Industrial Waste & Wastewater Treatment & Valorisation
21 – 23 May 2015, Athens, GREECE

The Comparative Study on Decolorization of Remazol Yellow Dye from Aqueous Solutions by Biosorption, Fenton and Photo-Fenton Processes

N. Ozbay[1], A.S. Yargic[1], M.F. Gozukizil[2], E. Onal[1]

[1] Department of Chemical and Process Engineering, Bilecik Şeyh Edebali University, Bilecik, 11210, TURKEY.

[2] Career School of Pazaryeri, Bilecik Şeyh Edebali University, Bilecik, 11800, TURKEY.

Corresponding author: seyda.guler@bilecik.edu.tr, Tel: +90 228 214 1244, Fax: +90 228 214 12 22

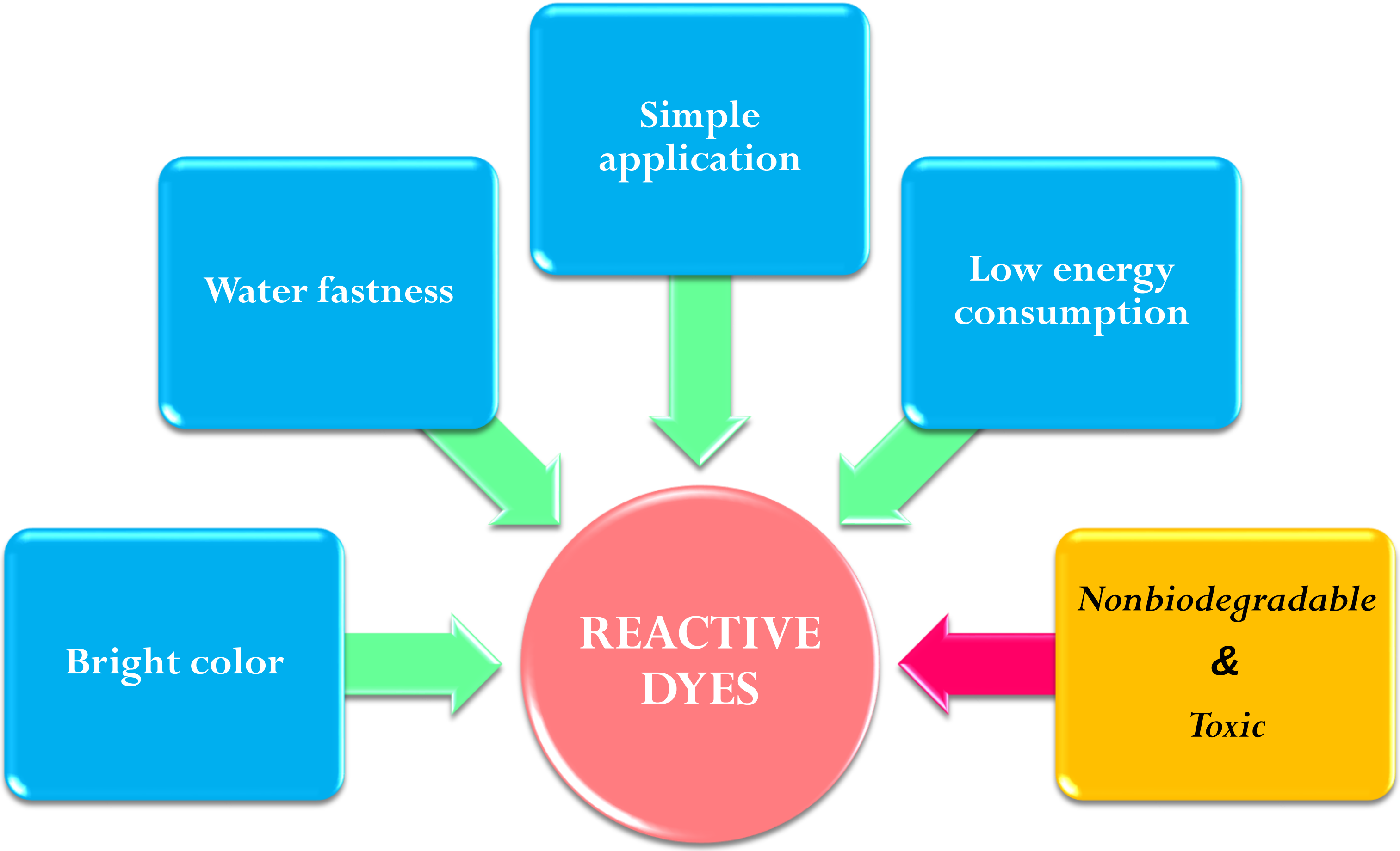
22.05.2015

CONTENTS

- MOTIVATION
- MATERIAL AND METHODS
  - ✓Preparation of SP
  - ✓Preparation of dye solutions
  - ✓Preparation of Fenton reagents
  - ✓Batch biosorption experiments
  - ✓Fenton and photo-Fenton oxidation experiments
- CHARACTERIZATION
  - ✓Ultimate and proximate analysis
  - ✓Fourier transforms infrared spectroscopy (FT-IR)
- EXPERIMENTAL RESULTS
  - **BIOSORPTION**
    - ✓Effect of
      - solution pH
      - biosorbent dosage
      - initial dye concentration
      - contact time and temperature
      - electrolytes
    - ✓Isotherm, kinetic and thermodynamic study
  - **FENTON & PHOTO-FENTON**
    - ✓Effect of
      - Fe^{+2} concentration
      - H_2O_2 concentration
      - pH
      - Natural/artificial light
    - ✓Kinetic model
- CONCLUSION

MOTIVATION

Water pollution is one of the most unwanted environmental problems in the world and a great deal of investigation is improved to eliminate effluents from wastewaters.



Physical or chemical treatment processes

- Flocculati... combined with flotation
- Elect... ...on
-
- I... ...ation
- Ozonation
- Adsorption

These techniques are generally

- ❑Inefficient in color removal
- ❑Expensive
- ❑Less compatible to a wide range of dye wastewater.

Biosorption

- •low capital investment cost
- •simplicity of design
- •ease of operation

Fenton process

- •The chemicals are readily available at moderate cost
- •There is no need for special equipment

Low cost sorbents

- Peat
- Bentonite
- Fly ash
- Silica
- Bacterial biomass
- Biopolymers
- Coir pith
- Sugar beet pulp
- Sugarcane bagasse pith

Sunflower

(Helianthus annuus L.)

- Total world production: 38 million tons

MATERIAL AND METHODS

Preparation of SP and dye solutions

SP was attained from Central Anatolia region of Turkey

Air- dried → Crushed → Sieved →

Characterized

✓Elemental analysis
✓Structure and preliminary analysis
✓FT-IR spectroscopy

- Reactive textile dye Remazol Yellow (RY) was used without further purification.
- Stock solution containing 1000 mg/L of dye was prepared and diluted to arrange different working concentrations (50-250 mg/L).

Biosorption experiments

50 mL dye solution

SP

effects of

- pH
- biosorbent dosage
- initial dye concentration
- temperature
- contact time
- electrolyte

The suspensions were filtered.

Dye concentrations in the supernatant solutions were measured by UV/Visible Spectrophotometer (V-530 Jasco UV/VIS)

$\lambda_{max} = 422$ nm

The amount of dye biosorbed per unit mass:

$$q_e = [(C_0 - C_e)V]/W$$

The dye removal efficiency:

$$\eta = [(C_0 - C_e)/C_0]100$$

where V (L) is the volume of dye solution and W (g) is the amount of the biosorbent used.

Fenton and photo-Fenton oxidation experiments

100 mL dye solution

$FeSO_4 \cdot 7H_2O$
&
H_2O_2
addition

Lovibond Jar Test

effects of
- pH
- Fe^{+2} concentration
- H_2O_2 concentration
- natural/artificial light

Dye concentrations in the supernatant solutions were measured by UV/Visible Spectrophotometer (V-530 Jasco UV/VIS)

$\lambda_{max} = 422$ nm

EXPERIMENTAL RESULTS

BIOSORBENT CHARACTERIZATION

Ultimate and proximate analysis

Ultimate Analysis of SP	
Component (%)	SP
C	52.15
N	5.19
H	7.42
O*	35.26
HHV (MJ/kg)	28.34

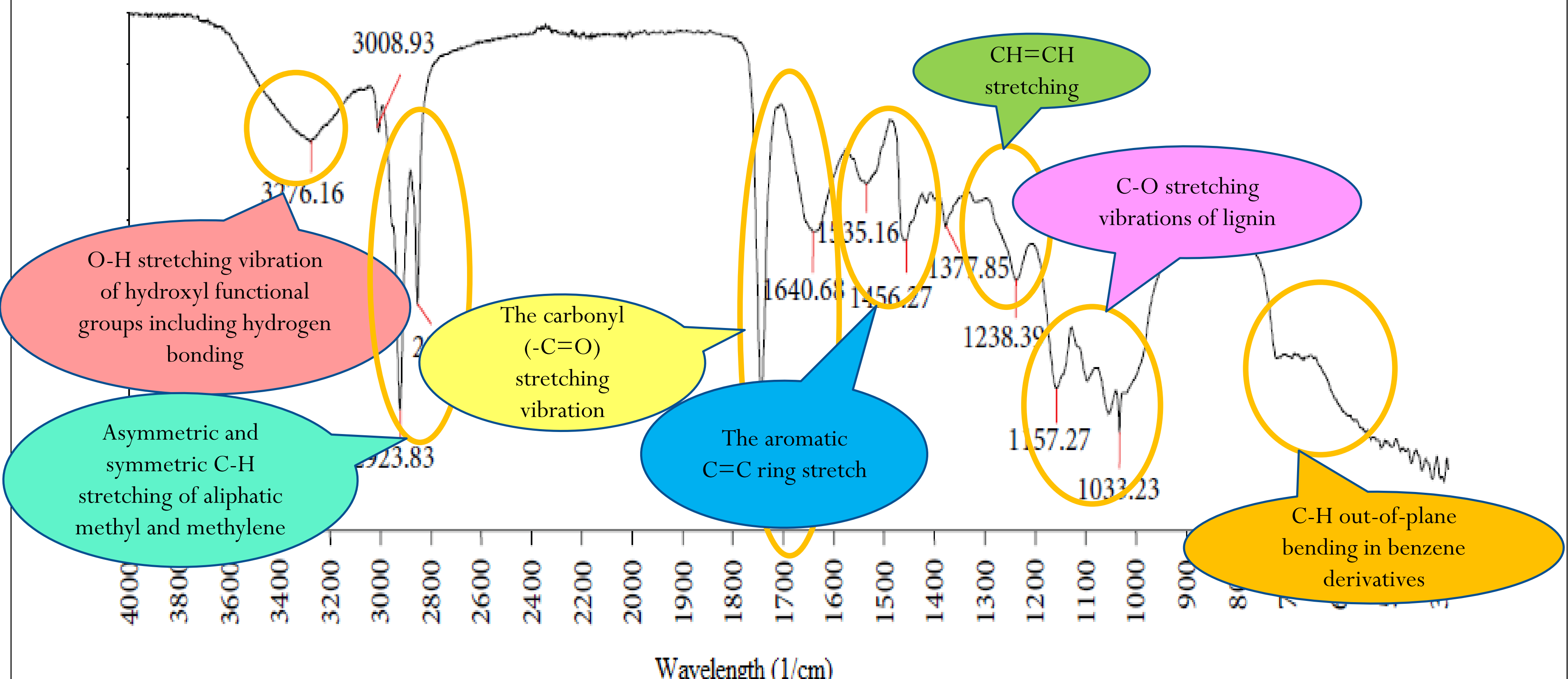
*Estimated by difference.

Elemental Analyzer (Leco CNH628 S628)

Proximate Analysis of SP	
Preliminary analysis	
Moisture	7.72
Ash	6.17
Volatile	75.15
Fixed carbon*	10.95
Structural analysis	
Holocellulose	22.90
Hemicellulose	10.92
Extractive material	23.59
Oil	30.30
Lignin	33.12
Cellulose*	12.53

*Estimated by difference.

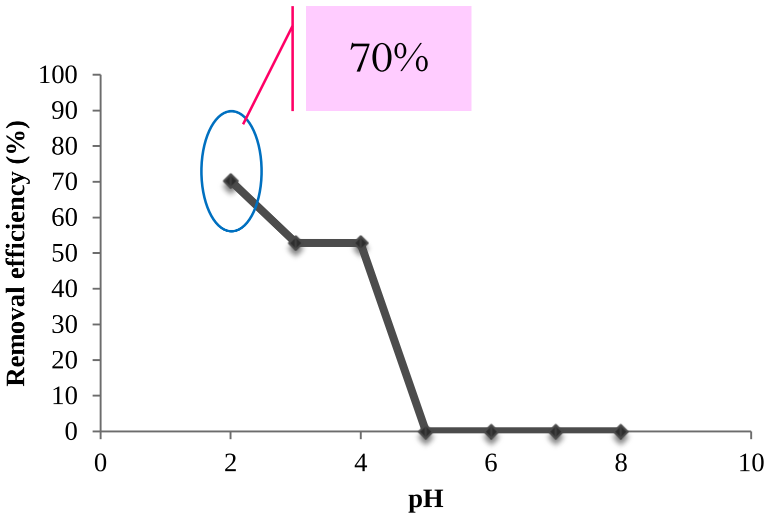
Fourier transforms infrared spectroscopy (FT-IR)



Perkin Elmer Spectrum 100

BIOSORPTION PERFORMANCE

Effect of solution pH



(initial dye concentration: 100 mg/L, contact time: 60 min, temperature: 293 K, biosorbent dosage: 0.1g/50mL dye solution)

- The pH of the dye solution influenced both ***the degree of ionization of the dye*** and ***the surface properties of the sorbent***.

pH increased → The dye removal efficiency decreased

- SP may get positively charged and the negative dye molecules will be ***electrostatically attracted*** to the surface and hence the removal efficiency is improved.

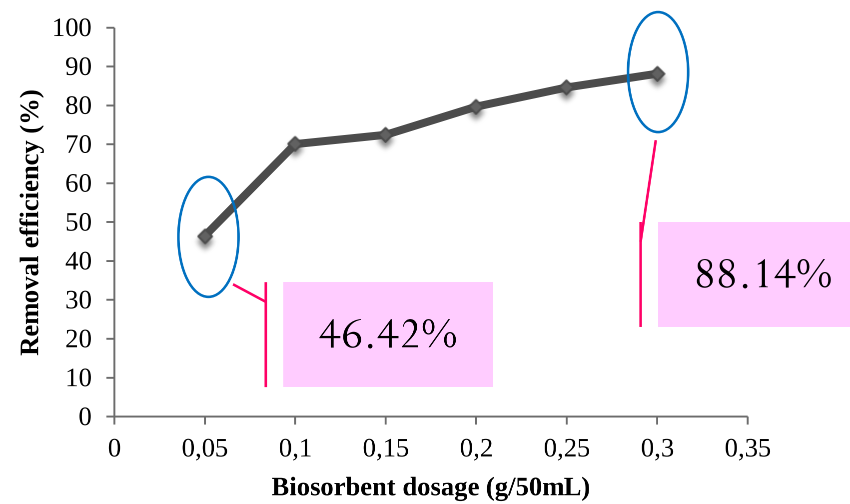
Effect of biosorbent dosage

Biosorbent dosage increased

The increase in biosorbent mass at fixed dye concentration and volume will lead to unsaturation of sorption sites through the biosorption process.

Removal efficiency (%) increased

Biosorbent surface area increased and more sorption sites occured



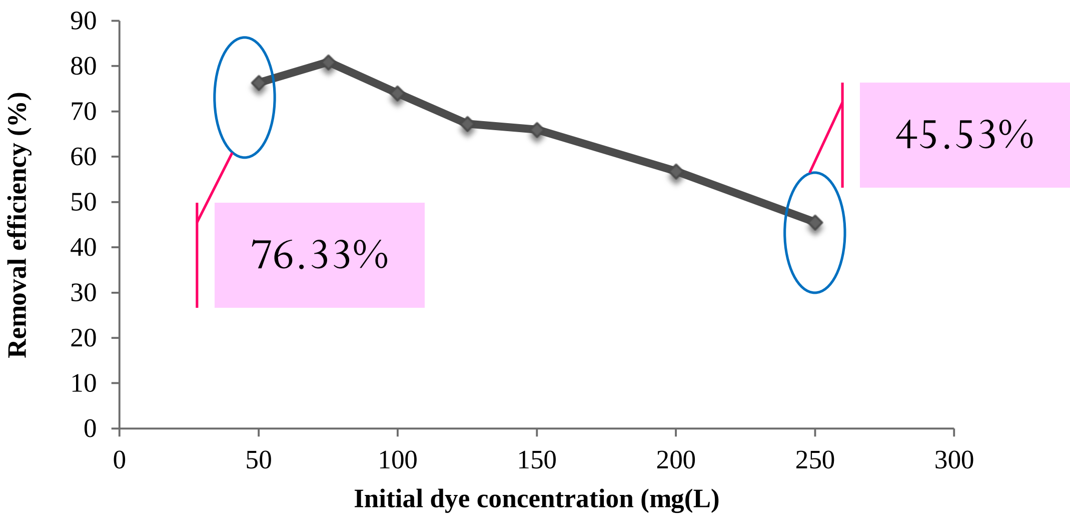
(initial dye concentration: 100mg/L, contact time: 60 min, temperature: 293 K, pH: 2)

Effect of initial dye concentration

Initial dye concentration increased

The dye removal efficiency decreased

This may be due to the saturation of surface area and active sites of sorbent.

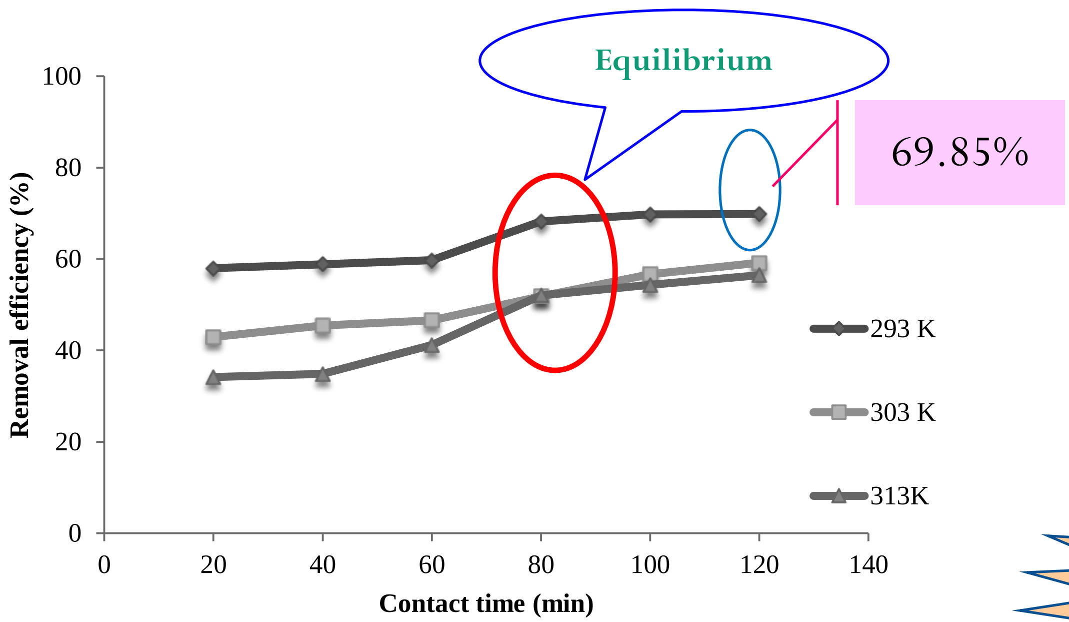


The initial dye concentration favors a **driving force to accomplish mass transfer resistances** between the solid and aqueous phases.

(biosorbent dosage: 0.1g/50mL dye solution, contact time: 60 min, temperature: 293 K, pH: 2)

Effect of contact time and temperature

- The diminishing in biosorption with temperature may be attributed to decrease in the number of active surface sites available for biosorption on sorbent, decrease in the porosity and in the total pore volume of the sorbent.

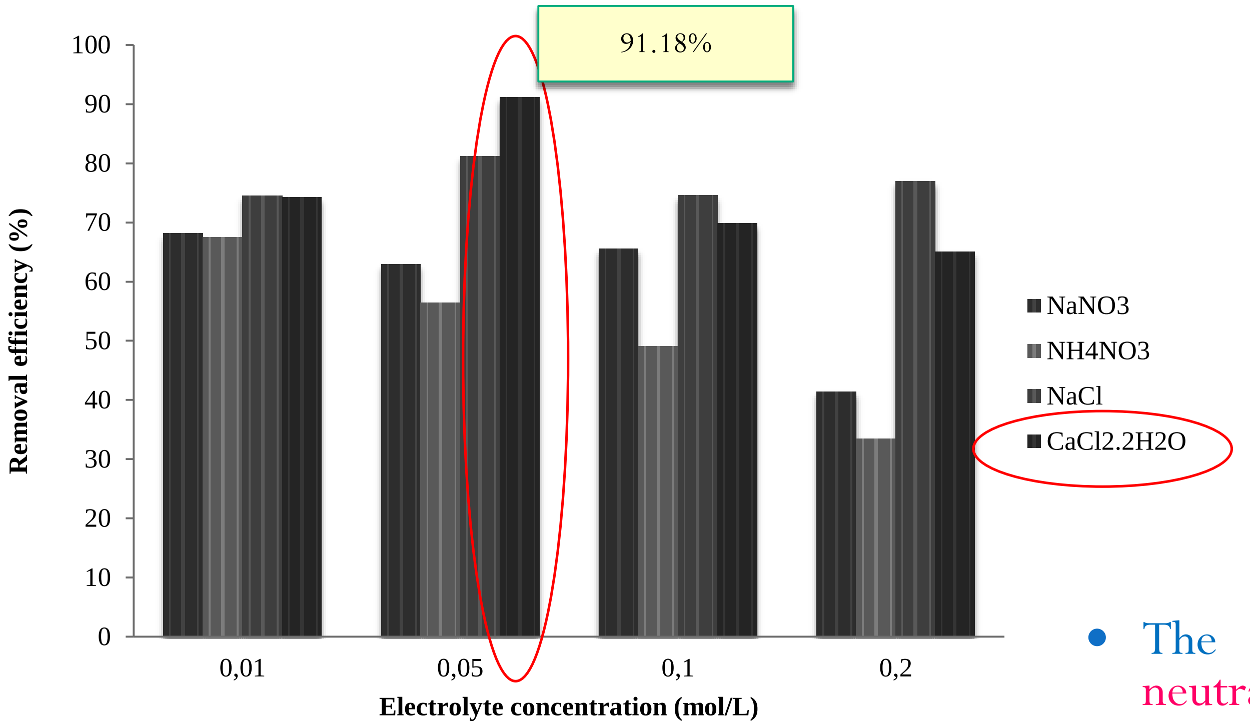


(biosorbent dosage: 0.1g/50mL, initial dye concentration: 100mg/L, pH: 2)

- It could also be due to the increase in the thickness of the boundary layer surrounding the sorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer increases.

EXOTHERMIC PROCESS

Effect of electrolytes



(biosorbent dosage: 0.1 g/50 mL, initial dye concentration: 100 mg/L, pH: 2)

- The electrolyte cations neutralize the *SP* surface's negative charge which provides biosorption of more molecules or cations to act directly on the negative adsorbate ions.

KINETIC, ISOTHERM AND THERMODYNAMIC STUDY

Isotherm models

- Interaction of adsorbate with the sorbent material is indicated by the adsorption isotherm which is important to evaluate the capacity of an sorbent.

Langmuir Isotherm			Freundlich Isotherm		
q_m (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g)	R^2
2.558	0.030	0.890	2.469	9.023	0.863

Isotherm	
Langmuir	
Freundlic[h]	

C_e: The dye ion concentration in the solution at equilibrium (mg/L)

…acity of the

…rate of

…maximum

- The Langmuir model displayed better fit to the biosorption data than the Freundlich model.

- Homogeneous biosorption patches was fulfilled by the interaction between *RY* dye and *SP* surface.

Kinetic models

All of the correlation coefficients obtained for pseudo-second order kinetic model were higher than pseudo-first order values.

RY biosorption on SP did not obey the pseudo-first order model.

- Biosorption was controlled by a chemisorption mechanism.

Kinetic Model
Pseudo-first ord
Pseudo-second (

Kinetic models

iosorbed at
der sorption
cond order

T (K)	$q_{e,exp}$ (mg/g)	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
		k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/(mg·min))	$q_{e,cal}$ (mg/g)	R^2
293	34.926	4.970	35.051	0.615	2.711	37.736	0.992
303	29.587	7.942	28.912	0.710	1.825	32.680	0.982
313	28.237	16.528	29.180	0.723	0.860	35.461	0.954

Thermodynamics

Van't Hoff Equation	$\ln K_D = \Delta S°/R - \Delta H°/RT$

T: the temperature (K)
R: the ideal gas constant (J/mol K)
K_D: the equilibrium constant (L/g)
$\Delta S°$: the entropy change (J/mol.K)
$\Delta H°$: the enthalpy change (J/mol)

T **(K)**	**$\Delta H°$ (kJ/mol)**	**$\Delta G°$ (kJ/mol)**	**$\Delta S°$ (J/mol.K)**
293		-1.92	
303	-22.25	-1.23	-69.39
313		-0.53	

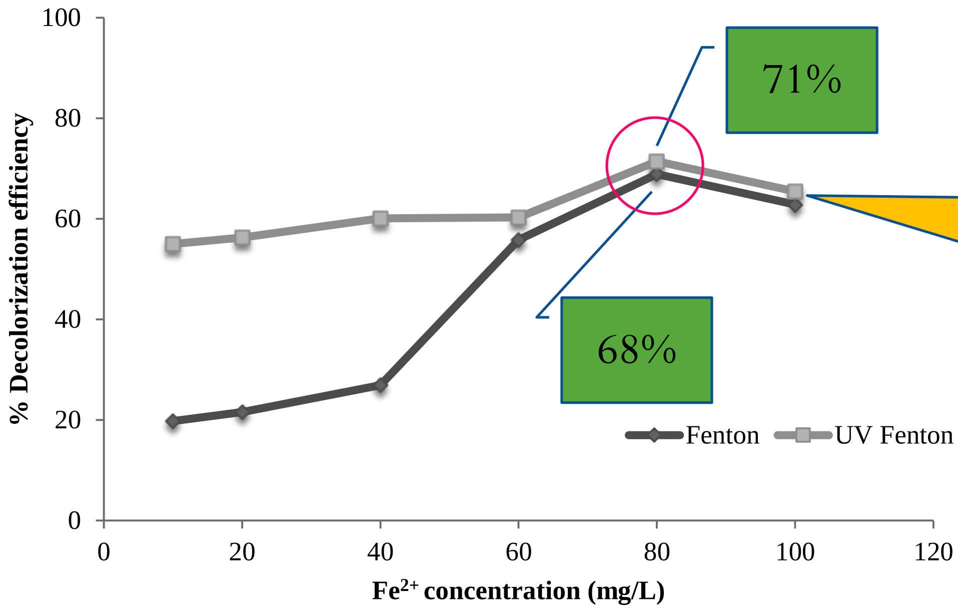
- ❑Biosorption of *RY* was enthalpy driven.
- ❑Randomness at the biosorbent/adsorbate interface decreased during process.

- ❑Biosorption rate decreased with increasing temperature.
- ❑*RY* biosorption onto *SP* was exothermic.

- ❑Thermodynamically biosorption was spontaneous.
- ❑The spontaneous nature of biosorption become greater with decreasing temperature.

FENTON AND PHOTO-FENTON PERFORMANCE

Effect of Fe^{2+} dosage



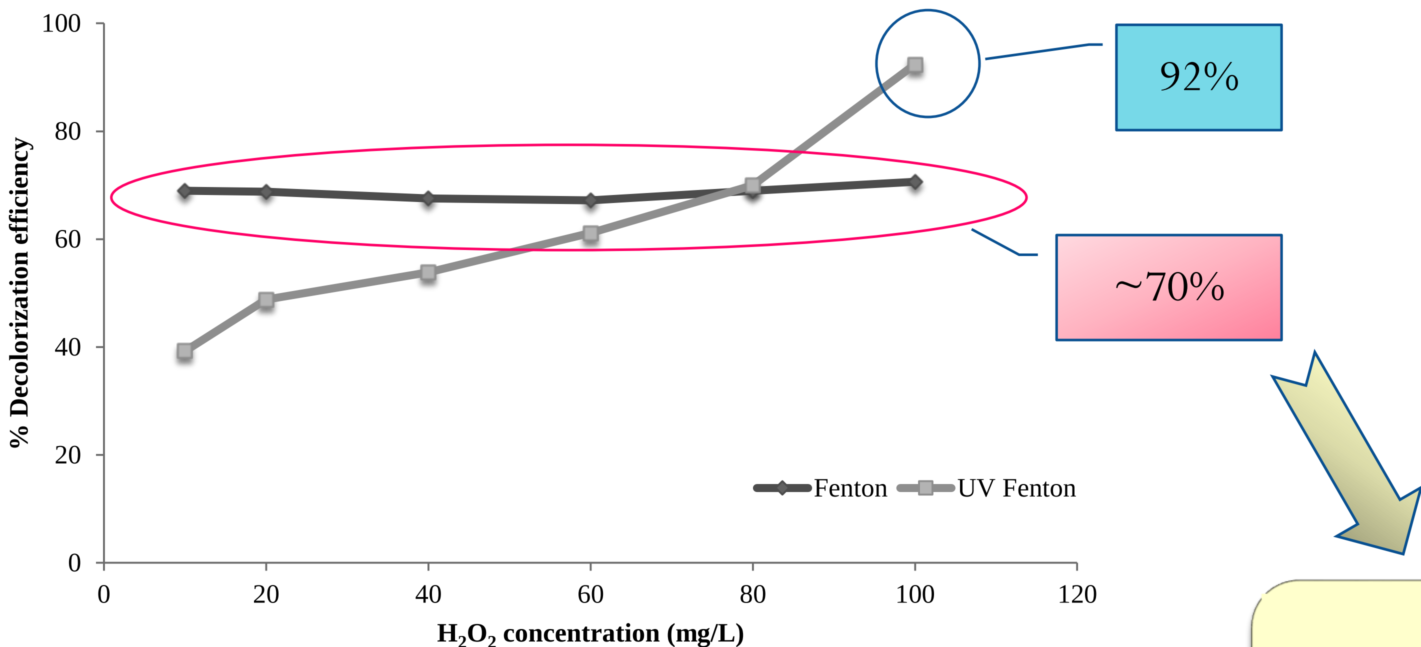
❑Red-ox reactions that •OH radicals may be scavenged either by the reaction with H_2O_2 present or with another Fe^{2+} molecule to form Fe^{3+}.

Fe^{2+} ions reacted with H_2O_2 generating more and more •OH radicals which remove the dye by degrading it into smaller molecules.

The degradation efficiency increased with a higher initial ferrous concentration.

Effect of H_2O_2 dosage

❑The concentration of •OH was expected to increase with increasing H_2O_2 dosage, leading to increased oxidation rates of organic compounds.

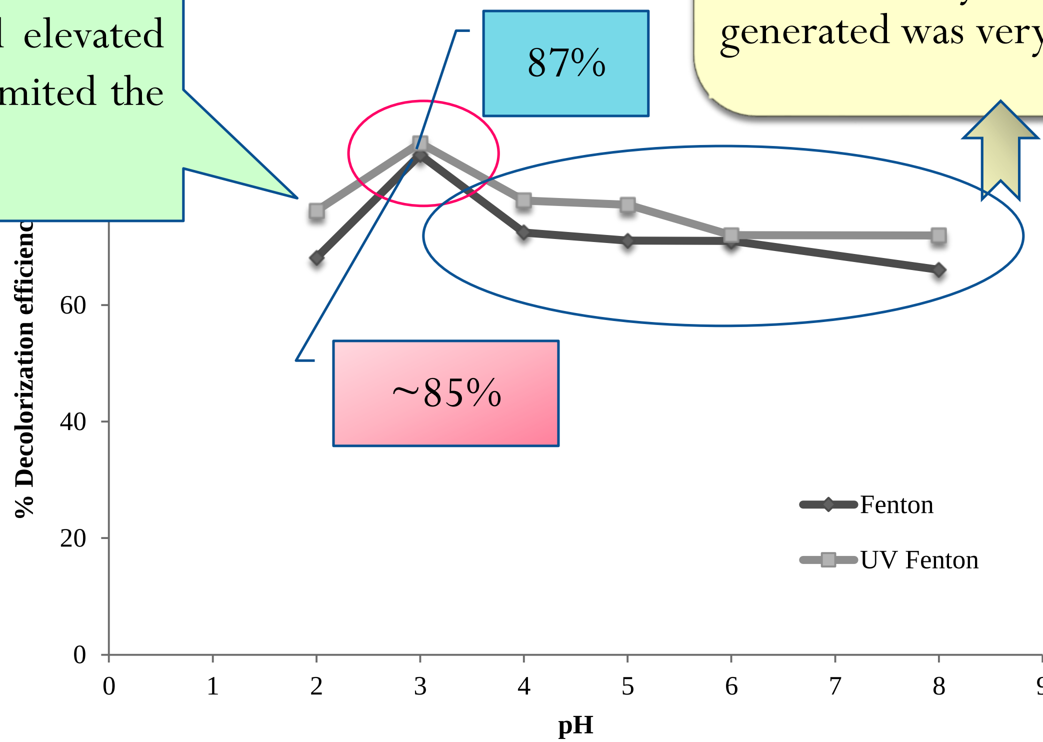


H_2O_2 alone was not effective in the removal of color.

Effect of initial pH

At lower pH values, the oxonium ion ($H_3O_2^+$) appeared and elevated the stability of H_2O_2 and limited the •OH formation.

The formation of ferrous/ferric hydroxide complexes led to the deactivation of ferrous catalyst, so the amount of hydroxyl radical (•OH) generated was very small.



❑The reaction rates of Fenton oxidation of dye were rather ***slow in alkaline medium*** while they were ***fast in acidic medium***.

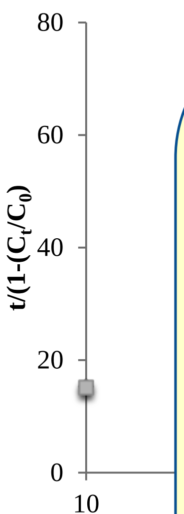
KINETIC MODEL

Kinetic model

Kinetic Model	Equation
Behnajady-Modirshahla-Ghanbery (BMG)	$C_t/C_0 = 1 - [t/(m + bt)]$ $t/[1 - (C_t/C_0)] = m + bt$

Kinetic model

b: constant relating to reaction kinetics
m: constant relating to oxidation capacity of the process



oloration

um
tion

Fento
UV-Fe

Long t value and approaching infinity → $1/b$ = the maximum oxidation capacity of Fenton process at the end of reaction.

The higher $1/m$ value → The faster initial discoloration rate of dye

CONCLUSION

- ***Sunflower pulp*** was a low cost and abundant material that could be used as an alternative biosorbent for reactive dye removal ***even at low amount***.

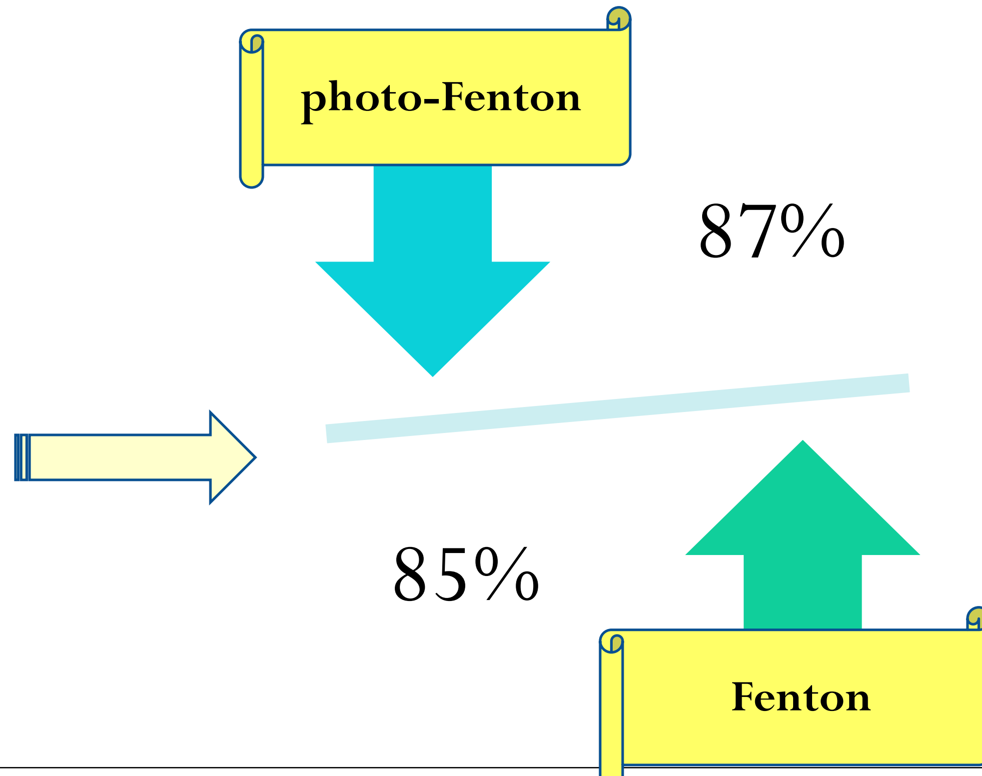
pH=2
Biosorbent dosage=0.1g/50mL solution
Initial dye concentration=100ppm
Contact time=100min,
Temperature=293 K,
Electrolyte=0.05M $CaCl_2 \cdot 2H_2O$

→ **91.18%**

CONCLUSION

- Experimental results verify that all of the methods including ***biosorption by sunflower pulp, Fenton and photo-Fenton processes*** can be used to treat water discharge containing dye such as **Remazol Yellow** with higher degradation efficiency, when convenient conditions are carried out.

Fe^{2+} concentration= 80 mg/L
H_2O_2 concentration= 100 mg/L
pH = 3



References

[1] Bingol, D., Tekin, N., Alkan, M.: Brilliant Yellow dye adsorption onto sepiolite using a full factorial design. Appl. Clay Sci. 50, 315–321 (2010).
[2] He, Y., Gao, J.F., Feng, F.Q., Liu, C., Peng, Y.Z., Wang, S.Y.: The comparative study on the rapid decolorization of azo, anthraquinone and triphenylmethane dyes by zero-valent iron. Chem. Eng. J. 179, 8–18 (2012).
[3] Nawi, M.A., Sabar, S., Jawad, A.H., Sheilatina, Wan Ngah, W.S.: Adsorption of Reactive Red 4 by immobilized chitosan on glass plates: Towards the design of immobilized TiO_2–chitosan synergistic photocatalyst-adsorption bilayer system. Biochem. Eng. J. 49, 317–325 (2010).
[4] Yola, M.L., Eren, T., Atar, N., Wang, S.: Adsorptive and photocatalytic removal of reactive dyes by silver nanoparticle-colemanite ore waste. Chem. Eng. J. 242, 333–340(2014).
[5] Ahmad, M.A., Rahman, N.K.: Equilibrium, kinetics and thermodynamic of Remazol Brilliant Orange 3R dye adsorption on coffee husk-based activated carbon. Chem. Eng. J. 170, 154–161 (2011).
[6] Safa, Y., Bhatti, H.N.: Adsorptive removal of direct textile dyes by low cost agricultural waste: Application of factorial design analysis. Chem. Eng. J. 167, 35–41 (2011).
[7] Yargic, A.S., ,Yarbay Sahin, R.Z., Ozbay, N., Onal, E.: The Effect of Different Operating Conditions on Removal of Reactive Dye by Green Carbon Adsorption. JOSUNAS. 498–510 (2013).
[8] Lucas, M.S., Peres, J.A.: Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation. Dyes Pigments. 71, 236–244 (2006).
[9] Özbay, N., Yargıç, A.Ş., Yarbay-Şahin, R.Z., Önal, E.: Full factorial experimental design analysis of reactive dye removal by carbon adsorption. J. Chem. 2013, 1–13 (2013).
[10] Santos, S.C., Vilar, V.J., Boaventura, R.A.: Waste metal hydroxide sludge as adsorbent for a reactive dye. J. Hazard. Mater. 153(3), 999–1008 (2008).
[11] Geethakarthi, A., Phanikumar, B.R.: Adsorption of reactive dyes from aqueous solutions by tannery sludge developed activated carbon: Kinetic and equilibrium studies. *Int. J. Environ. Sci. Tech.* 8(3), 561–570 (2011).
[12] Yargıç, A.Ş., Yarbay Şahin, R.Z., Özbay, N., Önal, E.: Assessment of toxic copper (II) biosorption from aqueous solution by chemically-treated tomato waste. J. Clean. Prod. 88, 152–159 (2015).
[13] Javadian, H., Ghaemy, M., Taghavi, M.: Adsorption kinetics, isotherm, and thermodynamics of Hg^{2+} to polyaniline/hexagonal mesoporous silica nanocomposite in water/wastewater. J. Mater. Sci. 49(1), 232–242 (2014).
[14] Fu, F., Wang, Q., Tang, B.: Effective degradation of C.I. Acid Red 73 by advanced Fenton process. J. Hazard. Mater. 174, 17–22 (2010).
[15] Lucas, M.S., Peres, J.A.: Degradation of Reactive Black 5 by Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes. Dyes Pigments. 74, 622–629 (2007).
[16] Kang, S.F., Liao, C.H., Chen, M.C.: Pre-oxidation and coagulation of textile wastewater by the Fenton process. Chemosphere. 46, 923–928 (2002).
[17] Ramirez, J.H., Duarte, F.M., Martins, F.G., Costa, C.A., Madeira, L.M.: Modelling of the synthetic dye Orange II degradation using Fenton's reagent: From batch to continuous reactor operation. Chem. Eng. J. 148, 394–404 (2009).
[18] Sun, S.P., Li, C.J., Sun, J.H., Shi, S.H., Fan, M.H., Zhou, Q.: Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: Effect of system parameters and kinetic study. J. Hazard. Mater. 161, 1052–1057 (2009).
[19] Ertugay, N., Acar, F.N.: Removal of COD and color from Direct Blue 71 azo dye wastewater by Fenton's oxidation: Kinetic study. Arabian J. Chem. Article in press. (2013).
[20] Xu, H.Y., Shi, T.N., Wu, L.C., Qi, S.Y.: Discoloration of Methyl Orange in the Presence of Schorl and H_2O_2: Kinetics and Mechanism. Water, Air, Soil Pollut. 224(10), 1–11 (2013).

Thank you for your attention…