REMTECH EXPO
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Session 14:
Effluents and wastewaters:
Challenges in managing odors and micropollutants

Synergetic Effect on gamma radiolytic degradation of micropollutants by addition of H_2O_2 towards radical based study

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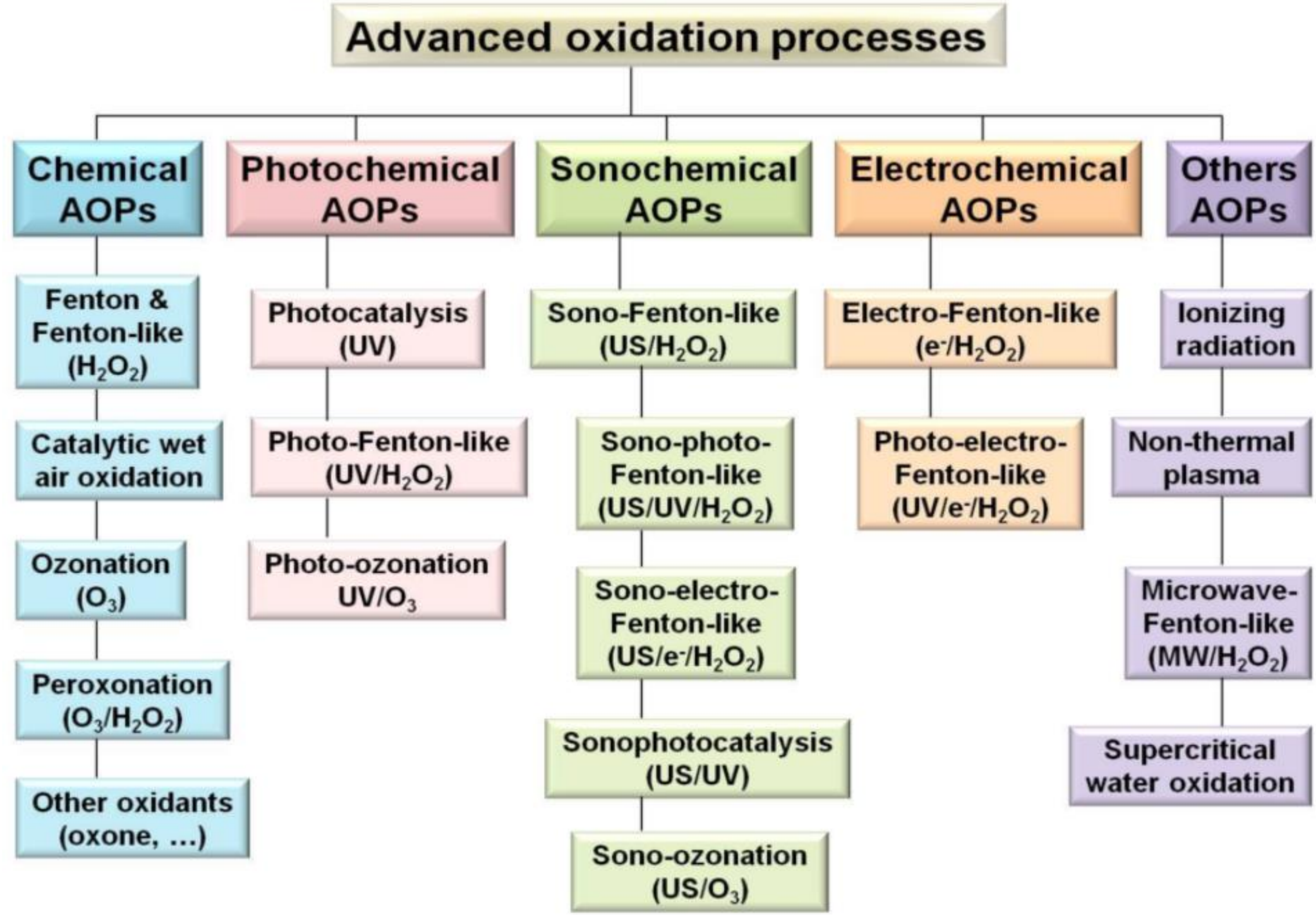

Sabine et al, Catalysts 2018, 8(10), 483

Sources used in gamma irradiation

Parameters	Cobalt-60	Caesium-137
Power Output (W/Ci)	3.35 x 10^{-3}	9.48 x 10^{-3}
Photon Energy (MeV)	1.33 & 1.17	0.66
Half Life	5.25	30.2
Chemical form	Sintered metal	$CsCl_2$
Water Solubility	Insoluble	Soluble
Nature of activity	^{60}Co decays by emitting a beta particle to the stable isotope nickel-60 (^{60}Ni). The activated nickel nucleus emits two gamma rays with energies of 1.17 and 1.33 MeV.	^{137}Cs decays by emitting high-energy beta decay to an excited nuclear isomer of ^{137}Ba, which in turn undergoes gamma decay with a half-life of about 150 seconds. The energy of the gamma decay is 0.66 MeV

Radiolytic Chemistry

The initial events in the radiolysis of water involves two step reaction,

(i) the direct ionization leads to the formation of water in its radical form and a free excited electron,

(ii) the transfer of energy excites the water molecule,

$$H_2O \xrightarrow{\gamma} H_2O^{\cdot +} + e^-$$

$$H_2O \xrightarrow{\gamma} H_2O^*$$

The above three species reacts with each other and other molecules to produce secondary species. It involves four important reactions,

(i) through dipolar interactions, water reacts with electrons and become solvated electron

(ii) interaction of electron with hydrogen to produce hydrogen radical,

(iii) dissociation of radical water to hydrogen ion and hydroxyl radical,

(iv) dissociation of excited water molecule to hydroxyl and hydrogen radicals.

$$e^- + H_2O \rightarrow e^-_{aq}$$

$$e^- + H^+ \rightarrow H^{\cdot}$$

$$H_2O^{\cdot +} \rightarrow H^+ + HO^{\cdot}$$

$$H_2O^* \rightarrow HO^{\cdot} + H^{\cdot}$$

The radiolysis of water leads to the generation of radicals as shown in the equation,

$$H_2O \rightarrow e^-_{aq} + H^\cdot + OH^\cdot + H_2 + H_2O_2 + H_3O^+$$

$$OH^\cdot + Dye \rightarrow Mineralisation$$

Species	Oxidation Potential (V)
Fluorine	3.03
Hydroxyl radical	**2.80**
Hydrogen Peroxide	1.78
Permanganate	1.68
Hypochlorous acid	1.49

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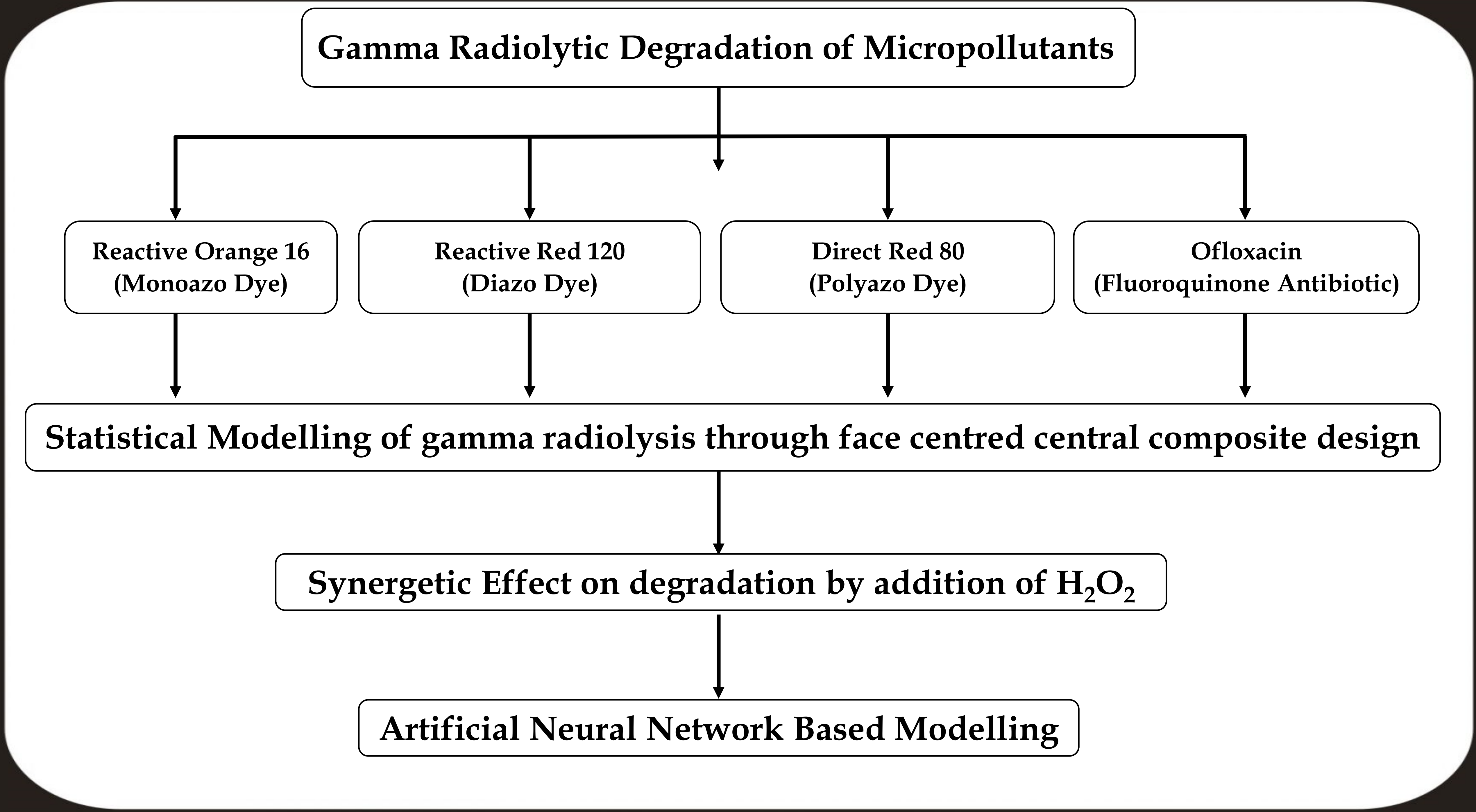
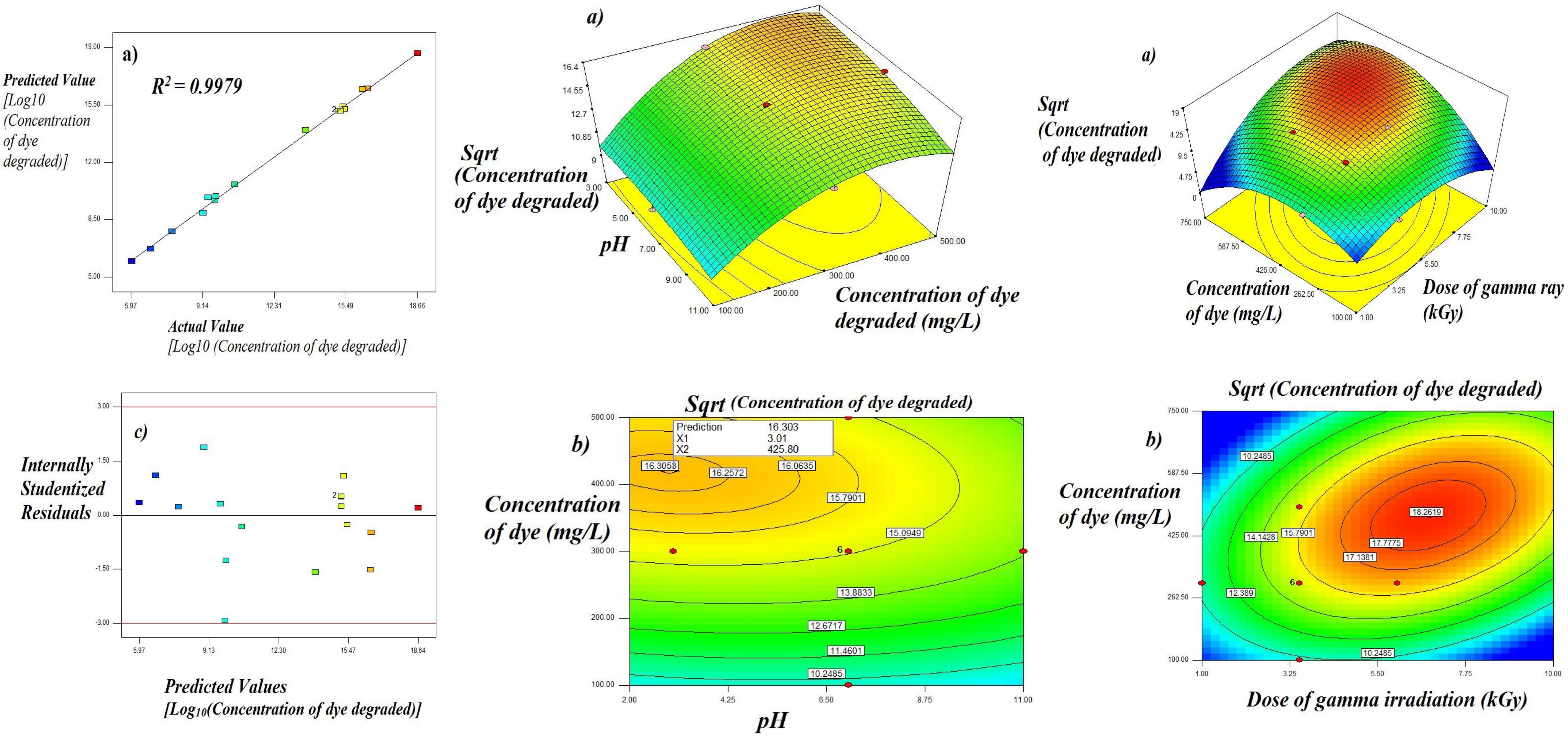

Gamma Radiolytic Degradation of Micropollutants
Reactive Orange 16 (Monoazo Dye)
Reactive Red 120 (Diazo Dye)
Direct Red 80 (Polyazo Dye)
Ofloxacin (Fluoroquinone Antibiotic)
Statistical Modelling of gamma radiolysis through face centred central composite design
Synergetic Effect on degradation by addition of H_2O_2
Artificial Neural Network Based Modelling

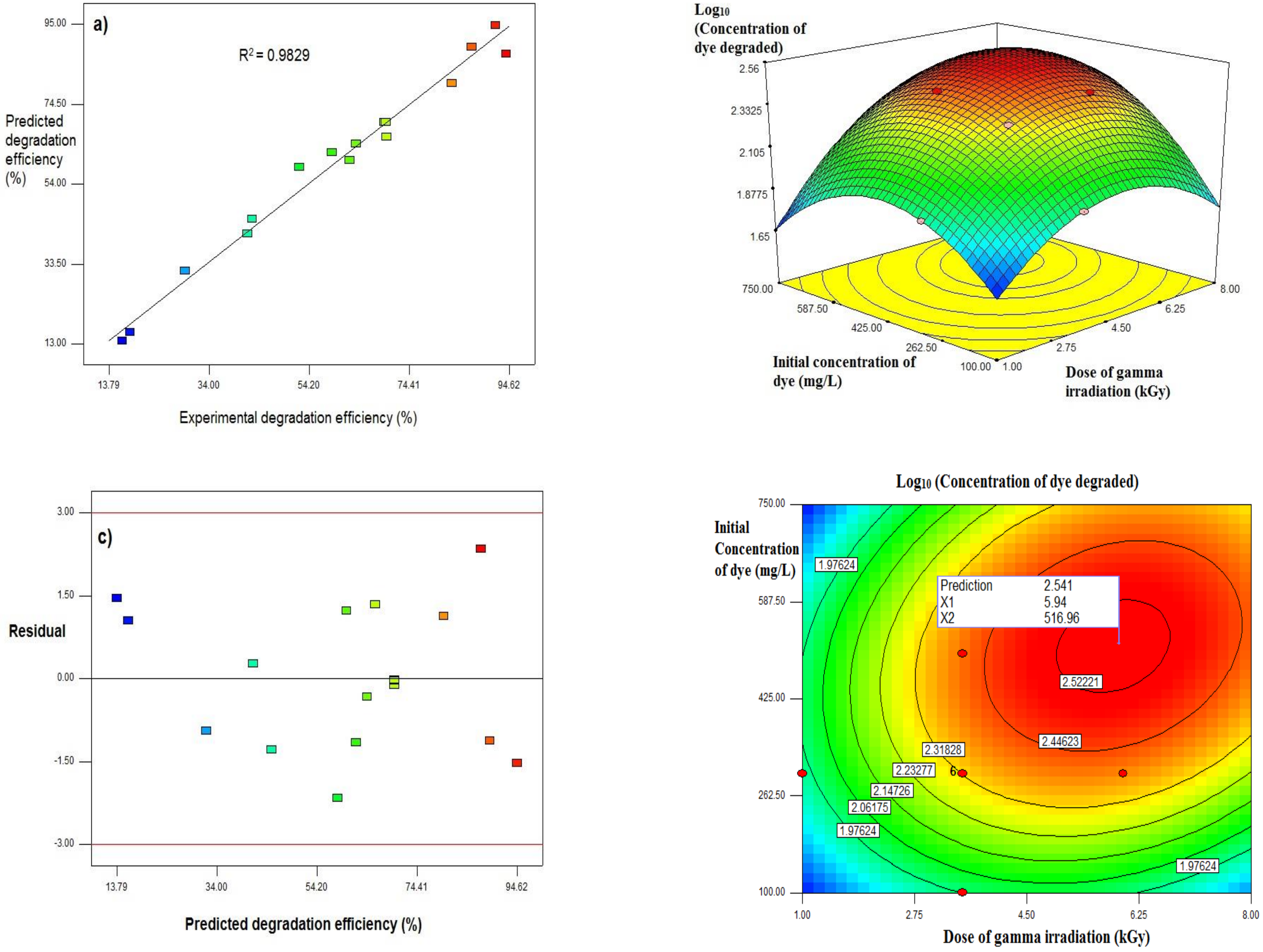
Degradation of Azo dyes

Design Summary - Face Centered Central Composite Design

Response Surface: Face Centered Central Composite Design							
				20 Runs		No Blocks	
Factor	**Name**	**Units**	**Type**	**Low Actual**	**High Actual**	**Mean**	**Std. dev.**
A	pH	-	Numeric	3	11	7	2.828
B	Dose of gamma Ray	kGy	Numeric	1	6	3.5	1.768
C	Conc. Of Dye	mg/L	Numeric	100	500	300	141.421
C	Conc. Of Ofx	mM	Numeric	0.1	1	0.5	0.16
Response	**Name**	**Units**		**Min.**	**Max.**	**Ratio**	**Model**
Y_1	Concentration of RO16 Dye Degraded	mg/L		36.120	348.300	9.643	Sq.Rt -Quadratic
Y_2	Concentration of RR120 Dye Degraded	mg/L		41.780	318.350	7.620	$Base_{10}log$ Quadratic
Y_3	Concentration of DR80 Dye Degraded	mg/L		54.690	359.150	6.567	$Base_{10}log$ Quadratic
Y_4	Conc. of Ofx degraded	mM		0.2	0.84	0.22	$Base_{10}log$ Quadratic

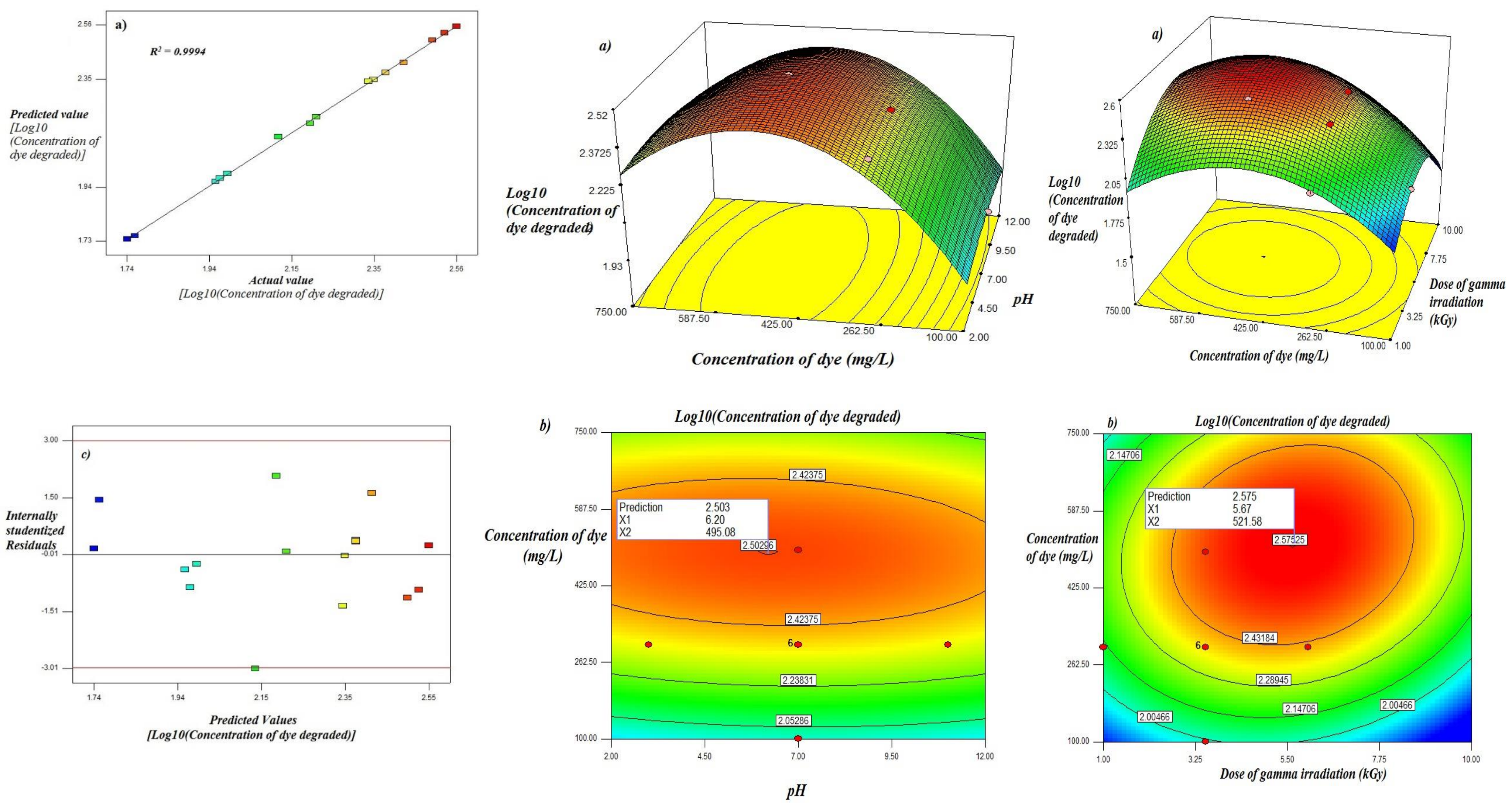


A plot of the actual vs predicted degradation and residual plots. The response surface plot (a) and the contour plot (b) of the degradation of RO-16 as the function of pH and concentration of dye (mg/L). Dose of γ- irradiation = 3.5kGy



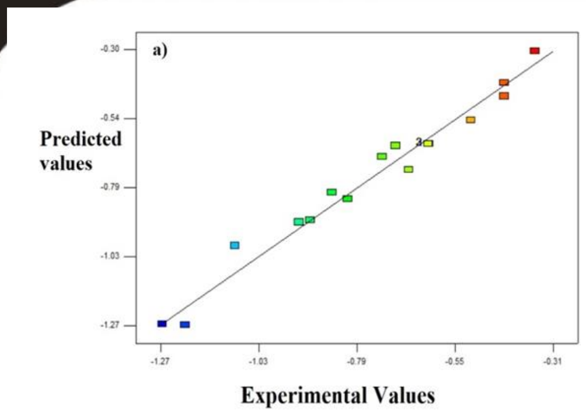
Padmanaban et al.
Water Science and Technology 73, no. 12 (2016): 3041-3048.

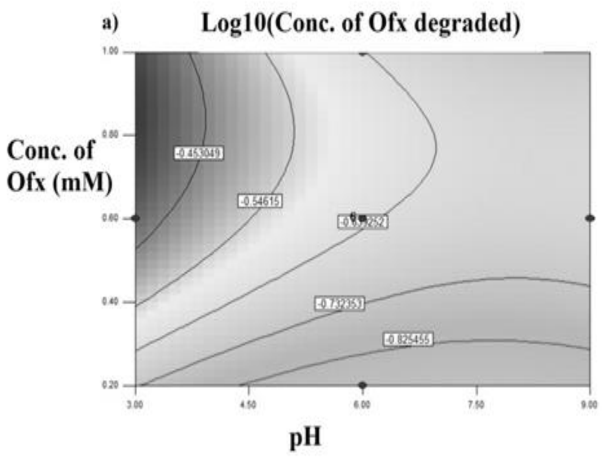
A plot of the actual vs predicted degradation and residual plots. The response surface plot (a) and the contour plot (b) of the degradation of RR-120 as the function of pH and concentration of dye (mg/L). Dose of γ- irradiation = 3.5kGy

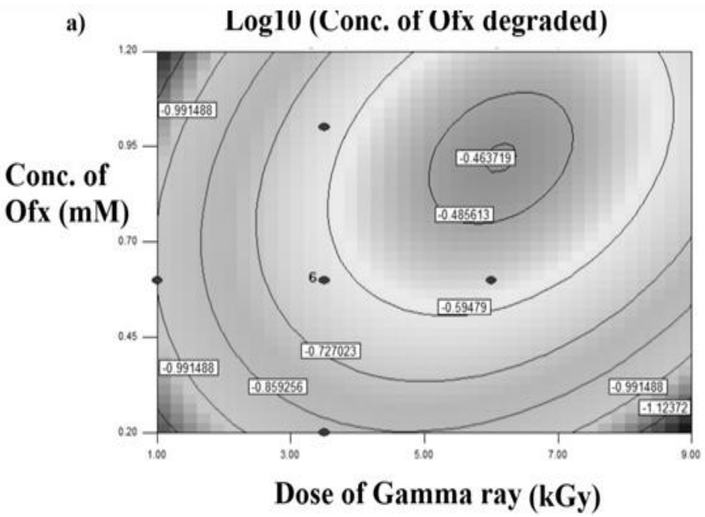


Padmanaban et al Reaction Kinetics, Mechanisms and Catalysis 125, no. 1 (2018): 433-447.

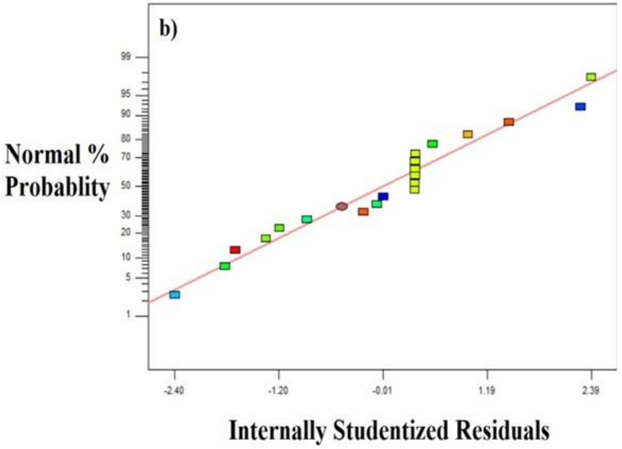
A plot of the actual vs predicted degradation and residual plots. The response surface plot (a) and the contour plot (b) of the degradation of DR 80 as the function of pH and concentration of dye (mg/L). Dose of γ- irradiation = 3.5kGy

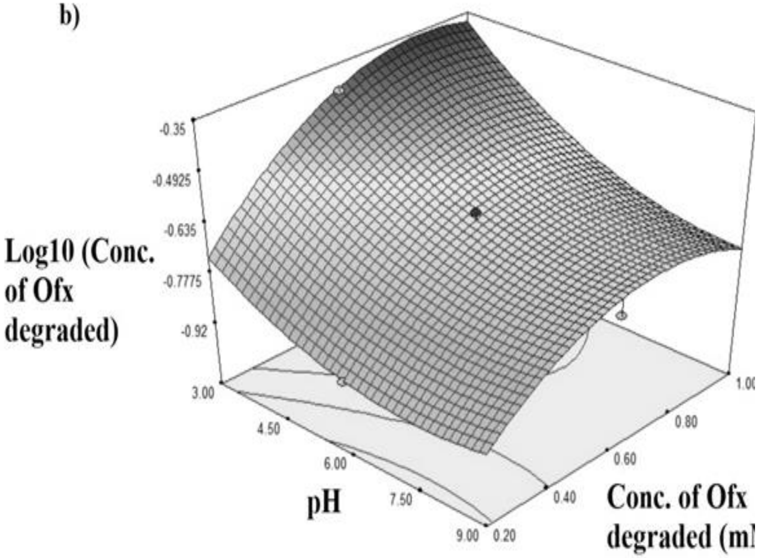


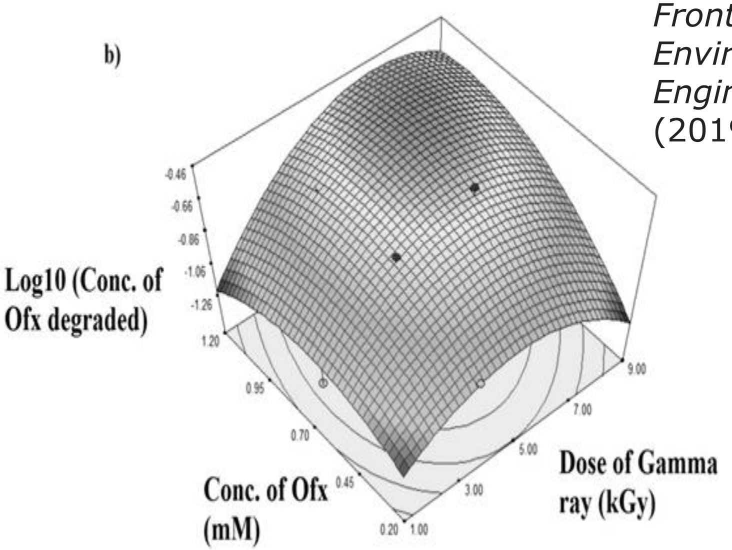




GS Muthu Iswarya et al, *Frontiers of Environmental Science & Engineering* 13, no. 3 (2019): 42.







A plot of the actual vs predicted degradation and residual plots. The response surface plot (a) and the contour plot (b) of the degradation of Ofx as the function of pH and concentration of Ofx (mM). Dose of γ- irradiation = 3.5kGy

Optimized numerical solutions for the maximum degradation (500mg/L) of Textile dyes & 1mM of Ofloxacin using the developed model

Sl.No	**Type of dye**	**pH**	**Dose of γ- irradiation (kGy)**	**Concentration of dye degraded in Transformed Scale**	**Predicted Conc. Of dye degraded (mg/L)**	**Experimental Conc. Of dye degraded (mg/L)**
1	Reactive Orange - 16 **(RO - 16)**	6.00	4.00	Sqrt (16.302)	279.861	282.34
2	Reactive Red – 120 **(RR - 120)**	7.02	5.93	Log_{10} (2.539)	347.509	349.12
3	Direct Red – 80 **(DR - 80)**	6.64	3.29	Log_{10} (2.5177)	329.5	314.15
4	**Ofloxacin (Ofx)**	3.00	2.09	Log_{10} (-0.535)	0.292	0.281

Synergetic Effect on degradation of dye by addition of H_2O_2

$$H_2O \rightarrow (0.27)e^-_{aq} + (0.06)H^{\cdot} + (0.27)OH^{\cdot} + (0.04)H_2 + (0.07)H_2O_2 + (0.27)H_3O^+$$

The **G value** is referred as the number of molecules of reactant consumed or product formed per 100 eV of energy absorbed.
The energy efficiency of dye degradation during ionizing radiation in terms of G value is calculated by,

$$G = 6.023 * 10^{23} * \frac{\Delta R_D}{D} * 6.24 * 10^{19}$$

where,

ΔR_D is the changed amount of the compound (mol/L);
D is the absorbed dose (kGy);
$6.24*10^{19}$ is a conversion constant for kGy to 100eV/L;
$6.023*10^{23}$ is the Avogadro constant.

$$H_2O \rightarrow (0.27)e_{aq}^{-} + (0.06)H^{\cdot} + (0.27)OH^{\cdot} + (0.04)H_2 + (0.07)H_2O_2 + (0.27)\ H_3O^{+}$$

Reducing species (e_{aq}^{-} & $H^{\cdot}$) can be converted into Oxidizing species($OH^{\cdot}$) by the addition of H_2O_2

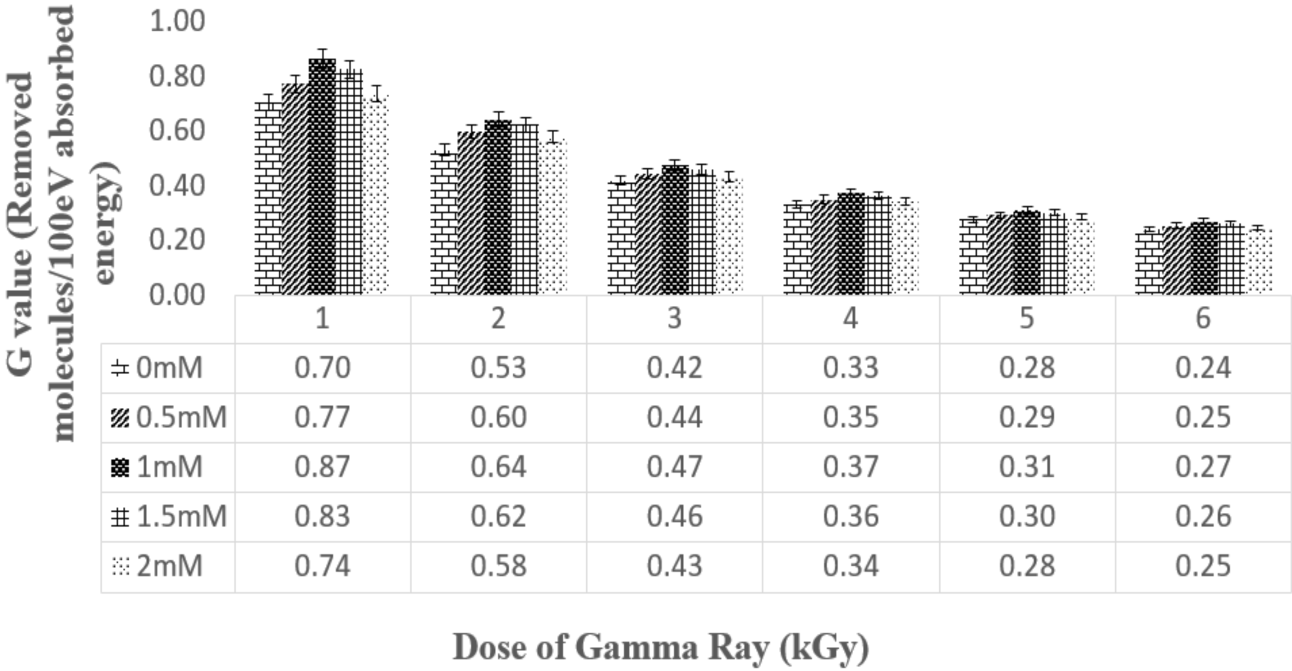
$$H_2O_2 + e_{aq}^{-} \rightarrow OH^{-} + OH^{\cdot}$$

$$H_2O_2 + H^{\cdot} \rightarrow H_2O + OH^{\cdot}$$

Synergetic Effect on degradation of pollutant by addition of H_2O_2

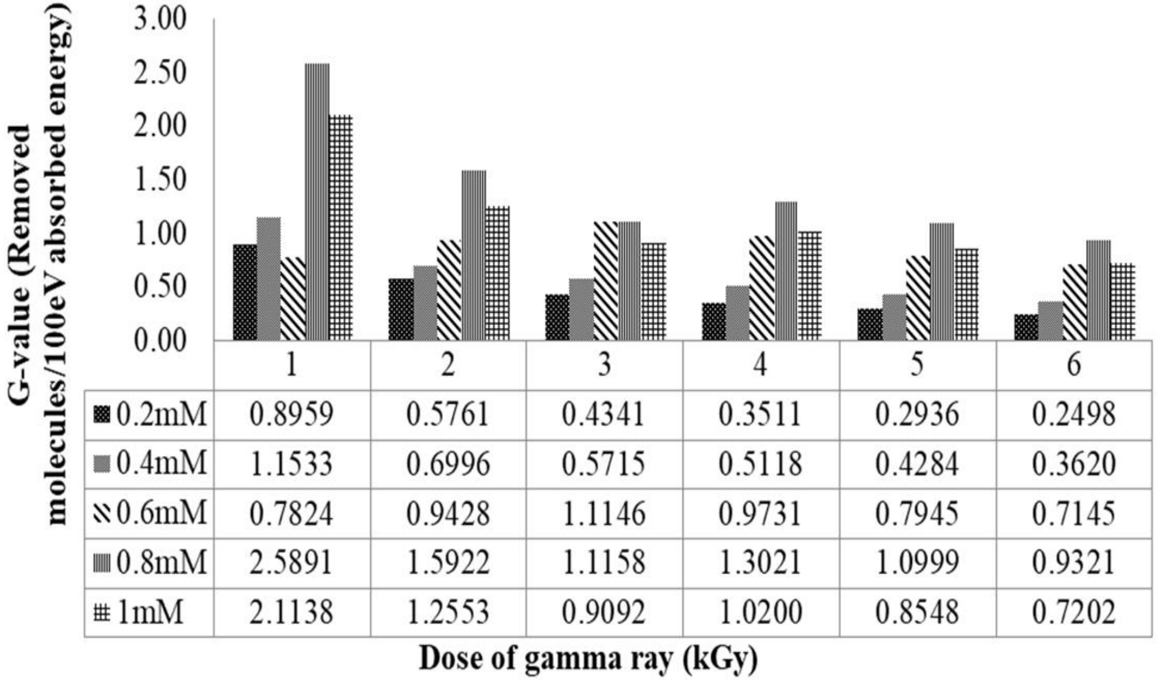
Reaction Conditions:

Initial dye concentration: 250mg/L & 1mM;
Dose rate: 2.5kGy/h; pH: 6.6)
Various Dose of gamma ray & Concentration of H_2O_2



	1	2	3	4	5	6
0mM	0.70	0.53	0.42	0.33	0.28	0.24
0.5mM	0.77	0.60	0.44	0.35	0.29	0.25
1mM	0.87	0.64	0.47	0.37	0.31	0.27
1.5mM	0.83	0.62	0.46	0.36	0.30	0.26
2mM	0.74	0.58	0.43	0.34	0.28	0.25

Direct Red 80



	1	2	3	4	5	6
0.2mM	0.8959	0.5761	0.4341	0.3511	0.2936	0.2498
0.4mM	1.1533	0.6996	0.5715	0.5118	0.4284	0.3620
0.6mM	0.7824	0.9428	1.1146	0.9731	0.7945	0.7145
0.8mM	2.5891	1.5922	1.1158	1.3021	1.0999	0.9321
1mM	2.1138	1.2553	0.9092	1.0200	0.8548	0.7202

Ofloxacin

Comparison of kinetic parameters for the removal of different recalcitrant at various concentrations of H_2O_2

Type of recalcitrant	Initial H_2O_2 Concentration (mM)	Dose constant, d (kGy^{-1})	Conc. Removed (kGy^{-1})	Ref.
p - Nitro Phenol (PNP) Conc: 50mg/L Dose rate: 185Gy/min	0.5	0.4332	21.66 mg/L	Yu S, Hu J, Wang J (2017)
	1.17	0.5725	28.625 mg/L	
	2.35	0.702	35.1 mg/L	
Sulfamethazine Conc: 20mg/L; Dose rate: 339Gy/min	0.294	0.0036	0.072 mg/L	Liu Y, Wang J (2019)
	0.882	0.0045	0.09 mg/L	
Direct Red 80 Conc: 250mg/L Dose rate: 2.5kGy/h (41.66Gy/min)	0	0.4022	100.55 mg/L	Current study
	0.5	0.4659	116.47 mg/L	
	1	0.6347	158.67 mg/L	
	1.5	0.5402	135.0 mg/L	
	2	0.4273	106.82 mg/L	
Ofloxacin Conc. of Ofx = 1mM (361.6mg/L). Dose rate: 1.72kGy/h (28.66Gy/min)	0	0.1157	0.1157 mM	
	0.5	0.1594	0.1594 mM	
	1	0.1985	0.1985 mM	
	1.5	0.232	0.232 mM.	
	2	0.1568	0.1568 mM	

Artificial Neural Network Based Modelling: Parameters

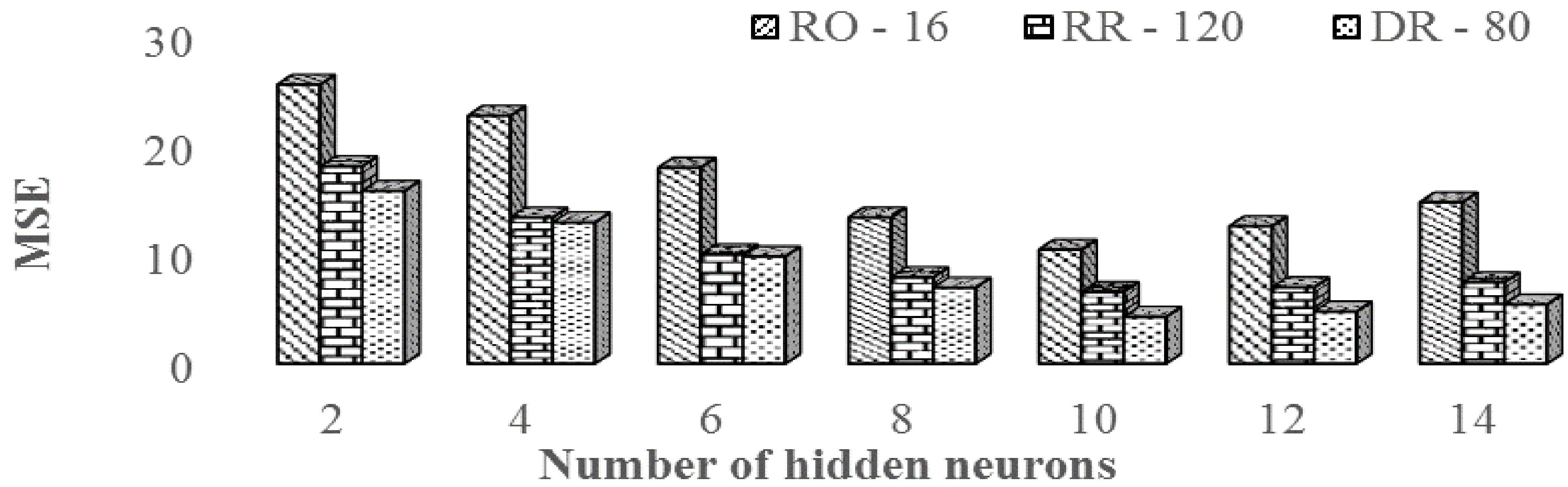
Layers	Parameters	Conditions
Input	Concentration of H_2O_2 (mM)	0 (control) 0.5 – 2.0
	Dose of gamma ray (kGy)	1,2,3,4,5,6
	pH	3.0, 5.0, 7.0, 9.0 11.0
	Concentration of dye (mg/L)	100 - 500
Output	**Response**	**% of degradation**
	Test & Validation	pH: 6.0 & 12.0

Three layer feed-forward network was trained using Levenberg - Marquardt back propagation algorithm with ten neurons in the hidden layer.

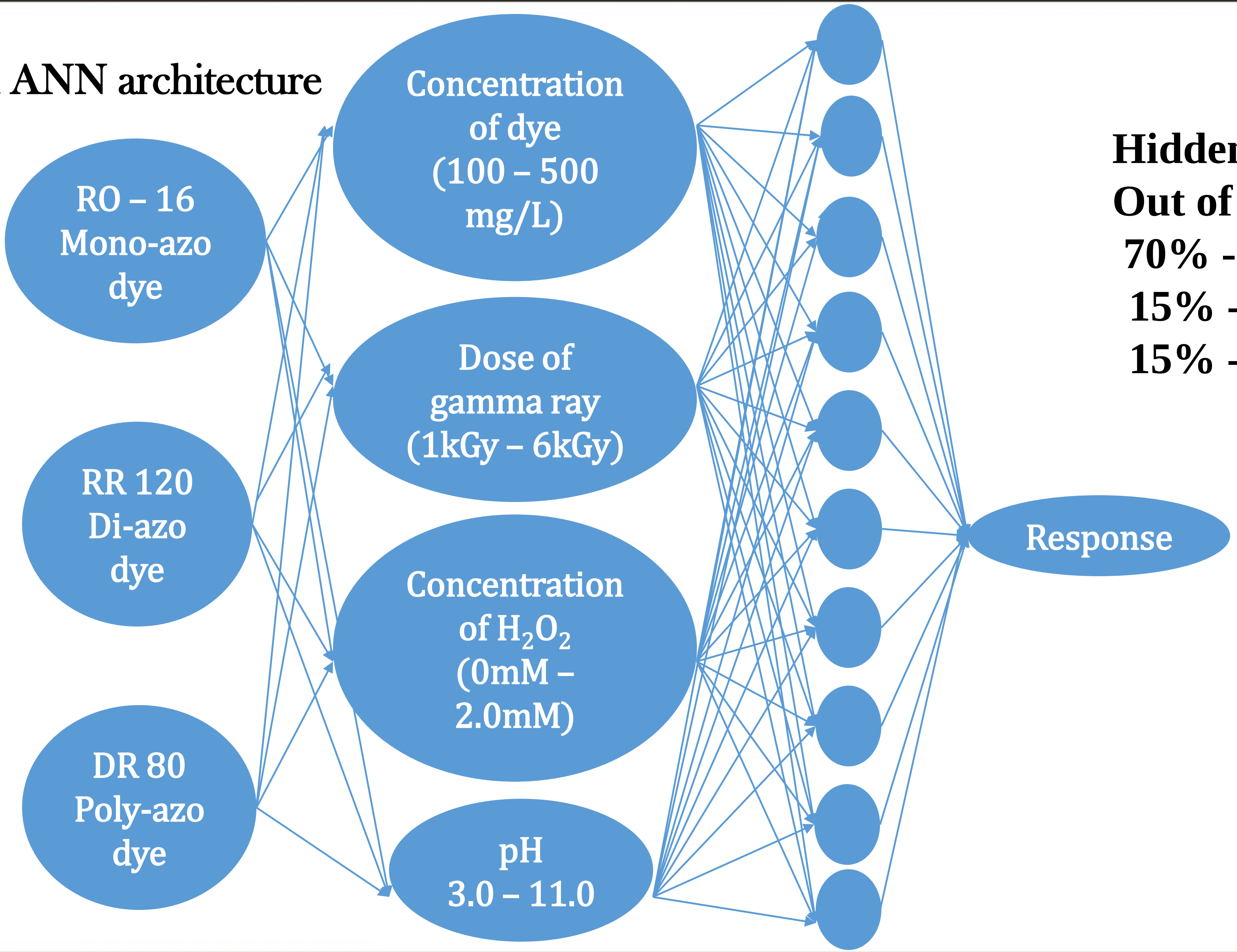
Optimization of neurons number

$$MSE = \frac{1}{Q}\sum_{i=1}^{i=Q}(y_{i,pred} - y_{i,exp})^2$$

Q is the number of data point,
$y_{i,pred}$ = prediction through network,
$y_{i,exp}$ = experimental response and i is an index of data.



Optimized ANN architecture



Hidden layers: 10

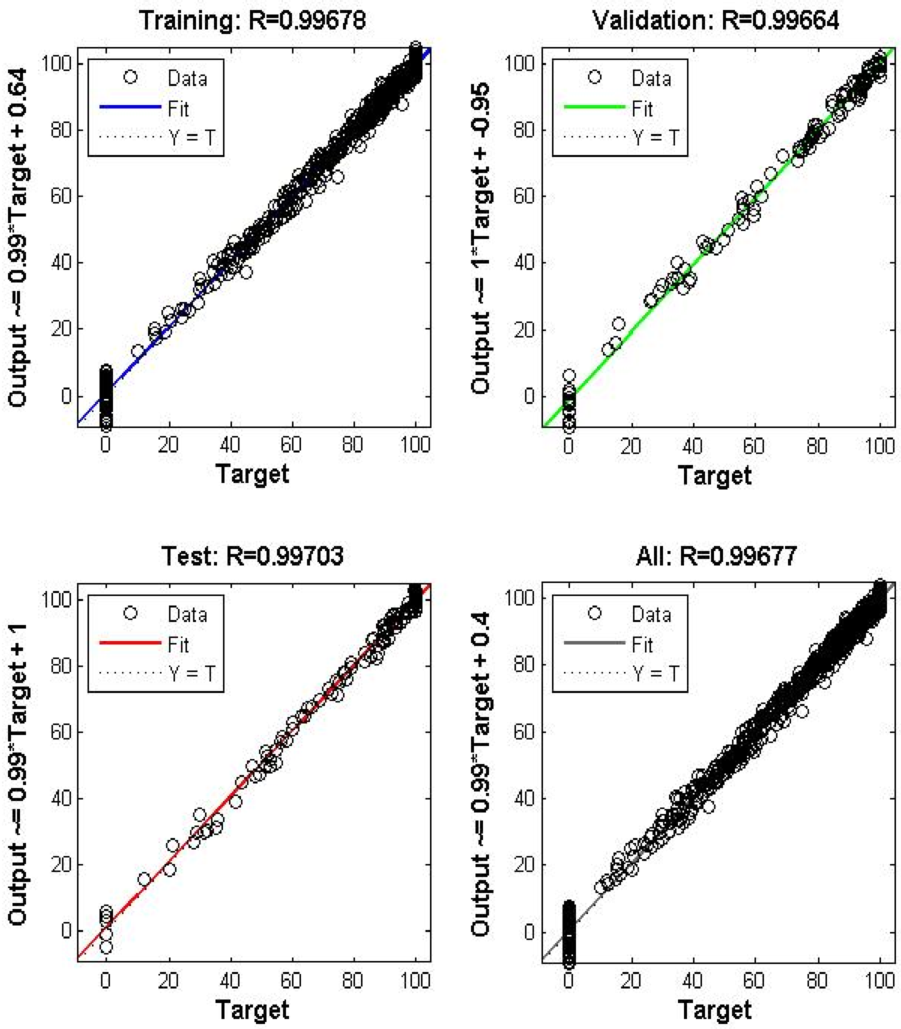
Out of 750 inputs:

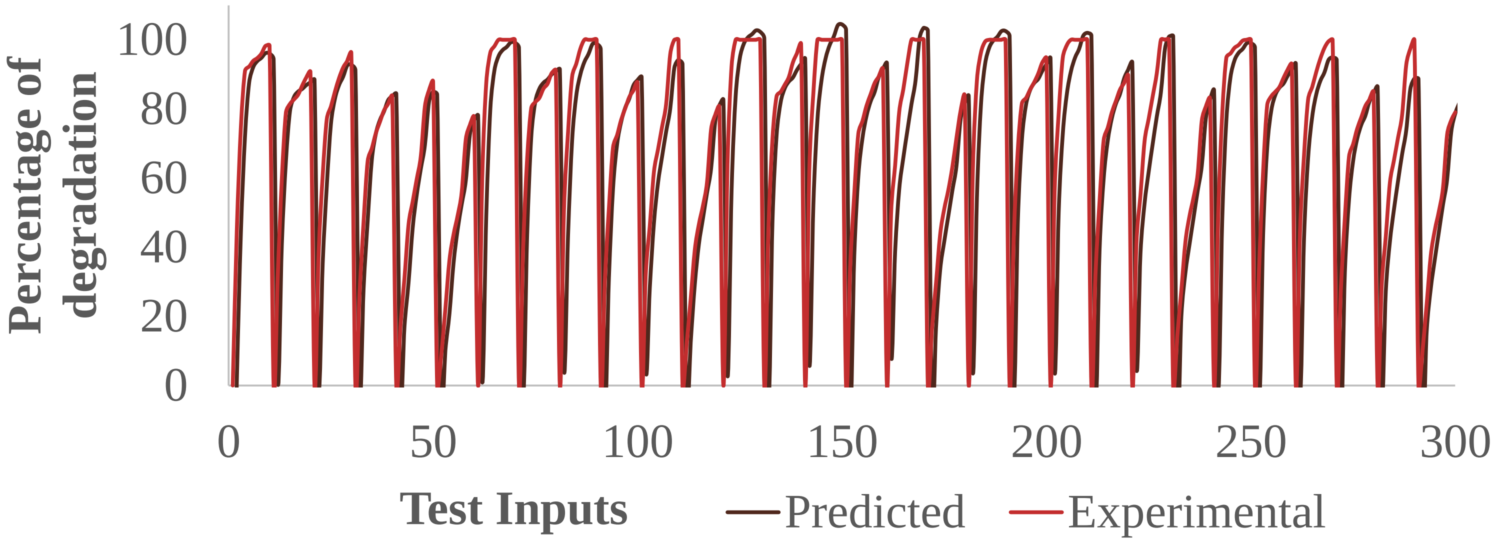
70% - Training

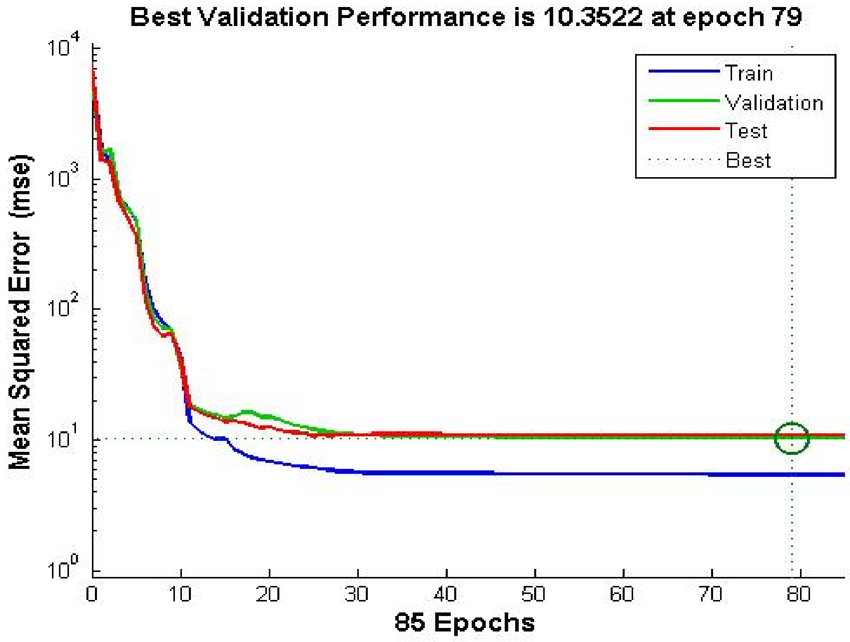
15% - Validation

15% - Test

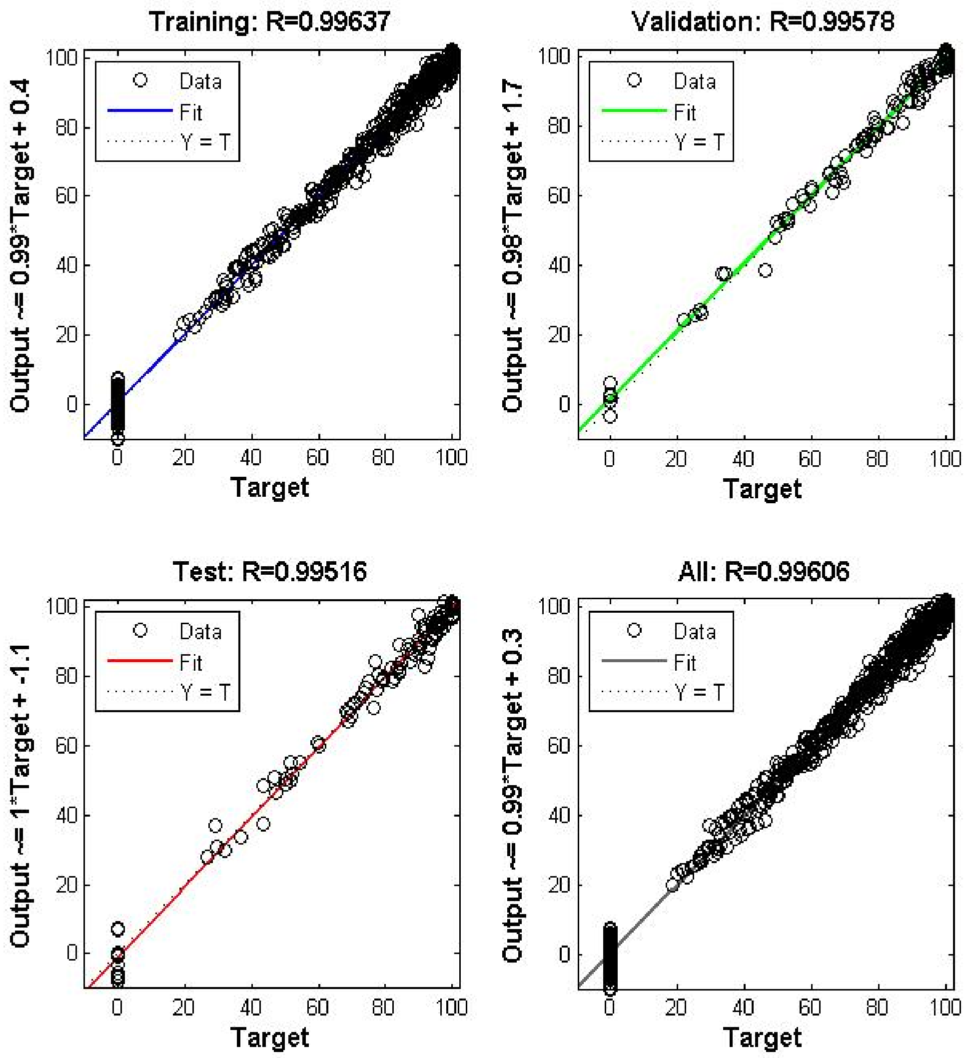
Mono azo Dye: Reactive Orange 16

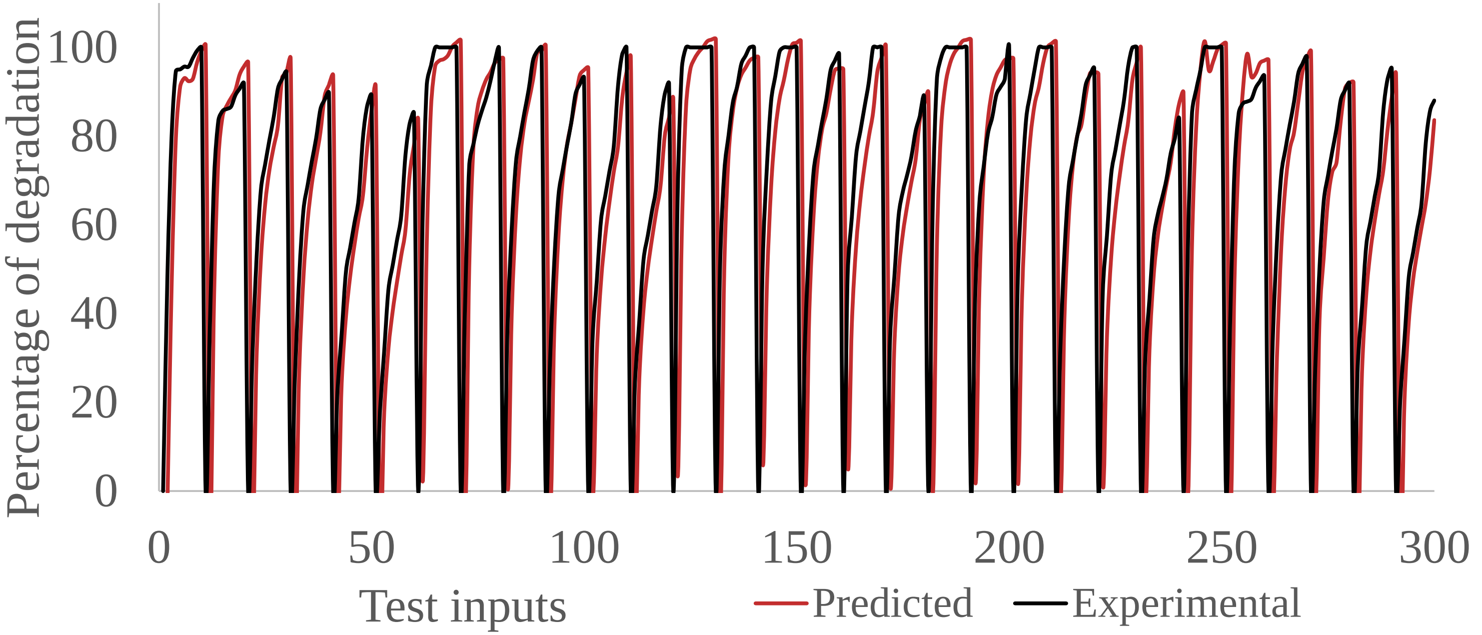


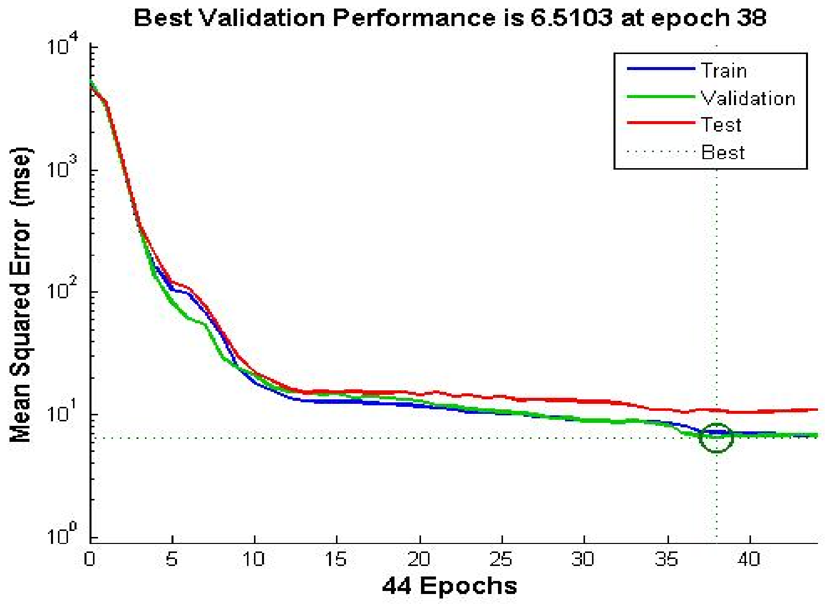




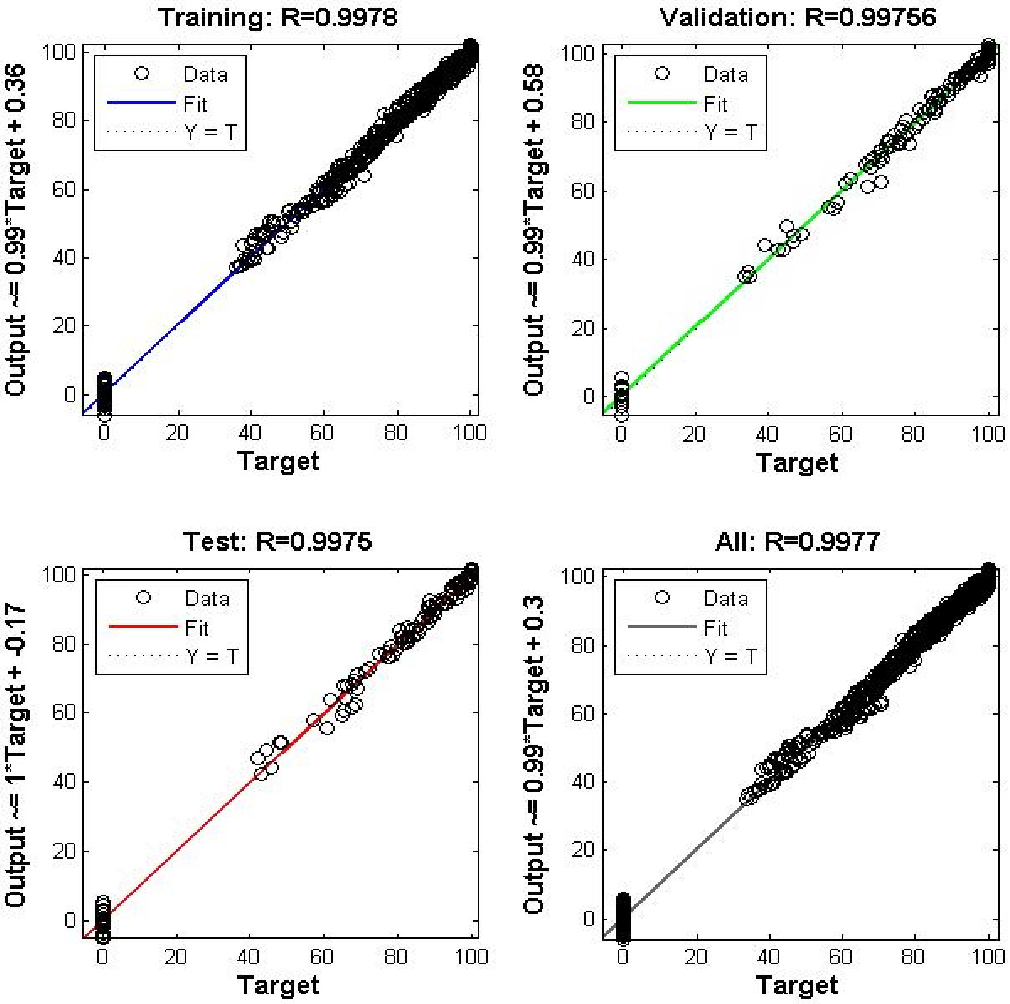
Di azo Dye: Reactive Red 120

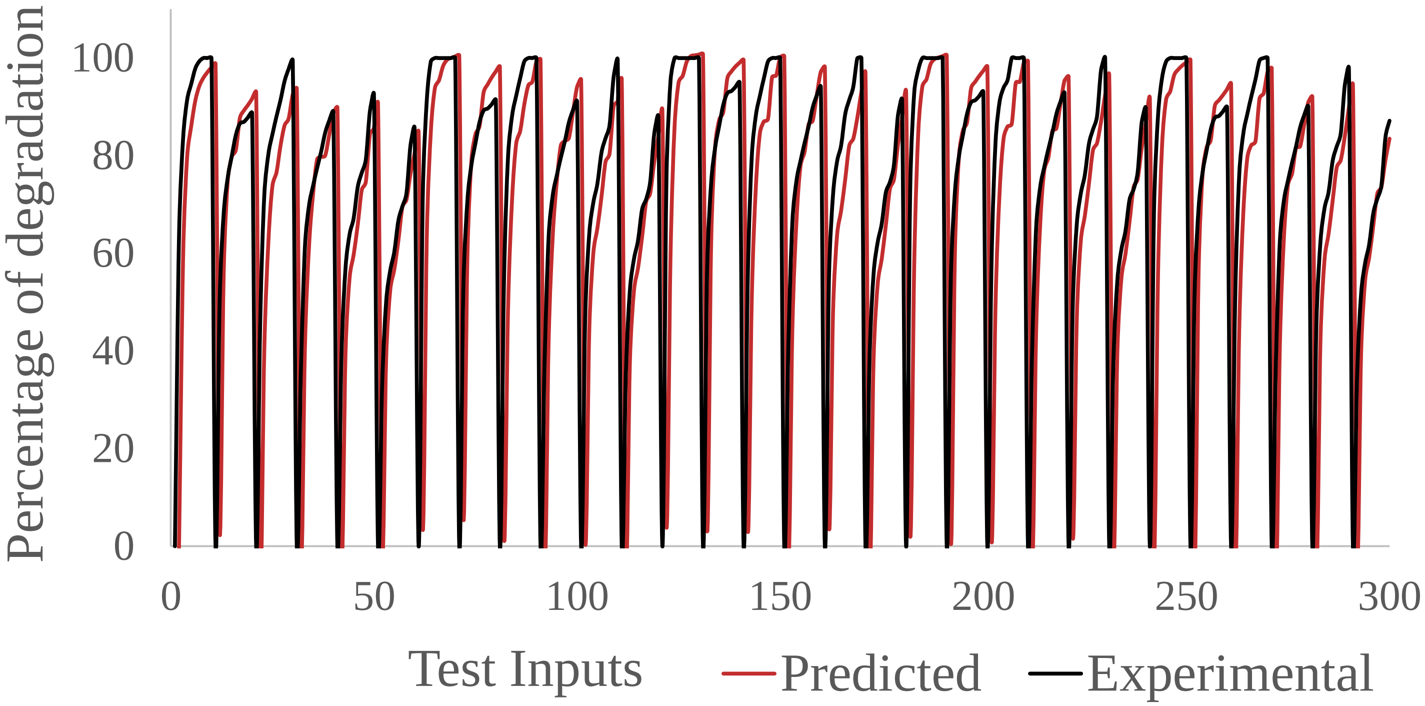


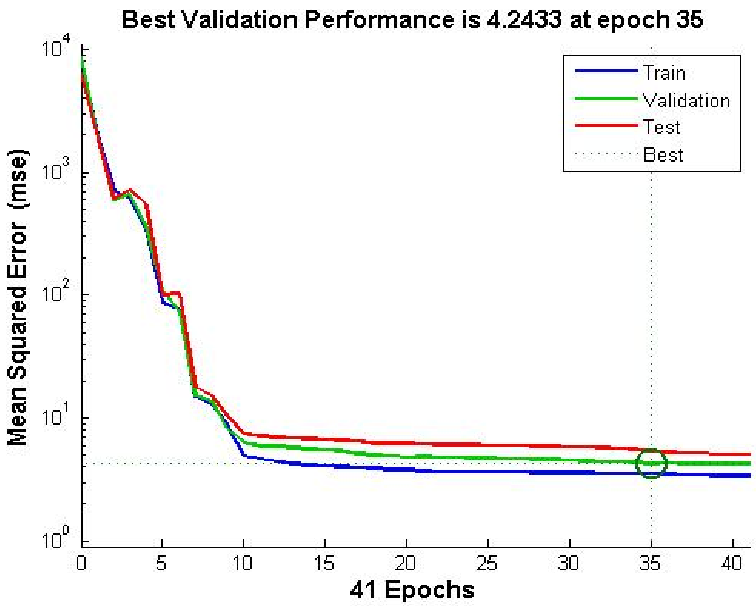




Poly azo Dye: Direct Red 80







Sensitivity analysis - Relative importance of the input variables Garson equation

$$Ij = \frac{\sum_{m=1}^{m=Nh}((|w_{jm}^{ih}|/\sum_{k=1}^{Ni}|w_{km}^{ih}|)\times |w_{mn}^{ho}|}{\sum_{k=1}^{k=Ni}\{\sum_{m=1}^{m=Nh}((|w_{jm}^{ih}|/\sum_{k=1}^{Ni}|w_{km}^{ih}|)\times |w_{mn}^{ho}|\}}$$

I_j is the relative importance of the j^{th} input variable on the output variable,

N_i and N_h are the number of input and hidden neurons, respectively and

W is connection weight,

'i', 'h' and *'o'* refers to input, hidden and output layers, respectively and

'k', 'm' and *'n'* refers to input, hidden and output neurons respectively

Relative importance of input variables for the degradation of reactive dyes.

Input variables	Relative Importance %		
	RO 16 – Mono azo	**RR120 – Di azo**	**DR 80 - Poly azo**
Conc. of H_2O_2 (mM)	28.75	20.47	39.49
Dose of gamma ray (kGy)	62.94	34.33	54.31
pH	7.74	17.43	5.24
Concentration of dye (mg/L)	0.57	27.77	0.96
Total	100	100	100

V C Padmanaban et al Desalination and Water Treatment 131 (2018): 343-350.

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