

Decolorization of Some Reactive Dyes Using Vegetable Extract

Anila Sameer¹, Saeed Umer Khan¹, Tehseen Ahmed¹, Humam Ahmed¹, Asad Khan Tanoli^{1*}, Amir Khan¹
Department of Chemistry, Faculty of Science, University of Karachi
asad.tanoli@uok.edu.pk

ABSTRACT

In this present study, an attempt was made to use the watery extract of most commonly use vegetables; onion (*Allium cepa.L*), potato (*Solanum tuberosum*) and garlic (*Allium sativum*) for the treatment of selected azo dyes. The selected azo-reactive dyes i.e. Jakofix-G yellow, Sumifix orange and Drimarene yellow are commonly used textile dyes. The vegetables extracts were made in the different ratio (v:v) for decolorization of these dyes. The reduction in the absorbance value of λ_{max} of these dyes indicates the decolorization. The color removal efficiency was calculated using change in the absorbance. It has been noted that garlic extract was able to decolorize dyes in high proportion as compared to onion and potato peel extract. All the color removal activity was done at the physiological pH of the selected vegetables. Furthermore, to uncover the nature of these reactive dyes, the solvatochromic behavior of the dyes were studies using solvent of different polarities.

Key words: Onion (*Allium cepa.L*), potato (*Solanum tuberosum*), garlic (*Allium sativum*), Azo dyes, decolorization

1. INTRODUCTION

Reactive and azo are extensively used category of dyes, not only in textile industry for coloring purpose but also in biomedical studies and advance application in organic synthesis^{1,2}. A number of reactive dyes are azo compounds that are linked by an azo group^{3,4}. Presence of aromatic groups and metal chlorides make reactive dyes toxic and direct threat to aquatic life⁵. Azo dyes can produce carcinogenic aromatic amines in the process of reductive degradation^{6,7}. High solubility, synthetic origin and complex aromatic molecular structure make their removal a very difficult task^{8,9}.

The main advantages of azo dyes that they have the tendency of degradation under aerobic condition. Below the anaerobic or micro aerobic subtractive bacteria, they will breed carcinogenic or lethal compounds that are harmful to the environment as well as human health². There are many physicochemical methods for degradation of dyes, but the aim of this study is to develop a method for the treatment of waste water to protect the ecosystem^{3,4}. This study ascertains the role of modern chemistry in society to treat textile waste water with different vegetable extracts⁵. For this purpose, synthetic dye solutions are prepared, which is usually use in dye industry and treated with different vegetable extract and the effect of decolorization was observed⁵. In some instance the oxidative enzymes have shown as an effective natural source of antioxidants and to degrade the recalcitrant pollutants^{6,7}. Phenolic compounds are also present in vegetable extracts which serves as major bioactive compounds⁸⁻¹¹. The use of vegetables and residue in the study is attractive, simple, cheap, easily accessible comparatively to other sophisticated and expensive methods and potentially important to reduce the pollution of food waste along with the peels are source of enzymes as some bioremediation treatments of decolorization and degradation process in textile industry¹².

2. Materials and Methods

2.1. Formation of vegetables extract

The selected vegetables (Onion, Potato and garlic) were purchased from local market, washed and grinded. The extract was prepared by weighing 10gm of grinded vegetables in 100 ml volumetric flask separately, water was used as a solvent. The supernatant was collected as a crude extract which is used for further process.

2.2. Decolorization of dyes using vegetables extract

For color removal efficiency, the fixed volume of selected vegetable extract (Onion, Potato and garlic) was mixed with a variable volume of selected dyes (Jackofix-G yellow, Sumifix orange and Dermarine yellow). The ratio was 1:1, 2:1, 3:1, 4:1 and 5:1 (v: v). Absorbance was recorded between 300 to 800 nm using UV-Vis spectrophotometer (Perkin-Elmer Lambda). The decolorization percentage was calculated as stated in equation-1¹³:

$$\% \text{ color removal efficiency} = \frac{A_o - A_t}{A_o} \times 100 \text{ ----- (1)}$$

Where A_o = initial absorbance and A_t = final absorbance.

2.3. Effect of Time on decolorization of dyes

Jackofix-G yellow, Dermarine yellow and Sumifix orange dyes were selected for this study. Each dye was mixed with fixed volume of selected vegetable extracts in ratio of 1:1, 2:1, 3:1, 4:1 and 5:1 (v: v) for time interval 10-30-40-50-60 minutes. Dye decolorization by selected vegetables (Onion, potato and garlic) was monitored at a specific wavelength. Untreated dyes were considered for the calculation of percent decolorization¹³.

2.4. Solvatochromic studies of dyes in different solvents

For solvatochromic studies of dyes, different solvents (ethanol, glycerol, CCl₄, dioxane and acetonitrile) were selected based on the polarity of selected dyes. The solution of each dye (A, B, C) was prepared in the series of different solvents in 25.0 ml volumetric flask and then further diluted with a fixed volume of dyes (A, B, C) and variable volume of selected solvents. Absorbance was recorded between 300 to 800 nm using UV-Vis spectrophotometer^{13,14}.

2.5. Effect of concentration on decolorization of dyes

The extract of selected vegetables as mentioned above were infused with increasing concentration of the three selected dyes (A, B, C) respectively for 1hr. Dye decolorization was observed at their individual wavelength maxima. The decolorization rate was calculated by taking untreated dyes as % removal¹³.

3. RESULTS AND DISCUSSION

3.1. Effect of time on decolorization of dyes using vegetables extract

Onion, garlic and potato were used in decolorization of dyes (A, B, C). The selected biological material is easily obtainable in native market throughout the year. Three reactive dyes were treated by keeping the volume of vegetables extract with increasing the volume of dyes. (Table 1). It has been noted that the color removal efficiency of three selected dyes is effectively increased in garlic extract at the ratio of 1:1. As compared to onion and potato peel extracts.

Table1: Color removal efficiency of dyes w.r.t ratios of selected vegetable extracts

Dyes	% color removal efficiency														
	Garlic Extract					Onion Extract					Potato peel Extract				
	1:1	2:1	3:1	4:1	5:1	1:1	2:1	3:1	4:1	5:1	1:1	2:1	3:1	4:1	5:1
Jackofix G yellow	87.02	22.42	13.56	8.45	8.47	11.81	14.59	21.42	33.81	5.29	46.41	22.94	14.71	10.90	7.93
Sumifix orange	81.85	61.90	49.03	19.44	17.24	41.73	50.79	29.68	24.15	21.64	12.77	16.87	19.93	79.39	11.54
Dermarine yellow	95.54	30.37	24.91	18.39	12.28	18.65	19.25	31.11	26.95	29.95	60.06	35.92	15.55	8.18	6.98

3.1. (a). Removal of dye A, B and C in onion extract

Five extraction ratios were considered to determine the best color removal efficiency of dyes A, B, C in onion extract. It has been noted in figure 1a that the dye B is decolorized by onion extract in a higher proportion that is 50.79% at ratio 2:1 as compared to dye A to 33.81% (4:1) and dye C to 31.11% (3:1) respectively. Similarly figure 2(a, b) and figure 3(a, b) shows the color removal efficiency of dye A and dye C by onion extract.

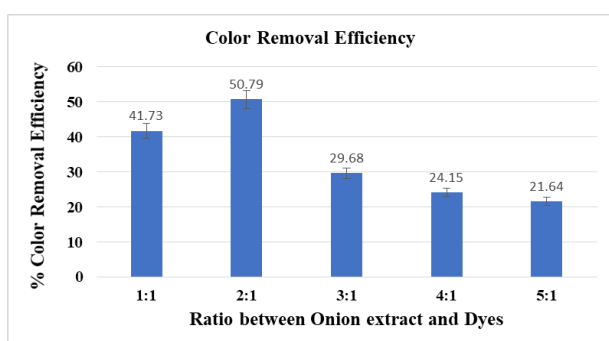


Fig-1a: Color removal efficiency of dye B by onion extract

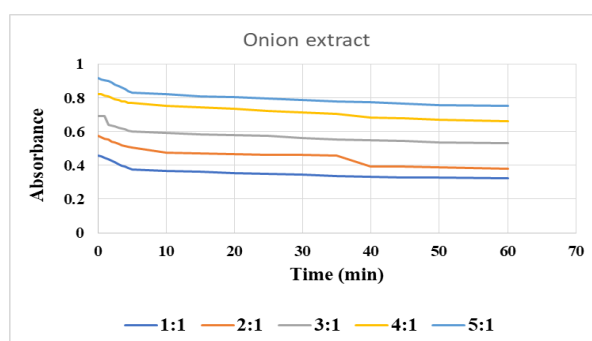


Fig-1b: Shows the absorption spectra of dye B at different interval of time w.r.t. ratios

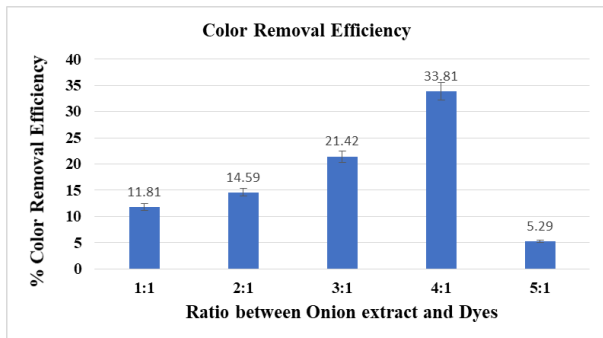


Fig-2a: Color removal efficiency of dye A by onion extract

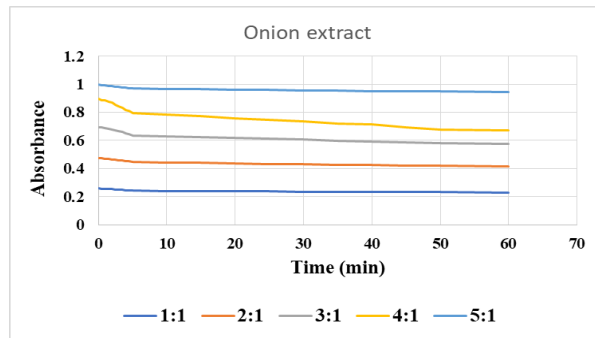


Fig-2b: Shows the absorption spectra of dye A at different interval of time w.r.t ratios

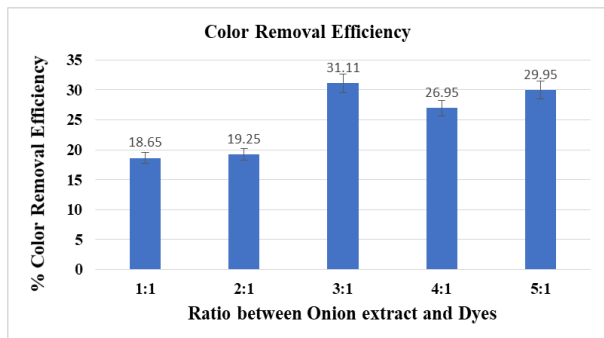


Fig-3a: Color removal efficiency of dye C by onion extract

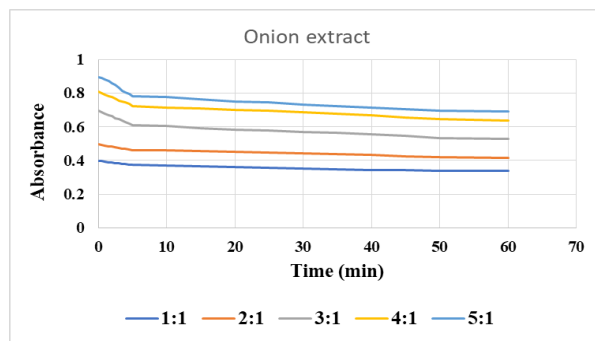


Fig-3b: Shows the absorption spectra of dye C at different interval of time w.r.t ratios

3.1. (b). Removal of dye A, B and C in Garlic extract

As shown in table 1, five extractions ratio was studied to observe the percent decolorizing rate of selected reactive dyes (A, B, C) in garlic extract. According to above-mentioned data, the higher the proportion of color removal efficiency was seen in dye C that is 95.54% at the ratio of 1:1. The other two dyes A and B were able to decolorize 87.02% and 81.85% respectively at a similar ratio. The graphical result of three dyes (A, B, C) is shown in figures 4, 5 and 6.

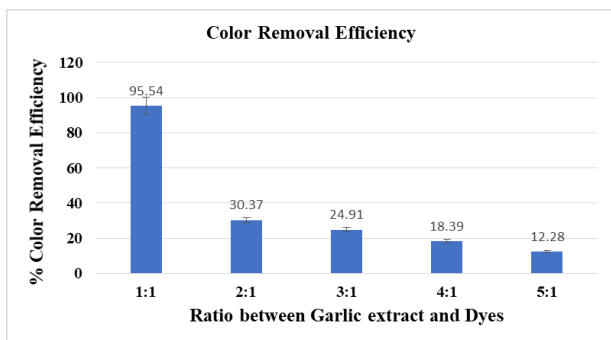


Fig-4a:Color removal efficiency of dye C by garlic extract

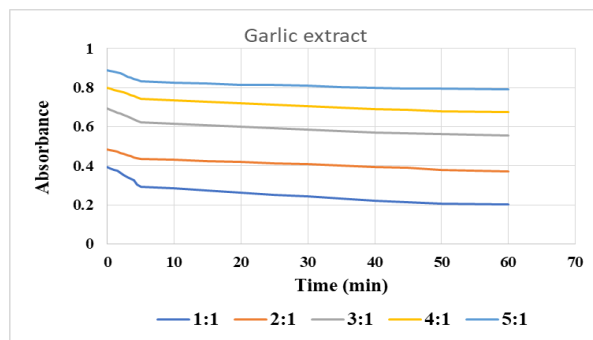


Fig-4b: Shows the absorption spectra of dye C at different interval of time w.r.t ratios

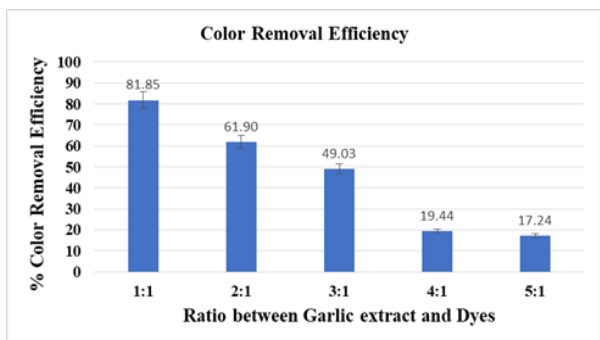


Fig-5a: Color removal efficiency of dye B by garlic extract

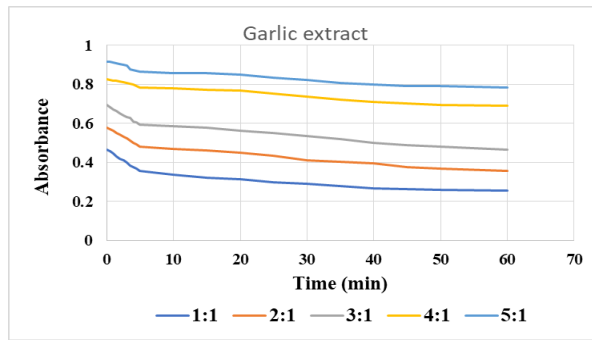


Fig-5b: Shows the absorption spectra of dye B at different interval of time w.r.t ratios

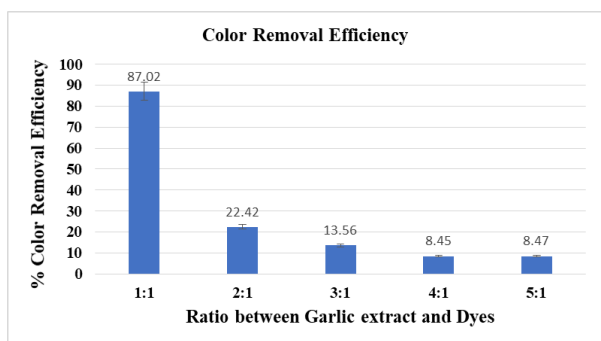


Fig-6a: Color removal efficiency of dye A by garlic extract

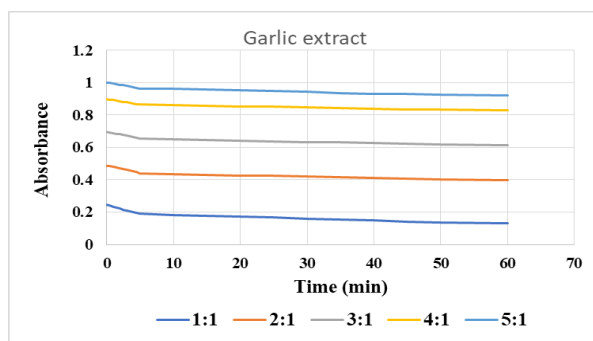


Fig-6b: Shows the absorption spectra of dye A at different interval of time w.r.t. ratios

3.1. (c). Removal of dye A, B and C in potato peel extract

The color removal efficiency in three selected dyes (A, B, C) in potato peel extract was evaluated in five extraction ratio, it has been noted that in figure 7 the potato peel extract was able to decolorized the dye B in higher amount i.e. 79.39% at a ratio 4:1 as compared to dye A to 46.41% and dye C to 60.06% at a same ratio of 1:1 (Fig. 8 & 9).

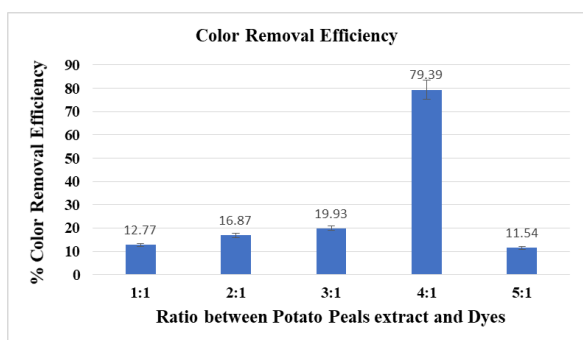


Fig-7a: Color removal efficiency of dye B by potato peel extract

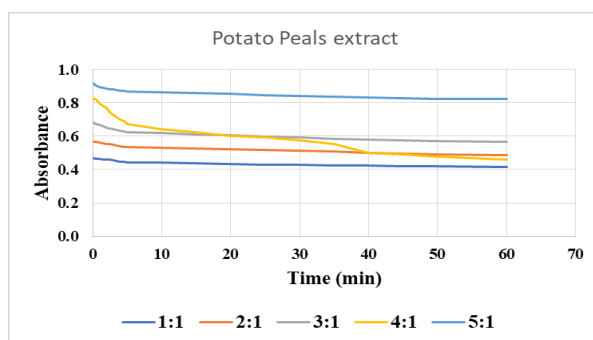


Fig-7b: Shows the absorption spectra of dye B at different interval of time w.r.t. ratios

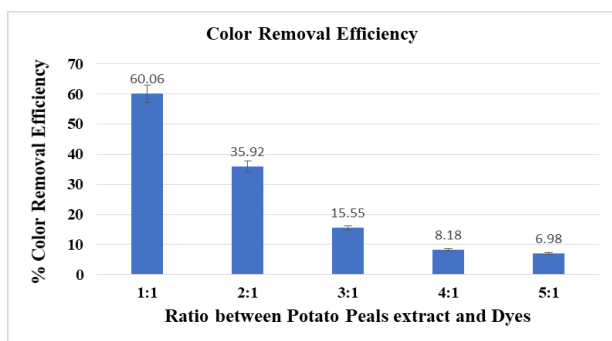


Fig-8a: Color removal efficiency of dye C by potato peel extract

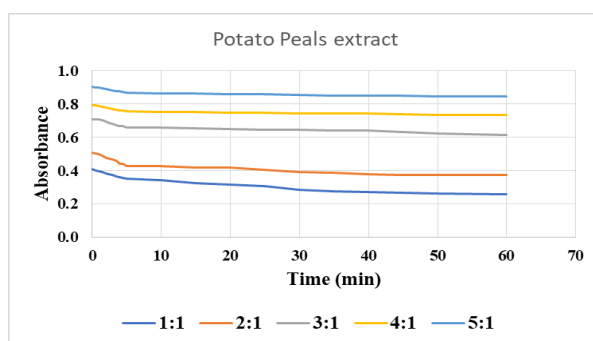


Fig-8b: Shows the absorption spectra of dye C at different interval of time w.r.t. ratios

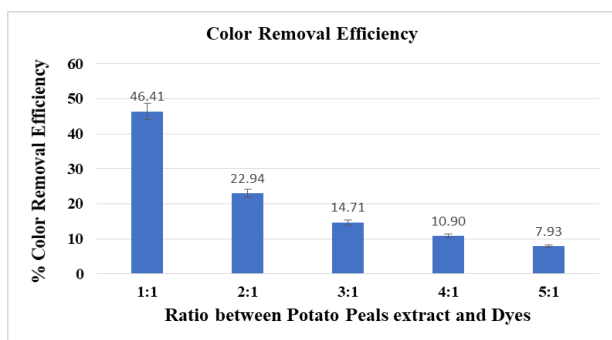


Fig-9a: Color removal efficiency of dye A by potato peel extract

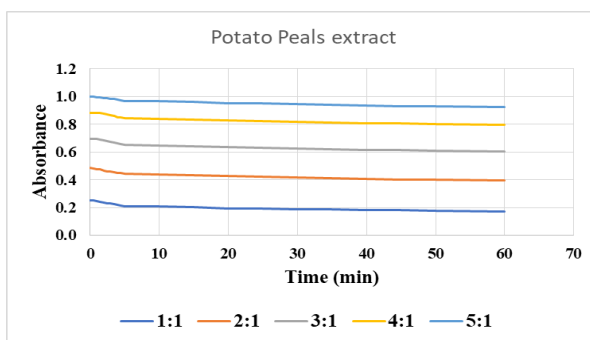


Fig-9b: Shows the absorption spectra of dye A at different interval of time w.r.t. ratios

3.2. Effect of concentration on decolorization of dyes

Table 2: % color removal efficiency of dyes at different concentration in 1 hour

Conc. of dyes in ppm	% color removal efficiency in 60 minutes
10	1.28
20	11.92
30	11.03
40	23
50	22.5

The data shown in above-mentioned table (2) shows that the percent color removal efficiency of selected dyes at 40 ppm were high as compared to 10, 20, 30 and 50 ppm for 60 minutes.

3.3. Solvatochromic studies of dyes in different solvents

3.3. (a). Analysis of dye A in binary solvent system

The spectrophotometric analysis of dye A in a binary solvent system was carried out in different water organic solvents. As shown in figure 10, the solvatochromic behavior of these solvents in the presence of dye A changes in the absorption intensity as a function of solvent mixtures. The spectra of those solvents show that it is greatly dependent on the solute-solvent interactions, and ultimately these interactions are affected by the photo physical nature of water-organic solvent mixture¹⁵. It has also been noted that in the presence of water molecule, the dielectric constant of the medium also increases and it also effect on the intensity, coordination property and spectroscopic properties of a solvent, absorption intensity values at different mole fraction are listed in table 3.

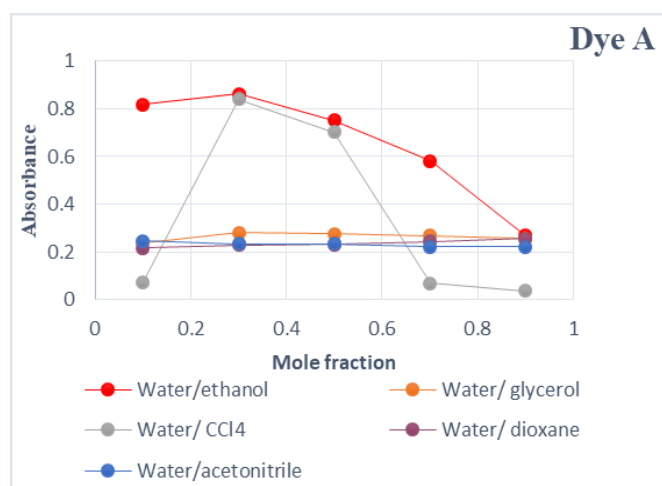


Fig-10: Analysis of dye A in binary solvent system

Table 3: Analysis of dye A in binary solvent system

Absorbance	Mole fraction				
	0.1	0.3	0.5	0.7	0.9
Water/ ethanol	0.817	0.863	0.751	0.582	0.269
Water/ glycerol	0.239	0.28	0.275	0.268	0.257
Water/ CCl ₄	0.075	0.84	0.702	0.069	0.036
Water/ dioxane	0.217	0.228	0.231	0.244	0.256
Water/ acetonitrile	0.247	0.235	0.233	0.222	0.221

3.3. (b). Analysis of dye B in binary solvent system

Table 4: Analysis of dye B in binary solvent system

Absorbance	Mole fraction				
	0.1	0.3	0.5	0.7	0.9
Water/ ethanol	0.763	0.919	0.754	0.631	0.342
Water/ glycerol	0.531	0.488	0.416	0.412	0.394
Water/ CCl ₄	0.098	0.77	0.448	0.406	0.336
Water/ dioxane	0.139	0.255	0.323	0.353	0.378
Water/ acetonitrile	0.3835	0.474	0.451	0.435	0.412

The data shown in above-mentioned table 4 shows that various water mixture organic solvents like water/ ethanol, water/ glycerol, water/ CCl₄, water/ dioxane and water/ acetonitrile were studied for the spectrophotometric analysis of dye B in binary solvent system. The solvatochromic behavior of these solvents in the presence of dye B changes in the absorption intensity as a function of solvent mixtures in different mole fractions. The absorption spectra, (Fig. 11)

shows that in order to improve the physical and chemical property of dye B, the mixtures of these water-organic solvents can be considered as an alternative method because the presence of binary compound (water) in organic solvents affects directly on physical and chemical behavior, and as a result changes the photo physical properties within the binary mixtures of solvent¹⁵.

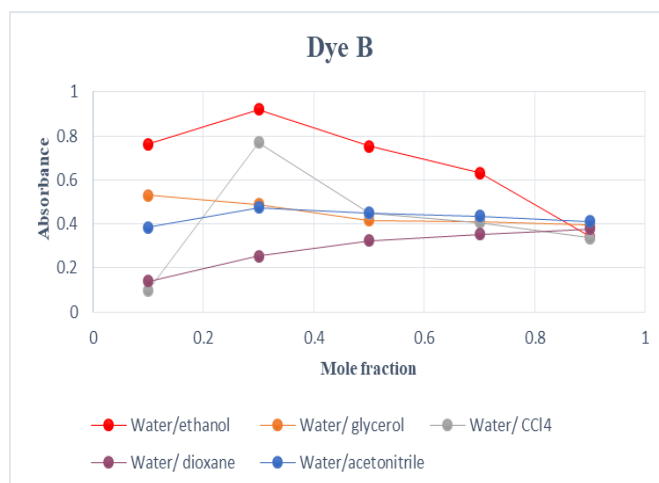


Fig-11: Analysis of dye B in binary solvent system

3.3. (c). Analysis of dye C in binary solvent system

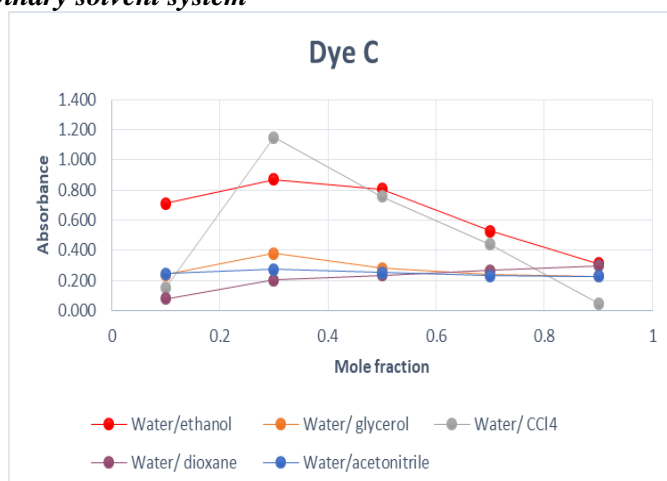


Fig-12: Analysis of dye C in binary solvent system

The analysis of dye C has been done in a binary solvent system. Different solvent was selected for this study at five different mole fraction as shown in table 5. The changes in absorption intensity as a function on the solvent mixtures can be observed in the absorption spectra (Fig 11). The water/ CCl_4 intensity is higher than other water/ organic solvent at the mole fraction 0.3 of dye C within the binary solvent system¹⁴⁻¹⁸. The physical and chemical property of dye C (solute) together with the polarity, protic and non-protic behavior noticed much cleared solvatochromic impact.

Table 5: Analysis of dye C in binary solvent system

Absorbance	Mole fraction				
	0.1	0.3	0.5	0.7	0.9
Water/ ethanol	0.710	0.871	0.806	0.529	0.311
Water/ glycerol	0.238	0.379	0.280	0.240	0.226
Water/ CCl_4	0.154	1.148	0.756	0.438	0.046
Water/ dioxane	0.077	0.203	0.235	0.265	0.296
Water/ acetonitrile	0.243	0.273	0.253	0.232	0.227

4. References

- [1]. Sarina, J.E.M., M.T. Brian and A.R.M. Reckhow. Evaluation of water reuse technologies for the textile industry. *Journal of Environmental Engineering*, (2006), 3: 315- 322.

- [2]. Chung, K. T. Azo dyes and human health: a review. *Journal of Environmental Science and Health, Part C*, (2016),34: 233-261. <https://doi.org/10.1080/10590501.2016.1236602>
- [3]. Wilson, M., McNab, R., & Henderson, B. Bacterial disease mechanisms: an introduction to cellular microbiology. *Cambridge University Press*. (2002).
- [4]. Robinson, T., McMullan, G., Marchant, R., & Nigam, P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource technology*, (2001), 77: 247-255. [https://doi.org/10.1016/S0960-8524\(00\)00080-8](https://doi.org/10.1016/S0960-8524(00)00080-8)
- [5]. Comninellis, C., Kapalka, A., Malato, S., Parsons, S. A., Poulios, I., & Mantzavinos, D. Advanced oxidation processes for water treatment: advances and trends for R&D. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, (2008), 83: 769-776. <https://doi.org/10.1002/jctb.1873>
- [6]. Anjaneyulu, Y., Chary, N. S., & Raj, D. S. S. Decolourization of industrial effluents—available methods and emerging technologies—a review. *Reviews in Environmental Science and Biotechnology*, (2005), 4: 245-273. <https://doi.org/10.1007/s11157-005-1246-z>
- [7]. Rao, M. A., Scelza, R., Scotti, R., & Gianfreda, L. Role of enzymes in the remediation of polluted environments. *Journal of soil science and plant nutrition*, (2010), 10: 333-353. <http://dx.doi.org/10.4067/S0718-95162010000100008>
- [8]. Gianfreda, L., Iamarino, G., Scelza, R., & Rao, M. A. Oxidative catalysts for the transformation of phenolic pollutants: a brief review. *Biocatalysis and biotransformation*, (2006), 24: 177-187. <https://doi.org/10.1080/10242420500491938>
- [9]. Ajila, C. M., Naidu, K. A., Bhat, S. G., & Rao, U. P. Bioactive compounds and antioxidant potential of mango peel extract. *Food chemistry*, (2007), 105: 982-988. <https://doi.org/10.1016/j.foodchem.2007.04.052>
- [10]. Ignat, I., Volf, I., & Popa, V. I. A critical review of methods for characterization of polyphenolic compounds in fruits and vegetables. *Food chemistry*, (2011), 126: 1821-1835. <https://doi.org/10.1016/j.foodchem.2010.12.026>
- [11]. Balasundram, N., Sundram, K., & Samman, S. Phenolic compounds in plants and agri-industrial by-products: Antioxidant activity, occurrence, and potential uses. *Food chemistry*, (2006), 99: 191-203. <https://doi.org/10.1016/j.foodchem.2005.07.042>
- [12]. Babbar, N., Oberoi, H. S., Uppal, D. S., & Patil, R. T. Total phenolic content and antioxidant capacity of extracts obtained from six important fruit residues. *Food Research International*, (2011), 44: 391-396. <https://doi.org/10.1016/j.foodres.2010.10.001>
- [13]. Solís, A., Perea, F., Solís, M., Manjarrez, N., Pérez, H. I., & Cassani, J. Discoloration of indigo carmine using aqueous extracts from vegetables and vegetable residues as enzyme sources. *BioMed research international*, (2013),2013: 1-6. <http://dx.doi.org/10.1155/2013/250305>
- [14]. Homocianu, M. Solvent effects on the electronic absorption and fluorescence spectra. *Journal of Advanced Research in Physics*, (2011), 2(1).
- [15]. Tanoli, M. A. K., Khan, Z., Maqsood, Z. T., Kamal, T., Khan, K. M., & Ahmed, T. Electronic Spectrum of different Bis-Schiff bases of Isatin and its Solvatochromism. *Pakistan journal of chemistry*, (2014), 4, 124-131.
- [16]. Van Driessel, B., & Christov, L. Decolorization of bleach plant effluent by mucoralean and white-rot fungi in a rotating biological contactor reactor. *Journal of bioscience and bioengineering*, (2001), 92(3), 271-276. [https://doi.org/10.1016/S1389-1723\(01\)80261-9](https://doi.org/10.1016/S1389-1723(01)80261-9)
- [17]. Yuan, X., Tian, G., Zhao, Y., Zhao, L., Wang, H., & Ng, T. B. Degradation of dyes using crude extract and a thermostable and pH-stable laccase isolated from *Pleurotus nebrodensis*. *Bioscience reports*, (2016) 36(4), 365-371. <https://dx.doi.org/10.1042/BSR20160163>
- [18]. Van Driessel, B., & Christov, L. Decolorization of bleach plant effluent by mucoralean and white-rot fungi in a rotating biological contactor reactor. *Journal of bioscience and bioengineering*, (2001), 92(3), 271-276. [https://doi.org/10.1016/S1389-1723\(01\)80261-9](https://doi.org/10.1016/S1389-1723(01)80261-9)