Treatment of Tea Industry Wastewater Using a Combined Adsorption and Advanced Oxidation Process

Dennis O. Otieno, Anil Kumar, Maurice S. Onyango and Ochieng Aoyi

Abstract—Tea, produced from the evergreen plant, *Camellia Sinensis*, is the most widely consumed beverage in the world after water. Although tea processing has now diversified into various speciality end products such as instant, white, oolong, iced, flavoured, and various blends, the most abundantly produced tea product in the world is fermented black tea. Black tea production is essentially a "dry" process, as no water is used at any of the production process steps. However liquid waste is generated due to the use of water for cleaning process equipment and factory premises. The waste exits the factory as coloured liquid effluent that must be treated before being discharged into rivers, lakes and other fresh water bodies. This paper presents findings of a study carried out to evaluate the performance of a combined adsorption and advanced oxidation process in removing colour from tea industry wastewater. The variables explored were the effects of sorbent mass, oxidant dosage, solution pH, agitation rate and temperature, on the decolouration of tea industry effluent. The results indicate that the combined adsorption and advanced oxidation is most effective at pH 3 wherein the effluent colour was reduced from 478 Pt-Co colour units to 8 Pt-Co colour units. The latter meets the NEMA recommended limit for discharge of colored effluents.

Keywords—Tea industry effluent, Water pollution, Colour removal, Adsorption, Advanced oxidation.

I. INTRODUCTION

THE problem of protecting the environment from pollution and contamination by both the natural and human causes is now in focus all over the world. In line with this global focus, this paper presents a simple and efficient industrial wastewater treatment process developed from a study carried out on effluents from the tea industry. According to Maghanga et al [1], effluents generated by tea factory is reddish-orange in colour, and is also found to have substantial amounts of organic and inorganic pollutants, and suspended solids. The colour of the effluent discharged from a tea factory is mainly caused by two phenolic compounds, *theaflavins* (TFs) and *thearubigins* (TRs), formed during the enzyme oxidation stage, also known as fermentation stage of tea processing. A number of techniques have been developed for the removal of pollutants from industrial wastewaters, including coagulation and flocculation [2], biological [3], [4], chemical [5], electrochemical [6], membrane separation [7], advanced oxidation processes (AOPs) [8], and adsorption [9]. These techniques have been used with varying degrees of success and shortcomings.

For example, it is observed that coagulation and flocculation require considerable land area and a continual supply of chemicals [10], hence operational costs are high; biological techniques such as activated sludge require fungi such as *coriolus*, *aspergillus*, *phanerochaete`* and certain bacterial species such as *bacillus*, *alkaligenes* and *lactobacillus* [4], which are highly sensitive to changes in operating conditions, and hence are costly to control; electrochemical techniques form metal hydroxide sludge from the metal electrodes, and pH control must be incorporated resulting in higher costs, in addition to the problem of metal hydroxide sludge disposal [10]; membrane separation techniques incur high capital and operational costs and are limited in application by the range of the molecular weights of the compounds being targeted for removal; advanced oxidation techniques are suitable for destroying dissolved organic contaminants, aromatic compounds, phenols and pesticides [11], but the operational costs of some AOPs such as ozonation, are considerably high. As for adsorption, one of the main shortcomings is the generation of sludge, the so-called secondary waste, and this results in the need for frequently changing or regenerating the adsorbent. However, recent studies show that the limitations and/or shortcomings of some of the adsorption methods can be remediated by making the right choice of adsorbent(s) [12] and/or combining adsorption with one or more of the other effluent treatment techniques to achieve the desired treatment efficiency in a cost effective manner [13], and with reduced environmental load.

The strategy of combining advanced oxidation with other treatment techniques has gained considerable attention in wastewater remediation [13]-[15]. In this study, the general objective was to investigate the application of a combined

D. O. Otieno, Department of Chemical, Metallurgical and Materials Engineering, TUT / Department of Chemical and Process Engineering, MU (phone; +27 61 772 6596; +254 703 775 716; e-mail: (e-mail: do99ke@yahoo.com).

A. Kumar, Department of Chemical and Process Engineering, MU (e-mail: ak3900@yahoo.com).

M. S. Onyango, Department of Chemical, Metallurgical and Materials Engineering, TUT (email: onyangoms@tut.ac.za).

O. Aoyi, Department of Chemical Engineering, Vaal University of Technology, South Africa (email: ochienga@vut.ac.za).

advanced oxidation and adsorption process, with a view to developing a novel technique for the treatment of tea industry effluents prior to discharge into receiving water bodies. The choice of adsorption is supported as being simple in design and operation, and applicable to many situations [12]; on the other hand, advanced oxidation has the advantage of being effective in destroying dissolved organic matter [11], [13]-[15]. Hence the application of a combined advanced oxidation and adsorption in purifying tea industry wastewater is potentially more effective than the individual processes; and further, the synergy of the combined advanced oxidation and adsorption process is a potential means of remediating the shortcomings of the individual processes, including reducing the quantity of secondary waste.

In this study, natural zeolite was used as the adsorbent, while hydrogen peroxide was used as the oxidant. No application of these materials in tea effluent treatment is reported in literature.

II. MOTIVATION

Tea production has contributed significantly to the Kenyan economy and it will continue to do so, as currently tea is the leading cash crop in Kenya. Effluent generated by tea factories is generally reddish-orange in colour, and originates mainly from washing the process equipment and factory premises. If discharged directly into rivers, lakes, and other surface water bodies, such wastewater reduces the availability of light over the water, thereby decreasing oxygenation of the water by photosynthesis, hence disrupting the growth of aquatic plants and micro-organisms; this subsequently adversely effects the rest of the aquatic community that depends on these organisms to survive. As industrial tea productivity has increased nationally over the recent years, so has water usage, creating a corresponding rise in wastewater quantities. Hence there is need for increased focus on developing more efficient techniques for the removal of pollutants such that the effluents discharged from tea industries are within the National Environmental Management Authority (NEMA) regulatory limit for coloured effluent discharge into the environment.

III. MATERIALS AND METHODS

In the first set of experiments, the variables explored were the effects of sorbent mass, oxidant dosage and solution pH on decolourization of the tea industry effluent. Pre-weighed amounts of the adsorbents ranging from 50 mg to 200 mg were contacted with 40 mL of the tea industry wastewater solutions contained in plastic sample bottles. The bottles were placed in a thermostatic shaker operated at 200 rpm for 24 h. At the end of this period the samples were removed from the shaker, filtered and the filtrate analyzed for residual colour concentration using a UV-visible spectrophotometer (Shimadzu UVmini 1240). Further analysis to establish the absolute colour units were done using Hach DR 4000.

Prior to this, the sorbent media was prepared using the procedure described by Onyango et al [12], which is summarized in Fig. 1.
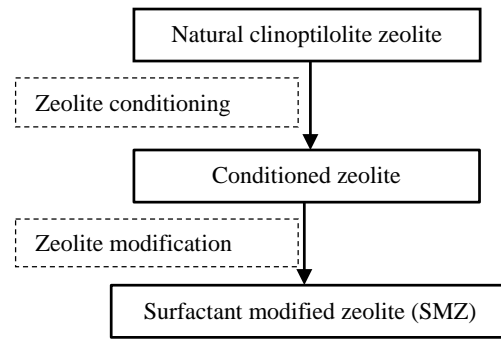

Fig. 1 Zeolite modification experimental process

The second sets of experiments carried out were kinetic experiments, and the variables explored were the effects of agitation rate and temperature, on decolourization of the tea industry effluent. These were carried out using a 1 L batch continuous stirred tank reactor (CSTR) operated, initially, at a stirring speed of 200 rpm. The adsorbent mass was fixed at 2.5 g, based on the optimal batch quantity of 50 mg in 40 mL bottle, while the temperature was initially set at 18 °C. To generate kinetic data, at time zero and at predetermined time intervals thereafter, samples were withdrawn from the reactor using a syringe. The samples were filtered and then analyzed for colour concentration, in the manner already described. These procedures were repeated with stirring speeds of 300 rpm and 400 rpm, and temperatures of 30 ºC and 40 ºC. The set up for kinetic experiments was as shown in Fig. 2.
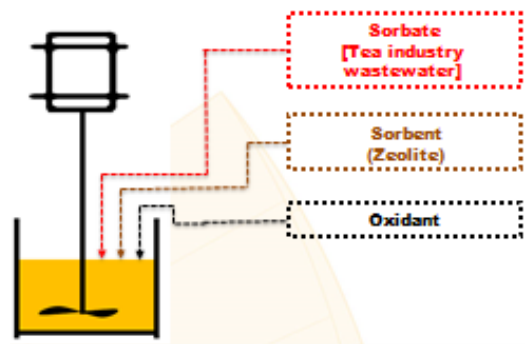

Fig. 2 Kinetic studies experimental process

Finally column experiments were carried out to study the effects of sorbent mass and oxidant dosage on decolorization of the tea effluent in a prototype flow situation. Perspex columns of internal diameter 20 mm and 30 mm respectively were used. Adsorbent bed heights were varied by using varying amounts of the sorbent mass. The sorption media was packed between glass wool while inert beads were placed at the bottom and top ends of the column. Tea wastewater solution was pumped vertically upward through the column to avoid channeling. Samples were collected from the top of the column at an interval ranging from 30 to 60 minutes, until the colour concentration at the column effluent was nearly the same as that of the influent. Both pre-oxidation and post-oxidation were considered. Fig. 3 illustrates the column studies experimental set up.
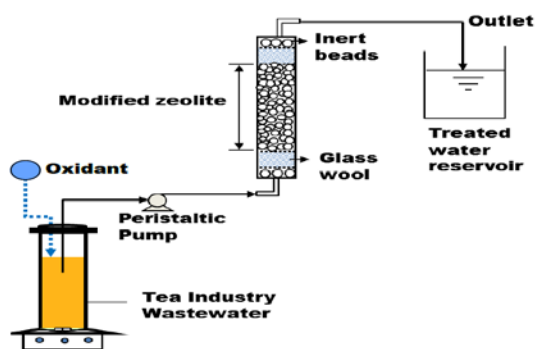
Fig.3 Column studies experimental set up

IV. RESULTS AND DISCUSSIONS

Results from this study are presented, in summary, in Table 1 to Table 7. With respect to the effects of sorbent mass, Table 1 shows that by progressively increasing the adsorbent mass, the absorbance correspondingly reduced, implying a reduction in colour concentration. Thus the decolourization of wastewater, expressed here as percent decolourizatiion, increased with corresponding increase of adsorbent mass. This observation is due to the fact that active sites available for sorption of colour compounds are proportional to the adsorbent mass.

The same trend similarly applies to the effect of oxidant dose, as shown in Table 2. In the case of oxidant dose, the decolourization efficiency increased with the increase in the volume of oxidant dose. The advanced oxidation step was incorporated in this study primarily to effect the breaking down of the aromatic organic chains of theaflavins and thearubigins into simpler forms, to ease their subsequent adsorption. It can therefore be concluded that the oxidant was successful in breaking down the aromatic chains, and further that excess or higher volumes of the oxidant enhanced the reaction rates.

The effect of pH on decolourization is given in Table 3, from which it is observed that the highest decolourization efficiency is achieved at the lowest pH, in this case pH 3. This observation can be explained in terms of adsorbate and adsorbent surface properties. The surface of SMZ is positively charged; hence if the decolourization efficiency at pH 3 is higher than that at PH 11, then changing the wastewater pH affects the net surface charge.

With respect to both the effect of temperature and the effect of agitation speed, shown in Table 4 and Table 5 respectively, the increased decolourization efficiencies at higher temperatures and higher agitation speeds can be attributed to increased motion of the molecules at higher temperatures and higher turbulence.

TABLE 2
EFFECT OF OXIDANT DOSE ON DECOLOURIZATION

Sample No	Sample pH	Oxidant dose (ml)	Absorbance (Abs)	% Relative Concentration	%Colour Removed
Wastewater	7.2	0	1.375	100	0
Distilled water	7.1	0	0.092	7	93
45	7.2	0.1	0.798	64	36
46	7.2	0.2	0.593	48	52
47	7.2	0.3	0.485	39	62
48	7.2	0.4	0.394	32	68

TABLE 3
EFFECT OF pH ON DECOLOURIZATION

Sample No	Sample pH	Sorbent Mass(mg)	Abs	% Relative Concentration	%Colour Removed
Wastewater	7.2	0	1.366	100	0
Distilled water	7.1	0	0.079	6	94
34	11.0	50	1.241	86	14
33	9.0	50	0.977	68	32
35	6.0	50	0.940	65	35
36	3.0	50	0.365	26	74

TABLE 4
EFFECT OF TEMPERATURE ON DECOLOURIZATION

Sample Temp ºC	Sample pH	Sorbent mass (mg)	Abs	% Relative Concentration	% Colour Removed
18	7.2	50	0.844	68	32
30	7.2	50	0.510	41	59
40	7.2	50	0.325	26	74
18	7.2	100	0.540	44	56
30	7.2	100	0.436	35	65
40	7.2	100	0.241	19	81
18	7.2	150	0.532	43	57
30	7.2	150	0.410	33	67
40	7.2	150	0.228	18	82
18	7.2	200	0.235	19	81
30	7.2	200	0.212	17	83
40	7.2	200	0.189	15	85

TABLE 5
EFFECT OF AGITATION SPEED ON DECOLOURIZATION

Agitation Speed (rpm.)	Sample pH	Sorbent mass (mg)	Abs	% Relative Concentration	% Colour Removed
200	7.2	50	0.844	68	32
300	7.2	50	0.821	66	34
400	7.2	50	0.790	64	36
200	7.2	100	0.540	44	56
300	7.2	100	0.535	43	57
400	7.2	100	0.507	41	59
200	7.2	150	0.532	43	57
300	7.2	150	0.510	41	59
400	7.2	150	0.499	40	60
200	7.2	200	0.235	19	81
300	7.2	200	0.232	19	81
400	7.2	200	0.224	18	82

TABLE 1
EFFECT OF SORBENT MASS ON DECOLOURIZATION

Sample No	Sample pH	Sorbent mass(mg)	Abs	% Relative Concentration	%Colour Removed
Wastewater	7.2	0	1.365	100	0
Wastewater	3.1	0	0.984	69	31
49	7.2	50	0.859	59	41
50	7.2	100	0.843	55	45
51	7.2	150	0.541	38	62
52	7.2	200	0.242	17	83

Table 6 and Table 7 show results for the effect of the combined adsorption and advanced oxidation on decolourization, respectively for batch studies and for column studies. Sorbent masses of 50 mg, 100 mg, 150 mg, and 200 mg were separately combined with oxidant dose of 0.1 ml. Batch tests done earlier had shown that 50 mg sorbent mass alone achieved decolourization efficiency of 41 % (Table 1), while 0.1 ml oxidant alone achieved decolourization of 36 % (Table 2). Now with the combined 50 mg adsorbent with 0.1 ml oxidant (Table 6), a decolourization efficiency of 64 % has been achieved, demonstrating that the combined adsorption and advanced oxidation process is more effective in purifying tea industry wastewater than the individual processes. This performance is replicated for 100 mg, 150 mg, and 200 mg, with 0.1 ml oxidant (Table 6) in comparison with that for individual adsorbents (Table 1).

TABLE 6
EFFECT OF COMBINED ADSORPTION AND ADVANCED OXIDATION ON DECOLOURIZATION

Sample No	Sorbent mass(mg)	Oxidant dose(ml)	Abs	% Relative Concentration	% Colour Removed
Wastewater	0	0	1.286	97	3
Distilled water	0	0	0.045	4	96
53	50	0.1	0.441	36	64
54	100	0.1	0.301	25	75
55	150	0.1	0.217	18	82
56	200	0.1	0.151	12	88

With respect to Table 7, the effect of the combined adsorption and advanced oxidation on decolourization in column flow studies was investigated at pH 3, the optimal pH. Both pre oxidation (that is, oxidation followed by adsorption) and post oxidation (adsorption followed by oxidation) were evaluated. The results indicate that post oxidation was the more effective of the two, in which the effluent colour was reduced from 478 Pt-Co colour units to 8 Pt-Co colour units.

TABLE 7
COLUMN POST-OXIDATION TREATMENT COLOUR ANALYSIS

Sample	Absorbance	Colour (Pt-Co)	% Colour Removed
Wastewater	1.271	480	3
Distilled water	0	0	96
Final adsorbate	0.082	30	64
Post oxidized adsorbate	0.022	8	75

V. CONCLUSIONS

This study has demonstrated that functionalization (modification) of zeolite increases its adsorption capacity and enables it to remove organic contaminants in tea industry effluent. The modified natural zeolite yielded a higher sorption capacity for tea colour compounds. It has been further demonstrated that the process of decolourization of tea industry effluent was affected by sorbent mass and oxidant dose, as well as the water quality parameters and hydrodynamic conditions including pH, temperature and agitation speed. And finally it has been demonstrated that the combined advanced oxidation and adsorption process is more effective in purifying tea industry wastewater than the individual processes. The combined adsorption and advanced

oxidation was most effective at pH 3 wherein the effluent colour was reduced from 478 Pt-Co colour units to 8 Pt-Co colour units. The latter meets the NEMA limit for discharge of colored effluent discharge into the environment.

However, further investigations need to be carried to generate more kinetic and breakthrough data. First, it is recommended that the effect of effluent flowrate through the column and the effect of column diameter on decolourization be investigated. It is also recommended that further investigations be directed towards internal recycling between the oxidation and adsorption stage in pursuit of developing the most cost effective strategy. This strategy of internal recycling could work in three stages, as follows. First the adsorption, aimed at removing simple organic colour compounds; this could be followed by an AOP, aimed at breaking the complex aromatic chains into simpler forms, with less chemical consumption. And finally, the adsorption step again, for polishing up, should this be deemed to be useful.

REFERENCES

[1] J. K. Maghanga, F. K. Segor, L. Etiégni & J. Lusweti. *Electrocoagulation Method for Colour Removal In Tea Effluent: A Case Study Of Chemomi Tea Factory In Rift Valley, Kenya*. Chemical Society of Ethiopia Vol. 23(3), 2009, pp. 371 – 381.

[2] O.S.Amuda, A. Alade. *Coagulation/flocculation process in the treatment of abattoir wastewater*. Desalination Vol. 196, 2006, pp. 22–31.

[3] T. Kuritz & C.P. Wolk. *Use of filamentous cyanobacteria for biodegradation of organic pollutants*. Applied and Environmental Microbiology Vol. 61, Jan. 1995, pp. 234–238.

[4] P. Kumar & R. Chandra. *Decolourisation and detoxification of synthetic molasse melanoidins by individual and mixed cultures of Bacillus spp.* Bioresource Technology Vol 97, 2006, pp. 2096–2102.

[5] J. Levec, & A. Pintar. *Catalytic oxidation of aqueous solutions of organics—an effective method for removal of toxic pollutants from waste waters*. Catalysis Today Vol. 24, 1995, pp. 51-58.

[6] C.A. Martinez-Huitle & S. Ferro. *Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes*. Chemical Society Reviews Vol. 35, pp. 1324-1340.

[7] H. Strathmann. *Membrane separation processes in advanced wastewater treatment*. Pure and Applied Chemistry Vol. 46, 1976, pp. 213-220.

[8] J. L. Wang & L. J. Xu. *Advanced Oxidation Processes for Wastewater Treatment: Formation of Radical and Application*. Critical Reviews in Environmental Science and Technology. Vol. 42, 2012, pp. 251-325.

[9] Ocampo-Pérez R., Abdel daiem M. M., Rivera-Utrilla J., Méndez-Díaz J. D., Sánchez-Polo M. *Modeling adsorption rate of organic micropollutants present in landfill leachates onto granular activated carbon*. Journal of Colloid and Interface Science Vol. 385, 2012, pp. 174–182.

[10] P. K. Holt, G. W. Barton & C. A. Mitchell. *The future for electrocoagulation as a localized water treatment technology*. Chemosphere, Vol. 59, 2005, pp. 355-367.

[11] D. D. Sun, J. H. Tay, K. M. Tan *Photocatalytic degradation of E. coliform in waters*. Water Research Vol. 37, 2003, pp. 3452–3462.

[12] M. S. Onyango, J. Kittinya, N. Hadebe, V.O.Ojijo, A.Ochieng. *Sorption of melanoidin onto Surfactant modified zeolite*. Chemical Industry & Chemical Engineering Quarterly Vol 17 (4), 2011, pp. 385−395.

[13] I. Oller, S. Malato, J.A. Sánchez- Pérez. *Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review*. Science of the Total Environment Vol. 409, 2011, pp. 4141–4166.

[14] T. Mandal, S. Maity, D. Dasgupta, S. Datta. *Advanced oxidation process and biotreatment: Their roles in combined industrial wastewater treatment*. Desalination Vol. 250, 2010, pp. 87–94.

[15] A. H. Konsowa, M. E. Ossman, Y. Chen, J. C. Crittenden. *Decolorization of industrial wastewater by ozonation followed by adsorption on activated carbon*. Journal of Hazardous Materials Vol. 176, 2010, pp. 181–185.