



PECTIN-CHITOSAN HYDROGEL SYNTHESIS AND ITS DYE ADSORPTION APPLICATION

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Abstract:

In this work we have synthesized Pectin-Chitosan hydrogel using extracted pectin from citrus fruits solid waste and synthesized chitosan from extracted chitin of crustacean shells. An optimization study of synthesized P-C hydrogel using variables like chitosan/pectin ratio, concentration of acetic acid and potassium hydroxide and optimal conditions (1:2 ratio of chitosan and pectin, 30 ml 10% CH₃COOH and 15 ml 1M KOH) were exposed with maximum water uptake (3.1 gm) of synthesized P-C hydrogel. The hypothetical structures of hydrogels 'a', 'b' and 'c' were confirmed through structural characterizations like SEM & elemental analysis and thermal stability of hydrogel was determined by thermogravimetric analysis (TGA). This P-C hydrogel was applied for methylene blue dye adsorption application performing the time interval kinetic study of dye (MB) adsorption and UV-Visible spectra of dye bath with passage of time followed by adsorption isotherm study and then dye desorption study in various eluents.

Index Terms - Pectin-Chitosan hydrogel, Methylene blue dye adsorption, Dye adsorption kinetic study, Adsorption isotherms, Dye desorption

1. Introduction

Biodegradable polymer hydrogels having excellent biocompatibility are important for various applications (Rieger *et al.*, 2013 & Varghese *et al.*, 2006). Chitosan is second most abundant polysaccharide, the deacetylated derivative of chitin commonly used to synthesize hydrogels due to having biodegradability, non-toxicity, antibacterial property (Moura *et al.*, 2007). Chitosan is a polycation requires cross linking providing chemical stability and mechanical properties. Most commonly used cross linkers are glutaraldehyde (Xing *et al.*, 2009), carbodiimide (Ulubayram *et al.*, 2002) and diphenylphosphoryl azide (Marinucci *et al.*, 2003). Polyanion having hydrophilic property has also been used as an effective cross linker for chitosan based hydrogel (Bernabe *et al.*, 2005 & Lee *et al.*, 2012). Pectin is a heteropolysaccharide mainly found in plant cell walls comprised of partially esterified galacturonic acid residues, rhamnose residues, and a variety of sugar residues are prone to hydrogen-bonding interactions and are unable to interact electro statically (Ovodov *et al.*, 2009). The hydrophilicity of pectin is similar to polyanions (Barck *et al.*, 2005).

The electrostatic interactions between chitosan and pectin generate millibeads (Barck *et al.*, 2005), microbeads (Yu *et al.*, 2009, Oliveira *et al.*, 2010 & Kim *et al.*, 2003), nanoparticles (Birch *et al.*, 2014), thin films (Bernabe *et al.*, 2005) and thermo reversible hydrogel. Gelation and hydrogen bonding of pectin with another biopolymer can be enabled by protonating pectin with hydrochloric acid (HCl) (Nordby *et al.*, 2003). The desirable hydrogel is that which can be synthesized under physiological conditions.

In this study, we have synthesized pectin-chitosan hydrogel from extracted pectin from citrus solid waste (Dhobi *et al.*, 2022) and synthesized chitosan from extracted chitin from marine crustacean shells (Dhobi *et al.*, 2022). After then synthesized P-C hydrogel was characterized by SEM, elemental TGA analysis to explore its structure and thermal stability followed by swelling property, dye (MB) adsorption study, adsorption isotherm study and dye desorption.

2. Experimental

2.1 Raw materials, reagents & Pectin-Chitosan Hydrogel synthesis

Pectin powder extracted from citrus fruits (oranges, lemons, grapes, peaches, strawberries and apples) solid waste under microwave illumination (Dhobi *et. al.* 2022) and chitosan powder synthesized by microwave (Catalyst system, CATA-RI) deacetylation process of extracted chitin from crustacean shells (Prawn shell, crab shell, krill shell and craw fish shell) by modified deproteination and demineralization process (Dhobi *et. al.* 2022) were used to synthesize P-C hydrogel. All chemicals utilized in this work were laboratory grade bought from Merck chemicals, Mumbai, India.

As shown in Figure-1 & Table-1 given mmol chitosan powder dissolved in 15ml of x% acetic acid solution and given mmol pectin powder dissolved in 15ml of x% acetic acid solution were mixed, stirred for 5 hours using magnetic stirrer at room temperature, printed in Petri dish and dried in oven (BIOCRAFT, India) at 60 °C for 3 hours. After then membrane was removed from the mold by adding 15 ml y M potassium hydroxide solution and then again dried at 50 °C for 3 hours followed by breaking and grinding using laboratory mortar-pestle giving P-C hydrogel fine powder was stored in glass vial for further use.



Figure 1: P-C Hydrogel Synthesis

2.2 Characterizations

The surface morphology of synthesized hydrogels obtained using JEOL 7100-EDX (Tokyo, Japan) scanning electron microscope (SEM) at x750 magnification, 10µm scale and 5kV voltage. The calibration of CHNSO analyzer (Horriba EA3000) with standard sulphanilamide prior to the elemental analysis of same hydrogel samples was done. Thermal behavior of same hydrogels was studied using thermal analysis like thermogravimetric analysis (TGA) on a STA 449F1 Jupiter (Netzsch, Germany) type thermogravimetric analyzer under a flow of nitrogen (150 mL/min).

2.3 Swelling studies

As shown in Figure-2 and Table-1, 0.3 gm weighed dry powdered P-C hydrogel was taken in empty tea bag tied with thread and hung on glass rod and swelling properties of hydrogels a, b, and c were evaluated by dipping it in distilled water. The swelling ratio (SR) of hydrogels was calculated at specific time using below equation (Peng *et al.*, 2011). The swollen hydrogel was used for further dye removal application (Figure-3)

$$SR = \frac{M_t - M_0}{M_0}$$

Where,

M_0 = mass of hydrogel before swelling (0.3 gm)

M_t = mass of hydrogel after swelling at time t (30 minutes)

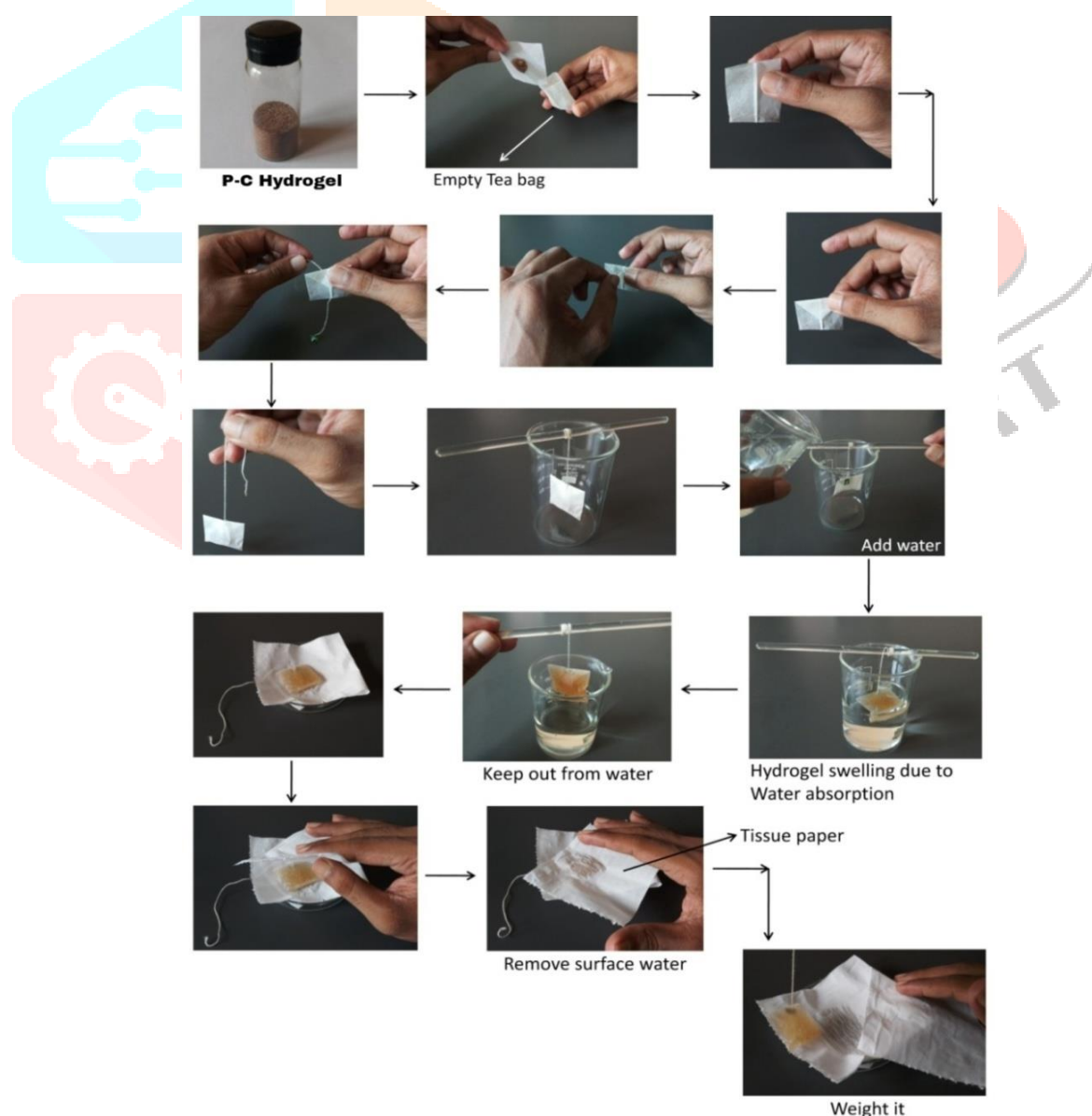


Figure 2: Swelling Test

2.4 Dye adsorption study

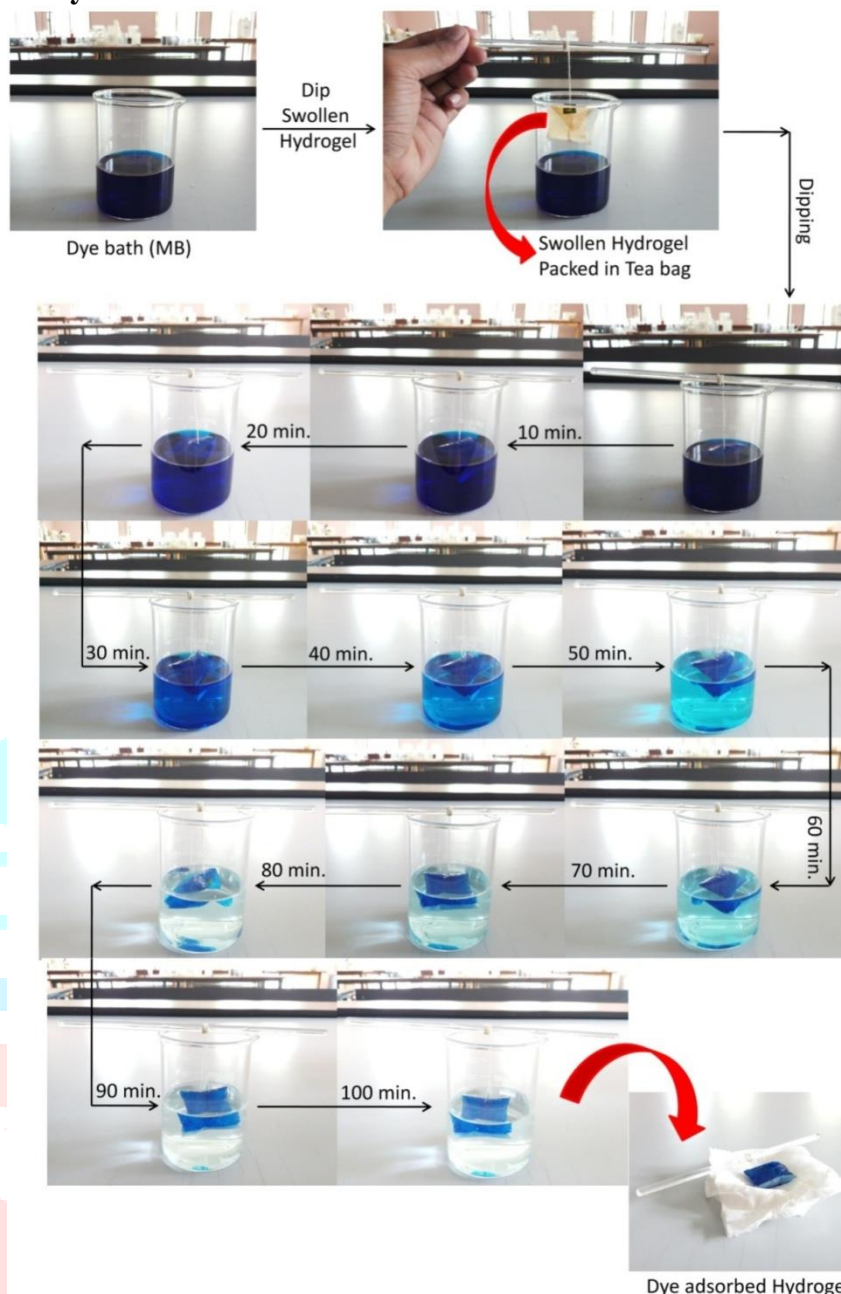


Figure 3: Time interval kinetic study of Dye (MB) adsorption by Hydrogel 'c'

As shown in Figure-3, Swollen hydrogel 'c' within a tea bag immersed in different pH (4, 7 & 9 adjusted with 0.1 N HCl or 0.1 N NaOH) aqueous solution of methylene blue dye (400 mg MB diluted to 200 ml with solvent) for 100 minutes at different room temperature (22, 25 & 28 °C). The dye solution was analyzed spectrophotometrically (Figure-7) using UV-VIS spectrometer at 663 nm at 10 minutes time intervals and different absorbance of unknown dye solution were obtained. After preparing MB dye solutions having different concentration (500mg/L, 1000mg/L, 1500mg/L, 2000mg/L and 2500mg/L), their absorbance were measured using UV-VIS spectrometer at 663 nm (Figure-10). After then calibration curve (Absorbance versus dye solution (mg/L)) was plotted and putting the absorbance values of unknown dye solution in calibration curve, respective concentrations of unknown dye solutions could be found were used to calculate dye removal percentage & adsorption capacity of hydrogel using following formulas (Figure-11 & Table-3) (Sharma *et al.*, 2015).

Dye removal percentage (R %) was calculated using following equation:

$$R \% = [(C_0 - C_t) / C_0] \times 100$$

Where, C_0 is dye concentration (mg/L) at time '0' and

C_t is dye concentration (mg/L) at time 't'

The adsorption capacity q_e (mg/g) was calculated using following equation:

$$q_e \text{ (mg/g)} = [(C_0 - C_t) / M] \times V$$

Where, C_0 is dye concentration (mg/L) at time '0' and

C_t is dye concentration (mg/L) at time 't'
 V is the volume of solution (in Liter) and
 M is the mass of adsorbent (gm).

2.5 Various Adsorption Isotherms

After getting parameters like C_0 , C_t & Q_e following adsorption isotherm (Desai *et al.* 2013) studies were done.

Langmuir Isotherm	$C_t \rightarrow C_t/q_e$	$Q_0=1/\text{Slope}$	$b=\text{Intercept} \times Q_0$
$C_t/q_e = [1/Q_0b + 1/Q_0 \times C_t]$			
Freundlich Isotherm	$\log C_t \rightarrow \log q_e$	$n=1/\text{slope}$	$K_f = \text{Antilog}(\text{Intercept})$
$\log q_e = \log K_f + (1/n)\log C_t$			
Temkin Isotherm	$\ln C_t \rightarrow q_e$	$b = \text{slope}$	$a = \text{Intercept}$
$X = a + b \ln C$			
BET Isotherm	$C_t/C_0 \rightarrow C_t / [(C_0 - C_t)q_e]$	$\text{Slope} = B - 1/B \times q_{\max}$	$1/B \times q_{\max} = \text{Intercept}$
$C_t / (C_t - C_0) = 1/B \times q_{\max} + (B - 1/B \times q_{\max})(C_t/C_0)$			

2.6 Dye desorption study

At economic point of view regeneration and reusability of hydrogel is very useful. The desorption study of MB loaded hydrogel (adsorbent) was carried out using various solvents like ethyl alcohol, N,N-dimethyl formamide (DMF), Acetone, 0.1M HCl and 0.1M NaOH. MB loaded hydrogel was treated with these desorption solvents (eluent) of 200 mL for 24 hours at 25 °C under magnetic stirring. After then, dye concentrations within different eluents were determined using UV-Visible spectrophotometer and MB dye desorption capacity & desorption efficiency (%) for each eluents were calculated from following formulas (Duman *et al.*, 2020).

Desorption capacity (q_e , desorption, mg/g) = $V (C_f)/M$

Where, V = Eluent volume (L) (0.2 L)

C_f = Dye concentration in desorbing solution (mg/L)

M = Dye saturated hydrogel weight (g) (3.4 g)

Desorption efficiency (%) = $(q_e, \text{desorption} / q_e, \text{adsorption}) \times 100$

Where, $q_e, \text{desorption}$ = MB dye desorption capacity (mg/g)

$q_e, \text{adsorption}$ = MB dye adsorption capacity (mg/g) (117.65 mg/g)

3. Results and Discussion

Table 1: Optimization of Hydrogel synthesis

Hydrogel	Amount of Chitosan	Amount of Pectin	CH ₃ COOH Concentration (x%) 30 ml	KOH Concentration (yM) 15 ml	Weight of Hydrogel Product (gm)	Mass of hydrogel before swelling (M ₀ gm)	Mass of hydrogel after swelling (M _t gm)	Swelling ratio (SR)
Hydrogel 'a'	1.0 mmol (0.161 gm)	1.0 mmol (0.382 gm)	5	1.0	0.533	0.3	0.9	2.00
				1.5	0.538		0.7	1.33
				2.0	0.540		0.5	0.66
			10	1.0	0.541		1.2	3.00
				1.5	0.537		0.4	0.33
				2.0	0.535		1.1	2.67
			15	1.0	0.534		0.6	1.00
				1.5	0.539		0.8	1.03
				2.0	0.536		1.0	2.33
Hydrogel 'b'	2.0 mmol (0.322 gm)	1.0 mmol (0.382 gm)	5	1.0	0.697	0.3	1.8	5.00
				1.5	0.699		2.0	5.67
				2.0	0.694		1.6	4.33
			10	1.0	0.702		2.3	6.67
				1.5	0.700		1.5	4.00
				2.0	0.695		2.1	6.00
			15	1.0	0.696		1.9	5.33
				1.5	0.698		1.7	4.67
				2.0	0.701		2.2	6.33
Hydrogel 'c'	1.0 mmol (0.161 gm) 2.0 mmol (0.764 gm)	2.0 mmol (0.764 gm)	5	1.0	0.912	0.3	3.3	10.0
				1.5	0.914		3.0	9.00
				2.0	0.916		2.8	8.33
			10	1.0	0.919		3.4	10.33
				1.5	0.917		2.6	7.67
				2.0	0.911		2.9	8.67
			15	1.0	0.913		3.2	9.67
				1.5	0.915		2.7	8.00
				2.0	0.918		3.1	9.33

From the above Table-1 of optimization of Hydrogel synthesis, it could be seen that more convenient conditions for P-C hydrogel (Pectin-Chitin hydrogel) synthesis were 1:2 ratio of chitosan and pectin, 30 ml 10% CH₃COOH and 15 ml 1M KOH to yield maximum product i.e. 0.919 gm. Mole ratio of chitosan & pectin controls porosity of hydrogels and Hydrogel 'c' is superior than that of Hydrogel 'a' & Hydrogel 'b' due to its more porous behavior and having more amount of pectin permits more quantity of water absorption within it and hydrogel swelling is due to concentration gradient. The increasing order for swelling ratio of hydrogels was hydrogel 'c' (SR = 10.33) > hydrogel 'b' (SR = 6.66) > hydrogel 'a' (SR = 3.0), which had indicated the porosity order of hydrogels i.e. hydrogel 'c' > hydrogel 'b' > hydrogel 'a', which could be well understood from hypothetic structures of hydrogel 'a', hydrogel 'b' and hydrogel 'c' as shown in Fig.3 (Supported from SEM results Figure-5 and elemental analysis Table-2) showing two pores within hydrogel 'c', one pore within hydrogel 'b' along with H-bonded chitosan moiety and one pore within hydrogel 'a'.

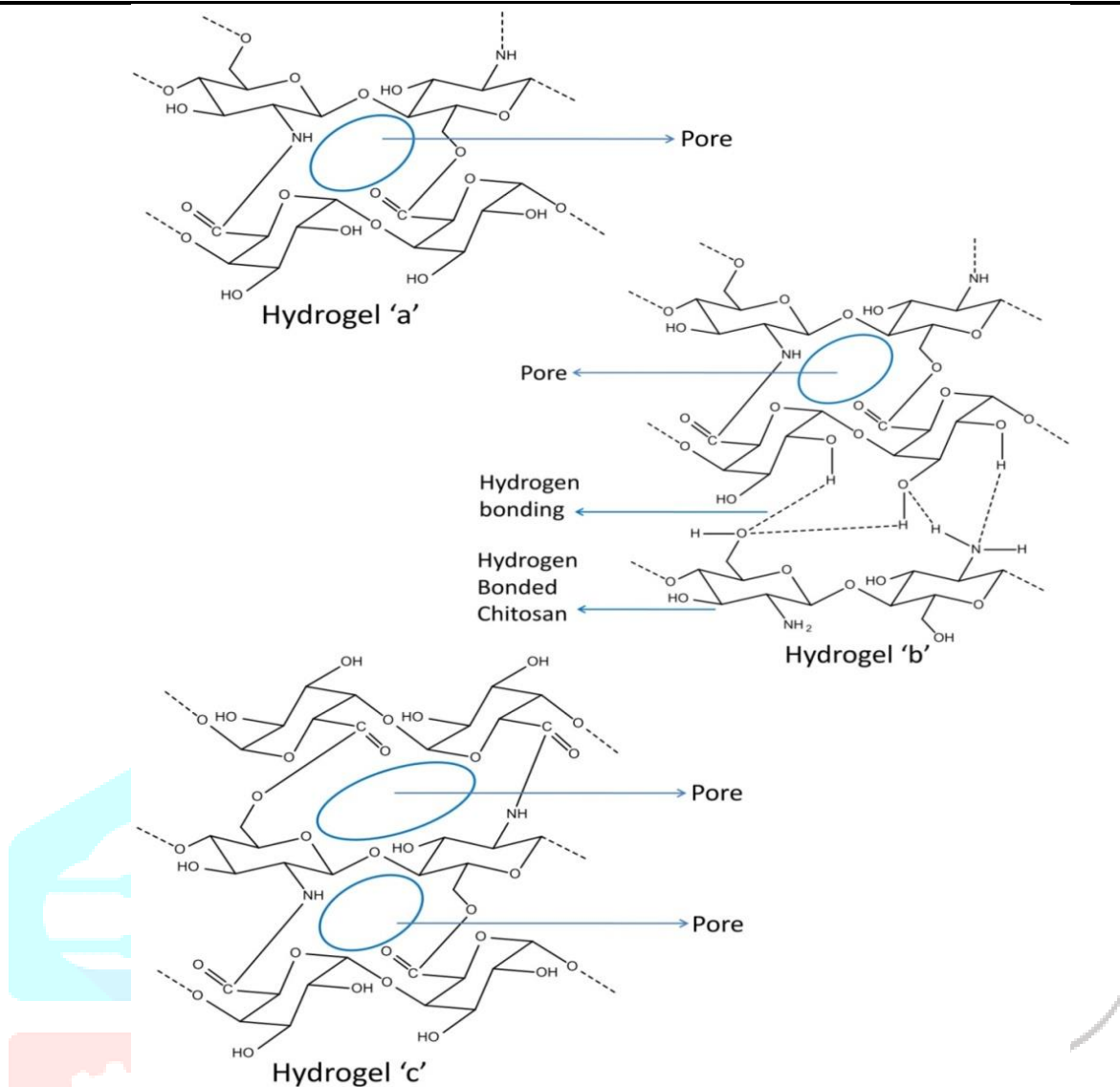


Figure 4: Hypothetic hydrogel Structure

4. Characterizations

4.1 SEM analysis of Hydrogels

Surface morphologies of synthesized hydrogels a, b and c could be seen from Figure-5 indicating order of roughness, craking and pores size order of the surfaces of hydrogels a, b and c was $a < b < c$, which pointed out that higher surface area of hydrogel 'c' provided for the water uptake and thus dye adsorption through concentration gradient from methylene blue dye bath to swollen hydrogel as shown in Figure-3.

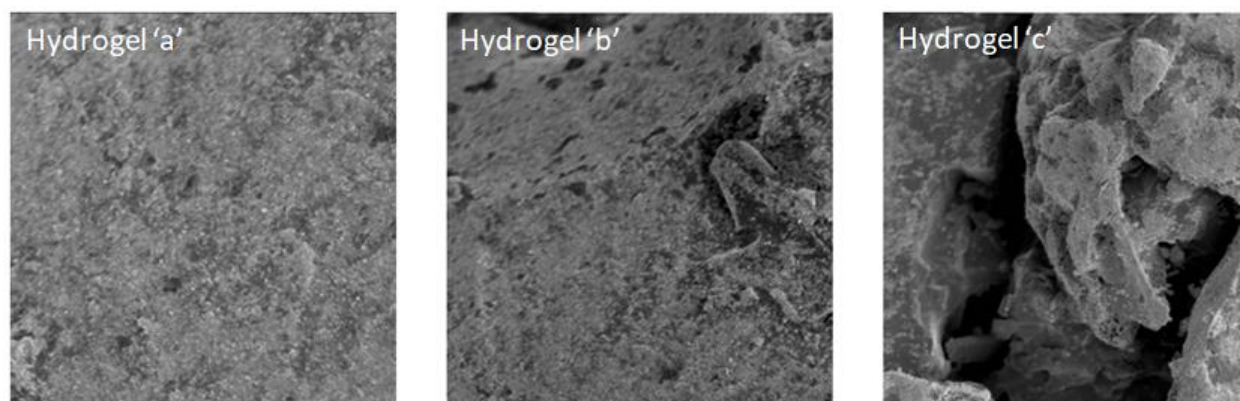


Fig. 5: SEM images of hydrogel a, b and c at magnification x750, 10µm scale & 5kV

4.2 Table 2: Elemental analysis of Hydrogels

Sr. No.	Type	Name	% C	% H	% N	% S	% S	Weight (mg)
1.	Standard	Sulphanilamide	42.05	4.74	18.75	21.52	12.94	0.985
2.	Standard	Sulphanilamide	40.91	4.67	15.81	18.58	20.03	1.125
3.	Sample	Hydrogel 'a'	44.23	5.01	4.31	0.01	47.11	1.116
4.	Sample	Hydrogel 'b'	44.39	6.14	6.04	0.00	44.36	1.131
5.	Sample	Hydrogel 'c'	43.79	5.09	2.91	0.00	49.17	1.095

Elemental analysis calculated value for $(C_{24}H_{32}O_{19}N_2)_n$ (Hydrogel 'a'): C (44.17%), H (4.91%), O (46.63%), N (4.29%) are matched very well with the experimental elemental analysis value: C (44.23%), H (5.01%), O (47.11%), N (4.31%); $(C_{36}H_{54}O_{27}N_4)_n$ (Hydrogel 'b'): C (44.44%), H (5.56%), O (44.44%), N (5.56%) are matched very well with the experimental elemental analysis value: C (44.39%), H (6.14%), O (44.36%), N (6.04%); $(C_{36}H_{46}O_{30}N_2)_n$ (Hydrogel 'c'): C (43.81%), H (4.67%), O (48.68%), N (2.84%) are matched very well with the experimental elemental analysis value: C (43.79%), H (5.09%), O (49.17%), N (2.91%); are shown in Table-2.

4.3 Thermal analysis (TGA)

As shown in Figure-6, TGA plot had shown that 92% weight loss of swollen hydrogel up to 121 °C was due to water elimination from hydrogel and then graph became steady up to 450 °C showing stability of dry hydrogel up to 450 °C and after then it had started to decompose.

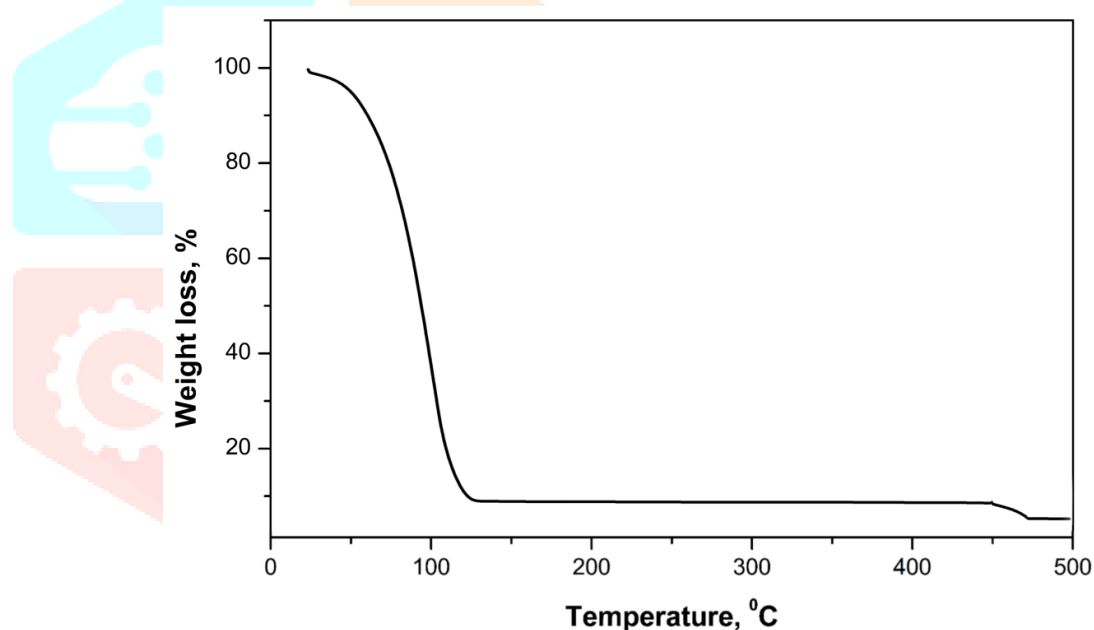


Figure 6: TGA plot of swollen hydrogel

5. Dye adsorption by swollen hydrogel**5.1 UV-Visible spectra of dye bath with passage of time**

From the plot of ABS (A) versus wavelength λ , it is clear that with increasing time the Absorbance of dye solution is decreasing (Figure-7), due to dye uptake by hydrogel. As a result concentration of dye in dye bath is decreasing; hence Absorbance is also decreasing in direct proportional, according to Beer's law. The adsorption of MB dye molecules by hydrogel was justified by electrostatic interaction between hetero atom bearing lone pair of electrons of hydrogel and tetravalent nitrogen atom bearing positive charge of methylene blue dye as shown in Figure-8.

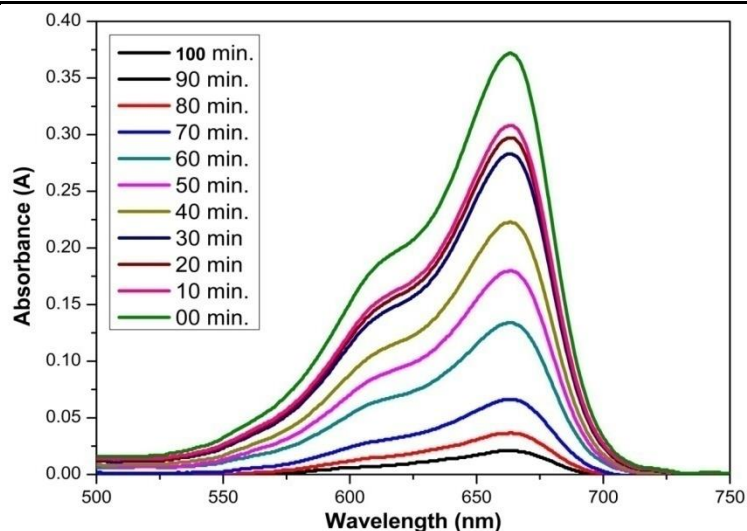


Figure 7: Absorbance vs. Wavelength plot at 10 minutes intervals

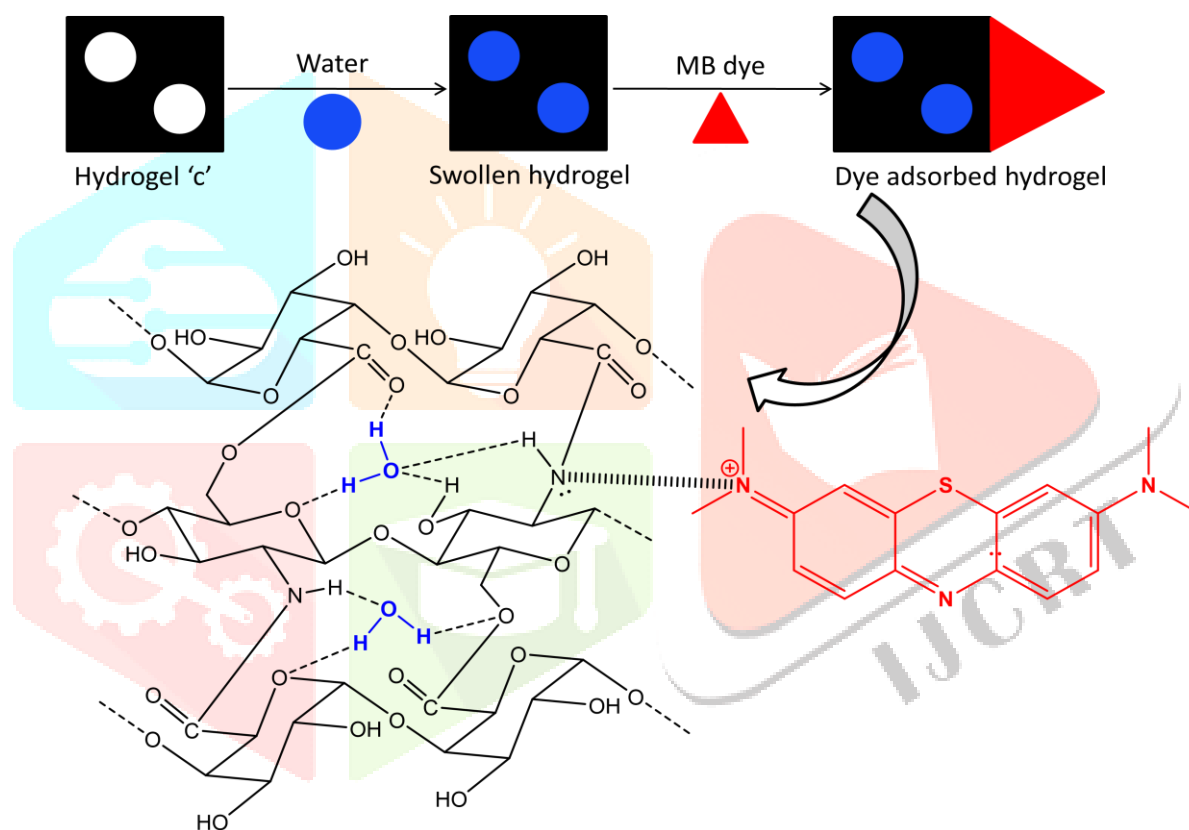


Figure 8: Electrostatic interaction between MB dye and P-C hydrogel 'c'

5.2 Optimization of dye adsorption with variables; pH & Temperature

It could be seen from Figure-9 that, 100 minutes time, 7 pH & 25 °C (R.T.) temperature were optimum condition for appropriate MB dye adsorption on swollen P-C hydrogel. At 4 pH it might be replacement of dye molecules of MB loaded hydrogel by H⁺ ions of acidic solvent and at 9 pH it might be attraction of dye molecules of MB loaded hydrogel by OH⁻ ions of alkaline solvent and at low temperature (22°C) rate of association of hydrogel and dye molecules might be decreased and at higher temperature (28 °C) decomposition of MB loaded hydrogel into hydrogel and dye molecules might be increased led to increased absorbance and thus the dye concentration in dye solution (Beer's law).

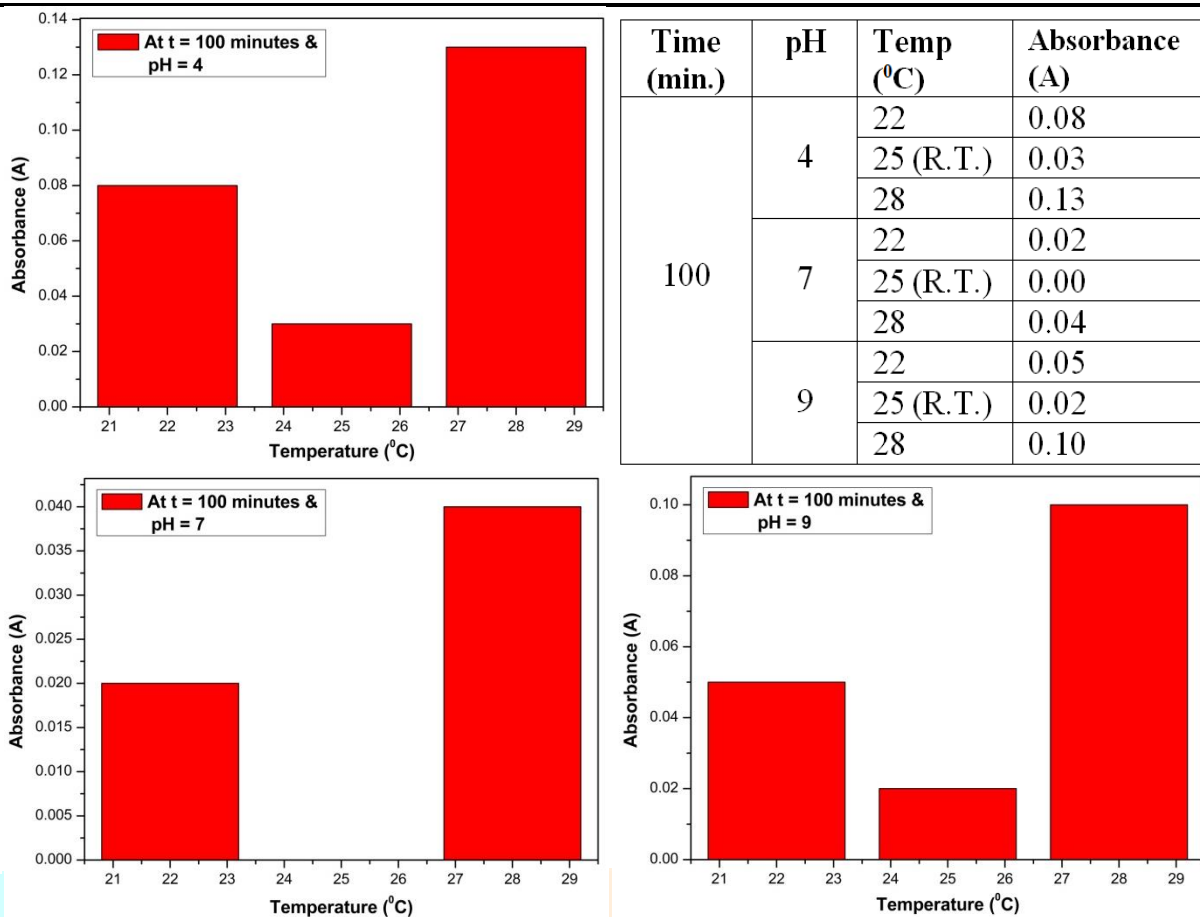


Figure 9: Absorbance vs. Temperature plots at specific time & pH

5.3 Determination of dye removal percentage & adsorption capacity of hydrogel with respect to time

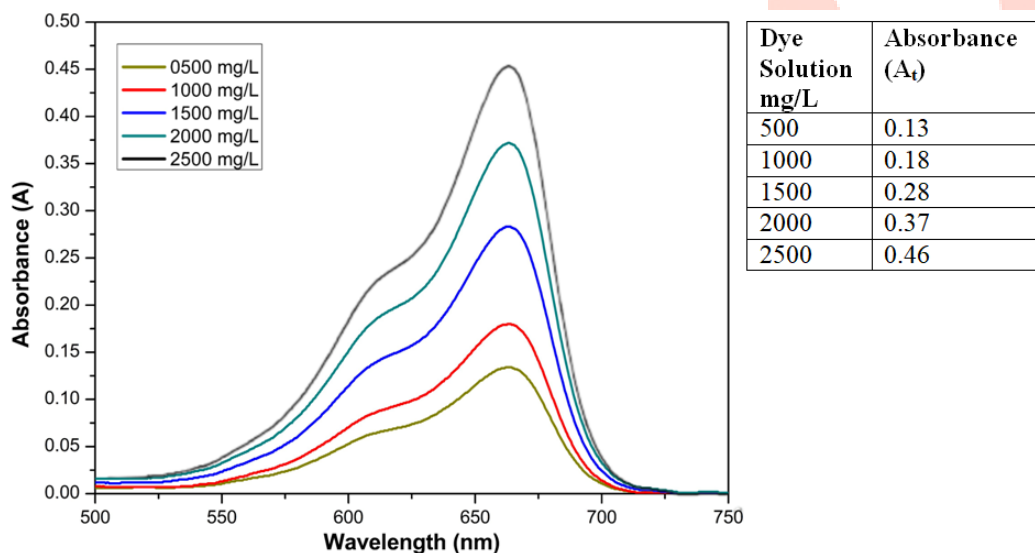


Figure 10: UV-Vis spectra of standard dye solutions (500, 1000, 1500, 2000 & 2500 mg/L)

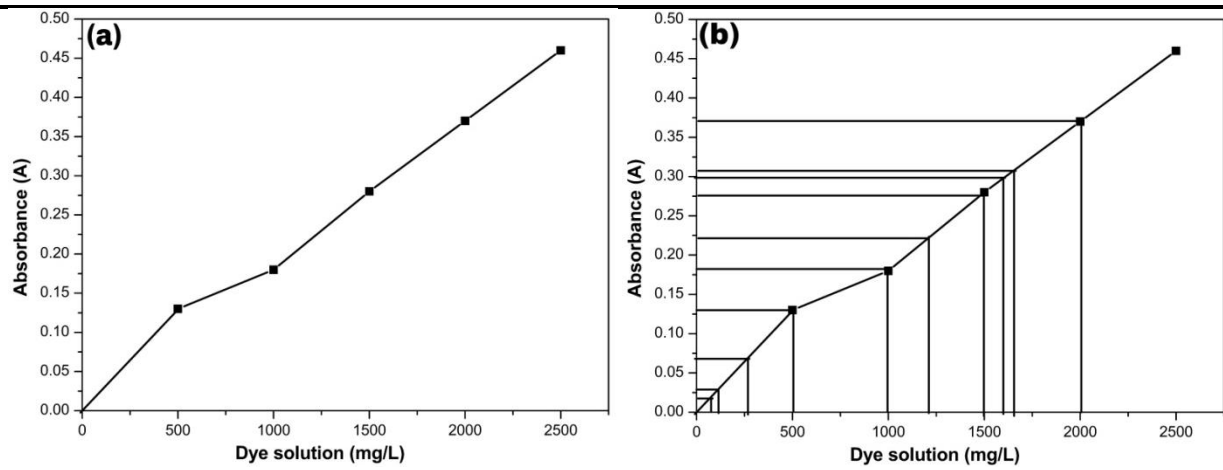


Figure 11: (a) Calibration curve and (b) Determination of unknown concentrations of dye solution with respect to time using calibration curve

Table 3: Dye removal percentage & adsorption capacity of hydrogel with respect to time

Sr. no.	Time (minutes)	Absorbance (A_t)	Dye solution Concentration (C_t) mg/L	Dye removal percentage (% R) = $[(C_0 - C_t)/C_0] 100$	Adsorption capacity q_e (mg/g) = $[(C_0 - C_t)/M]V$
1	00	0.37 (A_0)	2000(C_0)	0	0
2	10	0.31	1646	17.7	20.82
3	20	0.30	1590	20.5	24.12
4	30	0.28	1500	25.0	29.41
5	40	0.22	1210	39.5	46.47
6	50	0.18	1000	50.0	58.82
7	60	0.13	500	75.0	88.24
8	70	0.07	260	87.0	102.35
9	80	0.03	106	94.7	111.41
10	90	0.02	68	96.6	113.65
11	100	0.00	00	100	117.65

6. Adsorption isotherms study

Table 4: Various Parameters for Adsorption Isotherm

Sr. no.	C_t	C_t/q_e	$\log C_t$	$\log q_e$	$\ln C_t$	q_e	C_t/C_0	$C_t/[(C_0 - C_t)q_e]$
1	2000(C_0)	Infinity	3.30	Infinity	7.60	0	1.00	Infinity
2	1646	79.06	3.22	1.32	7.41	20.82	0.82	0.22333
3	1590	65.92	3.20	1.38	7.37	24.12	0.80	0.16078
4	1500	51.00	3.18	1.47	7.31	29.41	0.75	0.10200
5	1210	26.04	3.08	1.67	7.10	46.47	0.61	0.03296
6	1000	17.00	3.00	1.77	6.91	58.82	0.50	0.01700
7	500	5.67	2.70	1.95	6.21	88.24	0.25	0.00377
8	260	2.54	2.41	2.01	5.56	102.35	0.13	0.00146
9	106	0.92	2.03	2.05	4.66	111.41	0.05	0.00050
10	68	0.60	1.83	2.06	4.22	113.65	0.03	0.00030
11	00	0	Infinity	2.07	Infinity	117.65	0	0

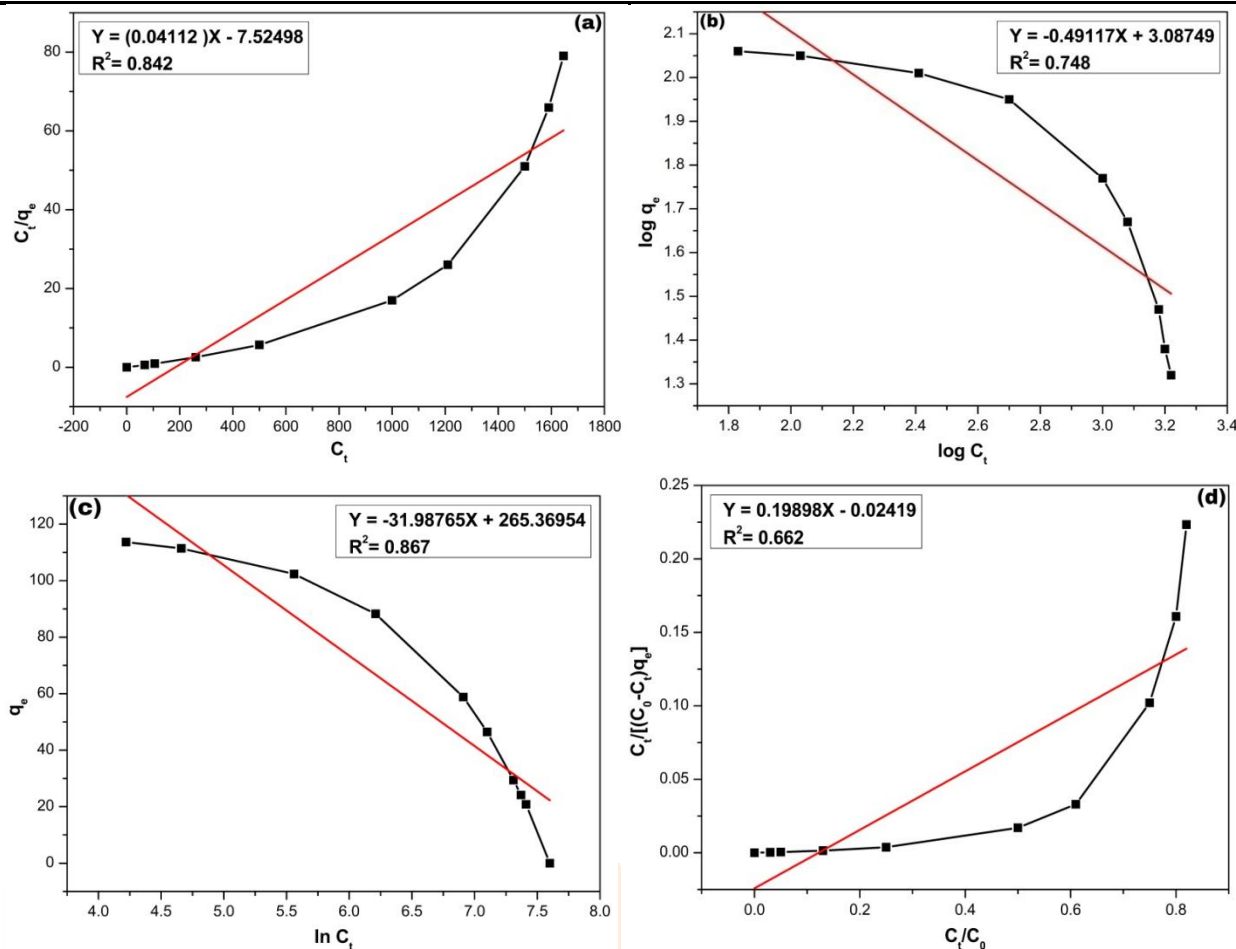


Figure 12: (a) Langmuir Isotherm, (b) Freundlich Isotherm, (c) Temkin Isotherm & (d) BET Isotherm

Table 5: Calculated Parameters from Adsorption Isotherm graphs:

Isotherm	Parameters		
Langmuir Isotherm	$R^2 = 0.842$	Q_0 (mg/g) = 24.32	b (1/mg) = -183.00
Freundlich Isotherm	$R^2 = 0.748$	K_f (mg/g) = 1223.17	n (1/mg) = -2.359
Temkin Isotherm	$R^2 = 0.867$	a (mg/g) = 265.37	b (1/mg) = -31.988
BET Isotherm	$R^2 = 0.662$	q_{max} (mg/g) = 117.65	B (1/mg) = -0.3514

Graphical representation of Langmuir, Freundlich, Temkin & BET adsorption isotherms are shown in figure 12. Various parameters for these isotherms are given in table 4 and calculated parameters from the isotherm graphs are shown in table 5. It was found that the value of correlation coefficients (R^2) for Langmuir, Freundlich, Temkin & BET adsorption isotherm were 0.842, 0.748, 0.867 & 0.662 respectively indicated more favorable adsorption isotherms for adsorption of MB dye on P-C hydrogel were Langmuir and Temkin adsorption isotherms and adsorbate (MB dye) was adsorbed on adsorbent (hydrogel) in monolayer as well as in multilayer fashion. Higher values of Q_0 (mg/g), K_f (mg/g), a (mg/g) and q_{max} (mg/g) had indicated high adsorption capacity and lower values of b (1/mg), n (1/mg), B (1/mg) had indicated slow rate of adsorption and low adsorption intensity.

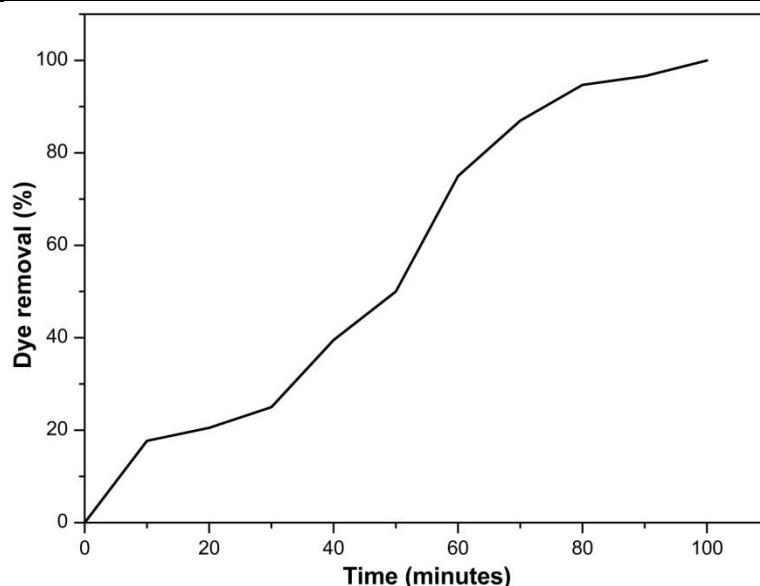


Figure 13: Dye removal (%) vs. Time

It could be seen from Figure-13 that with passage of time dye removal (%) was increased and there would be 100% dye removal at 100 minutes.

7. Dye desorption study

Table 6: Parameters for the calculation of desorption efficiency

Eluent	Absorbance (A_t)	C_f (mg/L)	q_e , desorption (mg/g)	Desorption efficiency (%)
Ethyl alcohol	0.29	1568	92.23	78.39
DMF	0.13	703	41.35	35.15
Acetone	0.22	1189	69.94	59.45
0.1M HCl	0.35	1892	111.29	94.59
0.1M NaOH	0.07	378	22.24	18.90

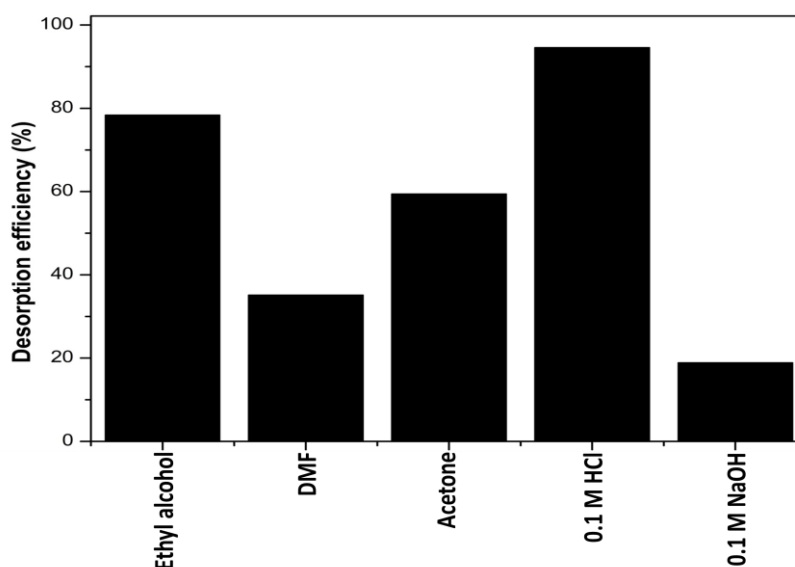


Figure 14: Desorption efficiency in various eluents

It could be seen from figure 14 that, desorption efficiency of MB loaded P-C hydrogel is superior (95%) in 0.1M HCl solvent may be due to replacement of MB dye molecules on P-C hydrogel by H^+ ions, which can be reused for MB dye adsorption from dye solution of given concentration.

8. Conclusion:

Due to less hydrophilicity of chitosan it is necessary to modify it to increase hydrophilicity and mechanical strength. Hypothetical structures of hydrogels were assumed from elemental & SEM analysis and thermal stability of hydrogel was determined from TGA analysis. Higher hydrophilicity of pectin provides increased hydrophilicity and improved mechanical properties to P-C hydrogel and thus, the improved water absorption property of porous hydrogel through concentration gradient and better dye adsorption characteristics through electrostatic interactions between chitosan-pectin composite and dye moiety at optimal conditions (Time = 100 minutes, pH = 7 & temperature = 25 °C). This MB loaded hydrogel can be recycled after dye desorption in 0.1 M HCl eluent at 25 °C temperature for 24 hours. Adsorption isotherms like Langmuir, Freundlich, Temkin & BET were employed for dye adsorption study. Among various eluents 0.1 M HCl was one of the best eluent for desorption of MB loaded P-C hydrogel.

9. References

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