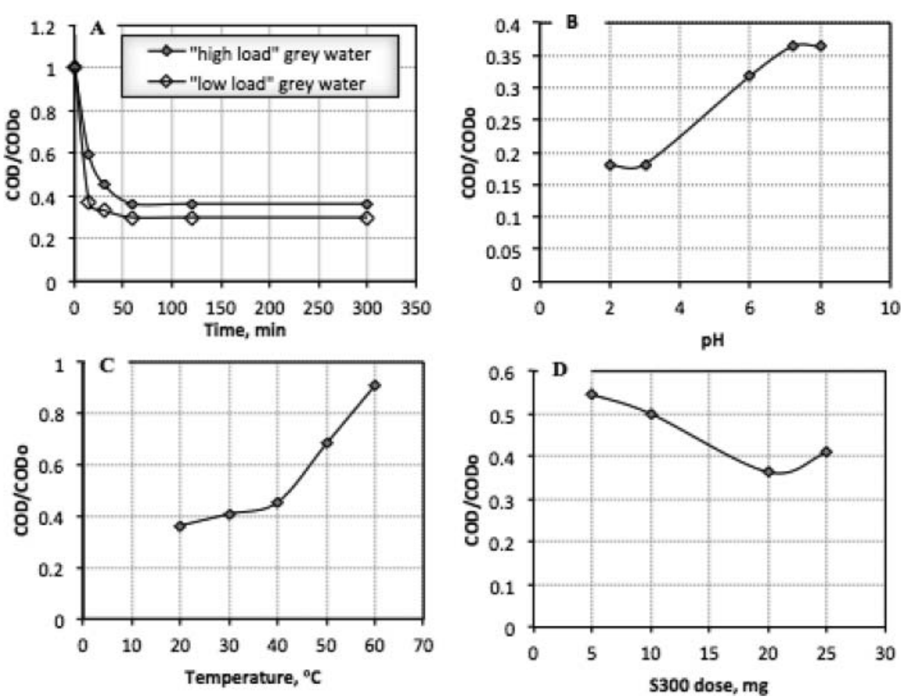


Figure 3. (a) Effect adsorption time of grey water pollutants versus COD removal the reaction time. (b) Effect of pH on adsorption of pollutant from grey water (S300). (c) Effect of temperature on adsorption of pollutant from grey water (S300). (d) Effect of S300 dose on adsorption of pollutant from grey water.

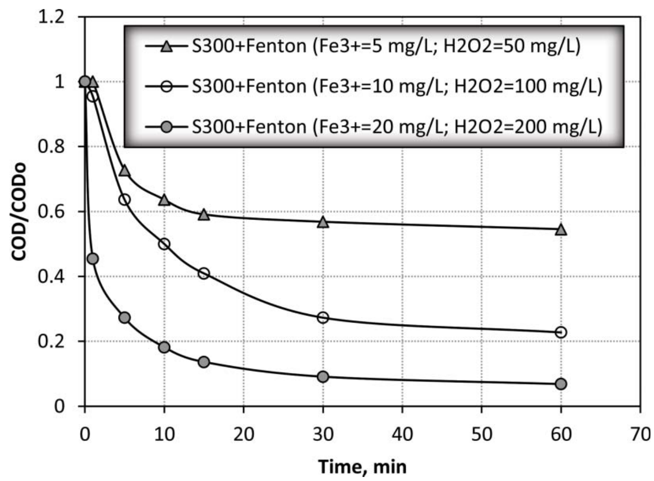


Figure 4. Effect of adsorption/oxidation process.

Conclusion

Laundry machine wastewater was subjected to laboratory treatment to investigate the Fenton's oxidation and Starbon adsorption treatment. The optimal treatment conditions were applied to maximise COD removal, e.g., different reagent concentrations, pH and temperature. The results showed that COD was reduced by 95% and 81% for the Fenton's reagent and adsorption treatment, respectively. When the combined adsorption/oxidation treatment was applied, the COD removal reached 93% but at a much lower concentration of the Fenton's reagent than that used in the individual experiment. This is the first time these two treatments have been used in combination, and the results show a significant promise for the treatment of laundry wastewater. Future work will involve testing this concept on a large scale, along with testing Starbon that is preloaded with iron.

Funding

The first author wishes to express her thanks to the Ministry of Higher Education, Missions Department, Egypt, for the financial support granted through the postdoctoral research.

References

[1] Jefferson, B.; Laine, A.; Parsons, S.; Stephenson, T.; Judd, S. Technologies for domestic wastewater recycling. Urban Water **2000**, *1*, 285–292.

[2] Friedler, E.; Hadari, M. Economic feasibility of on-site greywater reuse in multi-storey buildings. Desalination **2006**, *190*, 221–234.

[3] March, J. G.; Gual, M.; Orozco, F. Experiences on greywater re-use for toilet flushing in a hotel (Mallorca Island, Spain). Desalination **2004**, *164*, 241–247.

[4] Li, F.; Behrendt, J.; Wichmann, K.; Otterpohl, R. Resources and nutrients oriented greywater treatment for non-potable reuses. Water Sci. Technol. **2008**, *57*(12), 1902–1907.

[5] Kotut, K.; Nganga, V. G.; Kariuki, F. W. Physico-chemical and microbial quality of greywater from Various Households in Homa Bay town. Open Environ. Eng. J. **2011**, *4*, 162–169.

[6] Kim, J.; Song, I.; Oh, H.; Jong, J.; Park, J.; Choung, Y. A laboratory-scale graywater treatment system based on a membrane filtration and oxidation process-characteristics of graywater from a residential complex. Desalination **2009**, *238*, 347–357.

[7] Kim, S.; Vogelpohl, A. Degradation of organic pollutants by the Photo-Fenton-process. Chem. Eng. Technol. **1998**, *21*(2), 187–191.

[8] Bolong, N.; Ismail, A. F.; Salim, M. R.; Matsuura, T. A review of the effects of emergingcontaminants in wastewater and options for their removal. Desalination **2009**, *239*, 229–246.

[9] Gupta, V. K.; Carrott, P. J. M.; Carrott, R.; Suhas, T. L. Low-cost adsorbents: Growing approach to wastewater treatment—A review. Crit. Rev. Environ. Sci. Technol. **2009**, *39*, 783–842.

[10] Tony, M. A.; Zhao, Y. Q.; Fu, J. F.; Tayeb, A. M. Conditioning ofcaluminium-based water treatment sludge with Fenton's reagent: Effectiveness and optimising study to improve dewaterability. Chemosphere **2008**, *72*, 673–677.

[11] Babel, S.; Kurniawan, T. A. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. J. Hazard. Mater. **2003**, *B97*, 219–243.

[12] Parker, H. L.; Hunt, A. J.; Budarin, V. L.; Shuttleworth, P. S.; Miller, K. L.; Clark, J. H. The importance of being porous: Polysaccharide-derived mesoporous materials for use in dye adsorption. RSC Adv. **2012**, *2*, 8992–8997.

[13] Parker, H. L.; Budarin, V. L.; Clark, J. H.,; Hunt, A. J. Use of starbon for the adsorption and desorption of phenols. Am. Chem. Soc. Sustain. Chem. Eng. **2013**, *1*(10), 1311–1318.

[14] Budarin, V.; Clark, J. H.; Deswarte, F. E. I.; Hardy, J. J. E.; Hunt, A. J.; Kerton, F. M. Delicious not siliceous: Expanded carbohydrates as renewable separation media for column chromatography. Chem. Commun. **2005**, *23*, 2903–2905.

[15] Bauer, R; Fallmann, H. The photo-Fenton oxidation—A cheap and cefficient wastewater treatment method. Res. Chem. Interm. **1997**, *23*(4), 341–354.

[16] Coelho, A.; Castro, A. V.; Dezotti, M.; Sant'Anna, G. L. Treatmentcof petroleum refinery sourwater by advanced oxidation processes. J. Hazard. Mater. **2006**, *B137*, 178–184.

[17] Paterlini, W. C.; Nogueira, R. F. P. Multivariate analysis of Photo-Fenton degradation of the herbicides tebuthiuron, diuron and 2,4-D. Chemosphere **2005**, *58*, 1107–1116.

[18] Tony, M. A.; Purcell, P. J.; Zhao, Y. Q. Oil refinery wastewater treatment using physicochemical, Fenton and Photo-Fenton oxidation processes. J. Environ. Sci. Health **2012**, *A47*, 435–440.

[19] Neyens, E.; Baeyens, J.; Weemaes, M.; Deheyder, B. Pilot-scalecperoxidation (H_2O_2) of sewage sludge. J. Hazard. Mater. **2003**, *B98*, 91–106.

[20] APHA-AWWA-WEF. *Standard Methods for the Examination of Water and Wastewater*, 20th Ed.; American Public Health Association: Washington, DC, 1998.

[21] Kositzi, M.; Poulios, I..; Malato, S.; Caceres, J.; Campos, A. Solar photocatalytic treatment of synthetic municipal wastewater. Water Res. **2004**, *38*, 1147–1154.

[22] Cember, H. *Introduction to Health Physics*. McGraw-Hill: New York, 1996; 237.

[23] Litorja, M.; Ruscic, B. A photoionization study of the hydroperoxyl radical, HO_2, and hydrogen peroxide, H_2O_2. J. Electron Spect. Rel. Phenom. **1998**, *97*, 131–146.

[24] Chu, W. Modeling the quantum yields of herbicide 2, 4-D decay in UV/H_2O_2 process. Chemosphere **2001**, *44*, 935–941.

[25] Kang, Y. W.; Hwang, K. Y. Effect of reaction condition on the oxidation efficiency in the Fenton process. Water Res. **2000**, *34*(10), 2786–2790.

[26] Bekci, Z.; Seki, Y.; Yurdakoc, M. K. Equilibrium studies for trimethoprim adsorption onmontmorillonite KSF. J. Hazard. Mater. **2006**, *B133*, 233–242.

[27] Sanchez, M.; Rivero, M. J.; Ortiz, I. Photocatalytic oxidation of grey water over titanium dioxide suspensions. Desalination **2010**, *62*, 141–146.

[28] Salam, M. A.; Burk, R. C. Thermodynamics and kinetics studies of pentachlorophenol adsorption from aqueous solutions by multi-walled carbon nanotubes. Water Air Soil Pollut. **2010**, *210*, 101–111.

[29] Horsfall, M.; Spiff, A.I. Effects of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by Caladium bicolor (Wild Cocoyam) biomass. Electron. J. Biotechnol. **2005**, *8*(2), 162–169.
[30] Abdel-Ghani, N. T.; Hefray, M.; EL-Chaghaby, G. A. F. Removal of Lead from aqueous solution using low cost abundantly available adsorbent. Intern. J. Environ. Sci. Technol. **2007**, *4*(1), 67–73.
[31] Huling, S.; Arnold, R.; Sierka, R.; Jones, P.; Fine, D. Contaminant adsorption and oxidation via Fenton reaction. J. Environ. Eng. **2000**, *126*(7), 595–600.