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Decolouration of reactive dyes with ozone in a semi-batch and a continuous stirred tank reactor

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Wastewater treatment in the textile Industry

General points of the first examiner:

1-The title of the thesis needs to be changed.

Answer: Wastewater treatment in the textile Industry was changed to “Decolouration of Reactive Dyes with Ozone in a Semi-Batch and a Continuous Stirred Tank Reactor.

2-Inthe table of content in page xi, how can you have 5.7, 5.8, 5.9, 5.10 etc in Chapter 6?

Answer: All of them have been corrected.

3- It would have been great to have the list of all Abbreviations before chapter 1.

Answer: It has been included before chapter1.

Specific Comments

1-The Abstract of the thesis needs to be rewritten.

Answer: It has been corrected and written in past tense .Quantitative results have been mentioned in the abstract.

All grammatical errors from Chapter 1 to 6 as per the first examiners comments were corrected.

List of abbreviations was added before chapter 1.Aim and strategy of chapter one was corrected.

Second examiner’s questions and comments

Page 1: Give a reference to support the statement”…which generally use 0.2 – 0.5 m^3 of water to produce I kg of the textile finished goods”

Answer: Ref 3 has been given.

The type and name of dyes should be given early on the thesis, so the reader is informed.

Answer: It has been done.

Page 7, two lines from end: remove “below”

Answer: It was removed.

Page 7: explain why traditional methods fail to treat textile WW.

Answer: It has been added.

Page 8: add reference for the table

Answer: It was in wrong place and has been corrected.

Page 9: change “etcetera” to ‘etc.”

Answer: It has been changed.

Page 9: give Reference to the 2nd Para.

Answer: Ref has been given.

Page 12: remove the first empty row in Table 2.2

Answer: It has been removed.

Page 15: Write correct symbol for hydroxide ion.

Answer: It has been corrected to OH- .

Page 16: add the degree symbol for 70C

Answer: It was added as 70 °C .

Page 21: why was indigo dye mentioned here?

Answer: It is not soluble in the water and can be used in this membrane system to be removed.

Page 22: give the specific energy to produce ozone

Answer: Has been added.

Page 23: Table 2.4: should also add the chemical reaction equations showing the various attack discussed in the text.

Answer: It was added

Page 23: what’s the meaning of “0.0046 to 0.0123 k/s-1”are these rate constants? If so what’s k/S-1

Answer: It has been corrected.

Page 24, line 1: check and correct “1.57USD/t per 100 tonnes”?

Answer: It has been corrected.

Page 24, line 4: check and correct “Dor example: Foe”and “10-15mi”what’s mi?

Answer: All have been corrected.

Page 25: The word of “demolition “is not appropriate.

Answer: It was changed to destruction.

Page 25 and elsewhere: what do you mean by “feedback time”?

Answer: It was changed to reaction time.

Page 26: and elsewhere: use a consistent symbol hydroxyl radical (preferably $\cdot OH$)

Answer: It has been done.

Page 28:2.4.1, last Line: I don’t think it is a good idea to mix ozone and hydrogen!

Answer: It was changed to combining.

Page 29:”ozonation feedback”?

Answer: It was changed to ozonation reaction.

Page 31,3rd Para: not clear

Answer: It was corrected.

Page 31, 2.4.2:CO2 and H_2O are not organics

Answer: It has been corrected.

Page 34: check the direction of the arrow in Eq.2.14

Answer: It was completed.

Page 48: discuss the novelty of the work.

Answer: It was added.

Page 50: what do you mean by”a place in the spectrum”- please chose a different word.

Answer: It has been corrected.

Page 52: the unit for “gramme” is “g” and not “gr”

Answer: It was corrected.

Page 52: give more details on the pre-ozonated expts (e,g.what’s the volume of the dye solution that was added to the reactor and discuss if it is significant to change the total volume and other parameters in the system)

Answer: It was added.

Page 55: Eq(1) is not homogenous ,it should be dC/dt+Kla(C*-C).

Answer: V was removed to be homogenous.

Page 56, line 6: the condition C=0 at t=0 is an initial condition rather than a boundary condition.

Answer: It was corrected.

Page 56: Eq.2 is not correct! What are the assumptions used to develop Eq.2? Is C*constant? Why?

Answer: It is constant because it is the equilibrium value that is usually assumed to be independent of the amount absorbed

Page 58: the model is indeed NOT valid because as can be seen in Fig.3.4. the line does not pass by the origin, which according to your model should pass by the origin.

Answer: We notice this does not vary through the zero point as might be expected. We suggest this is due to the obtaining being such that it takes time for the ozone to mix completely in the solution

Page62: Fig.3.8: should plot C/C_0 vs.t.

Answer: In this Fig we have three different initial concentrations and we wish to show that. We could have plotted it as suggested.

The curve plotted in Fig.3.8 for when C0=0.5g/l is different from those at Fig 3.6 and 3.7 though the other conditions are similar –please explain

Answer: It was plotted C/C0 and seem to be all right. It can be seen that all the curves are self-similar

Page 63: Should explain why gas flow rates affected dye decolouration rates- is it because of changes in mass transfer?

Answer: Unfortunately the ozoniser was such that when one changed the flow rate the concentration of ozone changed and so experiments varying only one parameter were difficult. Because there was such a small difference between the curves, the effects were not important

Page 64: I have concerns about the methodology used to determine the stoichiometry since an amount of dissolved ozone may be lost during the titration period, which is significantly long, by auto-decomposition and volatilisation .this is ozone should be significant enough to obtain incorrect high stoichiometry values. There are other techniques to determine ozone/organics stoichiometry that should be used. The other point to note on stoichiometry is that the purity of the dye should also be considered in the calculation of the number of molecules 0_3 used per one molecule of dye. How the pH affects the stoichiometry is also important to know.

Answer: We have used buffer to keep pH unchanged. It is possible that there were errors in the measurement but the result that many dye molecules were decoloured for an ozone molecule stands and this suggests a chain reaction which is the important result not the value.

Page 65: explain how mass transfer is faster than reaction.

Answer: limited by reaction. When looking at the curves the mass transfer reaches completion in about 15 mins while the reaction takes about 30 mins

Page 70 and elsewhere: nomenclature should not contain the well-known symbols such as nm,o3.NaOH,etc. Nomenclature should be sorted by alphabetical order and the Greek symbols are placed at the end.

Answer: It has been corrected.

Page 78, line 4: inappropriate use of the word ‘healing’

Answer: It was changed to treatment.

Page 79, para 3 , line 2 and elsewhere: change the word genera with species.

Answer: It was followed.

Page 79, para 3, line 2: use of ‘probability for corrosion ’is not appropriate.

Answer: It was changed to decomposition.

Page 80, para1, last line: kla is the ‘volumetric mass transfer coefficient’

Answer: Yes corrected.

Page 83: should give a figure of the spectrum to show how λ max was chosen

Answer: It was explained

Page 83: do you really need to remind that $1nm=10^{-9}m$?

Answer: No, It was removed.

Page 83: check which item is no (6)

Answer: No 6 was corrected as sampling.

Page 84, line 5: According to fig 4.1.there is no flow of dye solution –is the system semi-batch or continuous? This is confusing.

Answer: Chapter 4 is concerned with CSTR only. The flow of dye into the vessel has been added to the Figure 4.1.

Page 84,par2,line4:reputation

Answer: It was removed.

Page 84: discuss the assumptions made to develop the mass transfer equation

Answer:? It is just that the system is perfectly mixed and the processes occurring are mass transfer, flow in and out and homogeneous reaction

Page 86: Eq 3 is incorrect –Check MB.

Answer: It was typing error and was corrected.

Page 86: vague methods and confusing –no explanations were given.

Answer: It was typo error and formulation was corrected

Page 88, line4: explain what you mean by 'We see very similar behaviour in dye decolouration in both semi-batch and CSTR experiments in the reports published by othe researchers in the field.

Answer: These experiments obviously varies similar behaviour in rate of decolouration to those of other researchers in the field.

Page 89, clearly the figure shows that series 2, 3 are reproducible but no 3.What are the errors?

Answer: The third series was replaced with new series which looks similar.

Page 90, 4.4.4, line 2: how did you find that a plot of log(Cdye-Cdyef)vs .t gives a straight line of slope(q/v +k/v)?

Answer: Have shown that this equation applies.

Should develop the equations here starting from basic mass balances. If you do that then you will find that in fact a different linearized equation describes your case. The remaining discussion is incorrect since the model was not correct in the first place.

Answer: Have shown the model was correct and this comment does not apply.

Page 92: Eq.3 is incorrect so can't be used and the discussion that followed should be rewritten.

Answer: It was corrected. Equation (3) as written in the thesis was incorrect because of a typo, but the correct equation was used in the analysis.

Page 93: it is common that the rates highest initially and then they decline, why the results here do not follow this trend?

Answer: Because the liquid was not pre-ozonated there is an initial slower portion as the ozone concentration in the solution increases.

Page 95, Fig 4.9: check symbols and units.

Answer: It was corrected.

Page 96-97: conclusion don't seem appropriate.

Answer: it was revised.

Page 104, introduction: lines4-5 should be on the same line and check the sentence in line 7.

Answer: it was corrected.

Page 104, introduction, line 11 and elsewhere: what do you mean by 'organic processes '?

Answer: Biological process.

Page 105, para.3: what type of creatures that reactive dyes kill?

Answer: It has been reported generally in the references.

Page 106, line 4: correct the symbol of the hydroxyl radical

Answer: It was corrected.

Page 107, table title: change ‘prosperities’ with ‘properties’

Answer: It was done.

Page 109, ozone dissolution rate was measured on clean water where only physical absorption takes place. That rate will be enhanced when the system involves chemical reactions and hence it cannot be used for absorption accompanied by chemical reactions. The mass transfer rate is enhanced and an enhancement factor is used to describe the mass transfer rate.

Answer: ? The enhancement factor is only used when one does not have a model for the chemical reaction. Once one has a model for the rate of chemical reaction in the model there is no enhancement factor. We therefore have made no changes.

Page 109: what’s the reason for developing a simple model? If the model is simple but does not predict reasonably the real case then it is not useful.

Answer The idea is to develop the simplest model that can effectively describe all the phenomena as well as fit the data reasonably accurately. The claim is that this model does that.

Page 110: Reaction (a) should include stoichiometric ratios. Also remove the symbole ‘0’from dye as if it indicates a radical.

Answer: In our model one ozone attacks one dye molecule to form one radical. The radical can react with many dye molecules to form inactive dye. Thus the right hand side of (b) should have a radical in it. This has been done

Page 110: it is not clear why two symbols for coloured dye are used, this does not make sense.

Answer: This is part of the model to allow for the fact that the inactive dye can still react with the radical to cause termination. This has been explained in the text.

Page 111: The first sentence is not clear and the termination rate equation is not suitable.

Answer: Can clarify the first sentence to read: “The assumption is that radical termination occurs between both active and inactive dye. The sum of these is just the initial dye concentration so we can write:”

Page 111, Eq.4: when chemical reactions are involved in the system, the mass transfer is enhanced and its rate is written as E.kla(C0-C);where E is an enhancement factor that is determined from Hatta

number and the instantaneous enhancement factor. The theory explaining absorption accompanied by chemical reaction is well established and references such as Charpeniter , J-C.(1981).Mass transfer rates in Gas-Liquid Absorbers and Reactors. Advances in Chemical Engineering .Academic Press.11:1-133 or the book chemical reaction engineering by Octave Levenspiel should give more details.

Answer: The enhancement factor is only used when one does not have a model for the chemical reaction. Once one has a model for the rate of chemical reaction in the model there is no enhancement factor. We therefore have made no changes.

Page 123: integration of Eq.A1 should be checked and corrected .For instance V appeared in A2 though it was not in A1.The mathematical integration is also incorrect .stoichiometric ratios should also be taken into account in the rate equations.

Answer: There is a typo in A1 and the integration has been checked. Finally in the model all stoichiometric ratios are one.

Conclusions should be revised and rewritten.

Answer: Quantitative results were added.

Page 135: The combination should be with biological methods in first place.

Answer: It was added.

Third examiner's comments on the minor corrections

Page 51, Table 1 is meant to be Table 3.1

Answer: It was corrected.

Page 52, Figure 1 meant to be Figure 3.1

Answer: It was corrected.

Page 53, unclear sentence "the existing assumptions on mass transfer such as penetration, surface renewal and film assume that the confirmation …."Please clarify.

Answer: The explanation in the text was revised.

Page 64,in section 3.5.3,the student mentions the molecular weight of Reactive Red 198.Firstly the units need to be corrected ,9grams/mol not just grams)and secondly a reference need to be supplied .The literature suggests a value of 968.21g/mol. I am uncertain where the student arrived at a value of 608.5.It will be also useful to discuss more fully the experimental procedure of determining the amount of ozone to decolourise the dye. The calculation could be included in an appendix.

Answer: they were corrected. It was added to the appendix.

Page 84, Reference 24-25 on pages 84 are missing in the reference section .These need to be included.

Answer: They were corrected.

Equation 26 on page 86 is incorrect.

Answer: It was corrected.

Figure 4.6 0n Page 91is unclear. It is very difficult to which line corresponds to each data set. This figure needs to be presented in a better fashion.

Answer: It was changed to simpler one.

Page 93, It is mentioned that the rate constant is “significantly different from value of 0.075 quoted in Figure 4.8’.What does this refer to? - is it meant to refer to the value $0.1min^{-1}$ascertained from figure 4.6.?There seems to be no analysis of why different rate constant values have been obtained.

Answer: It was corrected in the Thesis.