Journal of Faculty of Engineering & Technology

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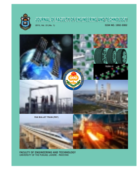

RIDDANCE OF SPENT DYE FROM TEXTILE RUNOFF

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Abstract

Textile effluents contain toxic and non-bio-degradable contents due to the high concentration of residual dyes. They impart colour to the waste water which hinders sunlight penetration and disturbs the ecosystem of water. The treatment of the textile waste water with biodegradable polymers has attained a vital importance as they are more environmental friendly and the sludge produced is bio-degradable due to their organic composition and may act as a nutrient for the micro-organisms. The aim of present experimental investigations was to make an effort to develop a feasible process for the removal of reactive dyes from the textile waste water using a plant based polymer (Potato Starch). Coagulation/flocculation studies were performed on a lab scale using jar-test apparatus. The dye removal was determined in terms of percentage reduction in turbidity of the treated solution. The effect of parameters, like coagulant dosage, temperature and pH, on percentage turbidity reduction, total dissolve solids (TSD) reduction and Sludge volume index (SVI) were graphically represented and critically discussed. The results indicate that the maximum dye removal was observed up to 36 %.

Keywords: Poly-saccharide, Potato starch, Reactive dye, Coagulation/Flocculation, Dye removal.

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1. Introduction

Textile, an eminent industrial sector, subsidizes 64 % of Pakistani export [1]. Consequently, due to the increasing demand of textile commodities, the textile industry has been growing proportionally. In addition, textile effluents contain toxic and non-bio-degradable contents caused by the high concentration of residual dyes. It can impart colour to the wastewater and hinder sunlight penetration results in perturbation of aqua-system. Moreover, due to the inefficient dyeing system, large bulks of dye are released into natural watercourses. It has been estimated that 50 % (approximately) of reactive dyes may be lost directly into waterways [2]. Reactive dyes are usually high molecular weight structured polymers that are difficult to decompose biologically. It may also be challenging if these dye are broken down an-aerobically due to the formation of toxic amines. In addition, other breakdown products of dyes are noxious and mutagenic to life [3]. Consequently, efforts have been made for the removal of spent dye from textile effluents using different processes, like chemical oxidation [4], filtration [5], bacterial decolorization [6] etc. However, coagulation and flocculation has proved to be simpler, cost effective and environmental friendly [7].

A variety of in-organic salts like aluminum chlorides and sulfates has been investigated as coagulants but they are now controversial due to the possible link of Alzheimer disease [8]. However, biopolymers, like Chitosan (animal based), Xanthan gum (microorganism base) and Guar gum (plant based), can be an attractive coagulant owing to its specific structure, physio chemical properties and high reactivity towards aromatic compounds and metals, which are eminent parts of reactive dyes. In addition, the biopolymers have the ability to associate by physical and chemical interactions with a wide variety of molecules [9]. It has been reported that there is a large swing of pH during cotton dying process through reactive dyes. So, it can limit the conventional biological and chemical treatment for dye removal [1]. Therefore, coagulation using bio-polymers has gained a vital importance as it may not disturb the pH of water body. A large numbers of plant extracted polymers have been investigated as coagulants by various researchers like turbidity of kaolin solution was reduced to 80% when a polymer extracted from strychnos potatorum (Nirmali) seeds was used as a coagulant [10]. Furthermore, M. oleifera seed extract was investigated for elimination of anthraquinone based reactive dye. It was, further, reported that the removal of dye was 95% when the coagulant dose and pH was kept at 100 mg/L and 7, respectively [11]. Later on, Lea in 2010 has also investigated the effectiveness of M. oleifera seed extract for the treatment of turbid water was examined and it was found that the turbidity removal was 99.5% at the dosage of 400 mg/L [12]. So, it can be concluded from the aforementioned discussion that it is eminent to refine the textile effluent so that the aquatic cycle may not be disturbed. Among the treatment processes, coagulation flocculation can be an effective choice. Moreover, owing to low cost, easily availability and biodegradability, plant based polysaccharide, i.e. potato starch, was used during current experimental investigations as a coagulant for removal of reactive dye from its solution. It may be act as a replacement of conventional biopolymers, like seeds extracted from strychnos potatorum and drumstick tree. Moreover, potato starch does not alter the pH of the solution, which other conventional coagulants may do [13]. Consequently, it makes potato starch a better choice as it can reduce the cost of pH adjustment. In addition, the sludge form as a result of coagulation flocculation process is biodegradable as the potato starch is biodegradable itself. This is in agreement with proposals from the literature [14].

2. Materials & Methodology

2.1 Materials

During present experimental investigations, the known concentrations (mentioned in Table 3) of Yellow reactive dye, which was supplied by Sandal Dye & Dye Stuff Industries Private Limited, was used due to the fact that the reactive class of dye has frequently been use for cotton fabric dying in Textile units [15]. The properties and characterization of dye has been depicted in Table The structure of dye as provided by society of dyes and colorist has been reported in Figure 1. Extracted potato starch, $(C_6H_{10}O_5)_n$, of reagent grade, was purchased from Deajung Chemicals & Metals Co. Ltd. Korean. The typical specifications of potato starch have been represented in Table 1.

Table 1: Properties of reactive dye and potato starch as reported by manufacturers

Dye	Reactive Yellow, MERL
CAS Registry Number	93050-80-7
C.I. Number	Y-145A
Molecular structure	Single AZO class
Molecular weight	1026.25
Molecular formula	$C_{28}H_{20}ClN_9Na_4O_{16}S_5$
Functional Groups	Bi-functional
	(Mono-chloro-triazine and Vinyl Sulfone)
Solubility	80 g\L
Use	Dying
Potato starch	
Molecular formula	$[C_6H_{10}O_5]_n$
Molecular weight	342.296 g/mol
Specific gravity	1.65

C.I. = Color Index, CAS = Chemical Abstract Service,

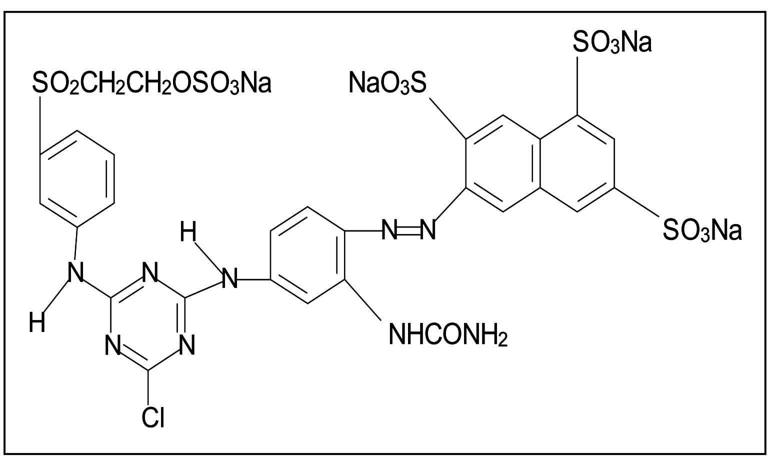

Figure 1: Chemical Structure of reactive dye [16]

2.2 Synthetic solution

A synthetic solution of dye was prepared rather than collecting spent dye solution from any dye house, so that the external disturbances can be reduced. The initial dye concentration of dye was fixed at 150 $mg.dm^{-3}$ as it was believed to be a typical high value of dye concentration in textile effluent [17]. The synthetic solution was prepared by dissolving known weight of dye (150 $mg.dm^{-3}$) in RO water. 10 gdm^{-3} of sodium carbonate was added and then solution is heated to 60 °C for 60 minutes. During heating, the value of pH of the solution was raised to 10.5 by the addition of 1N sodium hydroxide solution. The procedure for the preparation of synthetic dyeing effluent was in agreement with the reported method in literature [18].

2.3 Testing

The filtered stock solution was analyzed for turbidity using DRT 100B/HF Turbidity meter as the percentage reduction in turbidity can be co-related with the reduction in color [19]. The maximum turbidity (measured in Nephlometric turbidity units, NTU) of each filtered stock solution batch was determined for the reference, i.e. in the range of 1.2 to 8.5. Total dissolved solids (TDS) were determined using a standard JENWAY PCM3 meter. Further, pH of the solution was also measured by using a digital pH meter CORNING-440. The calibration of the pH meter was performed with the help of buffer solutions having pH 4.0 and 7.0 prior to start the tests. The results, along with its coding, have been depicted in Table 2.

Table 2: Characteristics of stock solutions prior to experimentations

Code	**Turbidity**	**TDS**	**pH**
	NTU	ppm of CaCO3	
S1	3.5	11150	10.33
S3B	8.5	11410	10.87
S37	5.2	11060	7.22
S27	1.2	10970	7.29
S4A	4	10520	3.19

NTU = Nephlometric Turbidity Unit, TDS = Total dissolved solids, ppm = parts per million

2.4 Experimental procedure

The effect of coagulation flocculation parameters, like pH, coagulant dosage and temperature on turbidity (an indication of dye removal), sludge volume index (SVI) and total dissolved solid (TDS) were determined using a series of experiments based on three-level factorial design, see Table 3. During each set of experiments, in coagulation phase, the stirring rate was kept at 200 rpm for 5 minutes. It was then slow down to 40 rpm for half an hour during second phase of the examination, i.e. flocculation phase. It was reported that the longer mixing time can cause flock's breakage as a consequent the rate of flocculation would reduce. In contrast, if the mixing time was too short, the collusions between the flocculants and colloids were inefficient to precipitate the suspended solids [19]. A blank Run was conducted using distilled water and colour intensity was recorded, for reference, before conducting the experimentations with the synthetic stock solution. The coagulation-flocculation tests were performed in a jar test apparatus [8]. 1 liter of stock solution was poured into the beaker and mixed homogeneously after the addition of fixed quantities of from 0.5 to 2 % (by weight) of potato starch as coagulant, see Table 3. The pH of the solution was controlled at 3 by the adding either acid (1N HCl) or base (1N NaOH) solution. As mentioned earlier, the solution was, initially, agitated at 200 rpm for 5 minutes and then at 40 rpm for 30 minutes. Afterwards, the agitation was stopped; the suspension was allowed to settle down for half an hour. A pipetted sample was drawn from the top inch of supernatant and the dye removal was measured by calculating the reduction in the value of turbidity. The scheme of the experimental procedure has been represented in Figure 2.

Table 3; Parametric levels and their limits for the application of three level full factorial design

Symbol	Parameter	Parameter Level		
		Low	**Medium**	**High**
		0	**1**	**2**
A	Coagulant Dosage (% w/v)	0.5	1	2
B	pH of waste water sample	3	7	10
C	Temperature of waste water (^{0}C)	25	40	55

The sludge volume index (SVI), introduced by Mohlman in 1934, can be defined as the volume of sludge in milliliters occupied by 1 g of a suspension after 30 min settling [20]. Further, SVI is an empirical measurement technique and can provide a rough estimate of sludge settling ability. It is frequently used in everyday operation of waste water treatment units and measuring the physical condition of sludge SVI and sludge density index (SDI). Both of these can be calculated using equation (1) and equation (2), respectively. The experiments were repeated by altering the pH, coagulant dosage and temperature to determine the effects of process parameters on SVI, TDS and turbidity.

$$\mathrm{SVI}\left(\frac{\mathrm{mL}}{\mathrm{gm}}\right) = \frac{\frac{\text{Setteled sludge volume (mL)}}{\text{Volume of sample (L)}}}{\text{Total suspended solids}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right)} * 1000\left(\frac{\mathrm{mg}}{\mathrm{gm}}\right) \quad (1)$$

$$\mathrm{SDI}\left(\frac{\mathrm{gm}}{\mathrm{mL}}\right) = \left(\frac{1}{\mathrm{SVI}}\right) * 100 \quad (2)$$

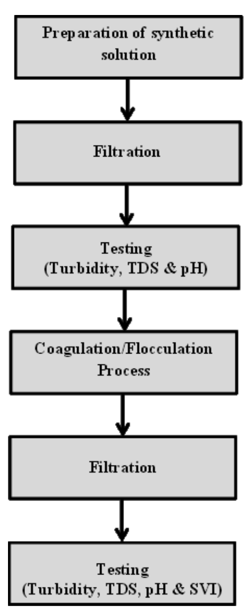

Figure 2: Schematic diagram of experimental procedure

3. Result and Discussion

As discussed in previous sections that the current experimental investigations are composed of the removal of reactive dye through coagulation-flocculation technique when potato starch, a plant based biopolymer, was selected as a coagulant. Furthermore, the experiments have been performed in a jar test apparatus. In proceeding section, the effect of parameters (i.e. temperature, pH and coagulant dosage) on turbidity, total dissolved solids (TDS) and sludge volume index (SVI) were determined, graphically reported and critically discussed.

3.1 Effect on Turbidity

Residual turbidity of textile waste water is considered as the most eminent parameter, so it has been used as an indicator of the dye removal [19].

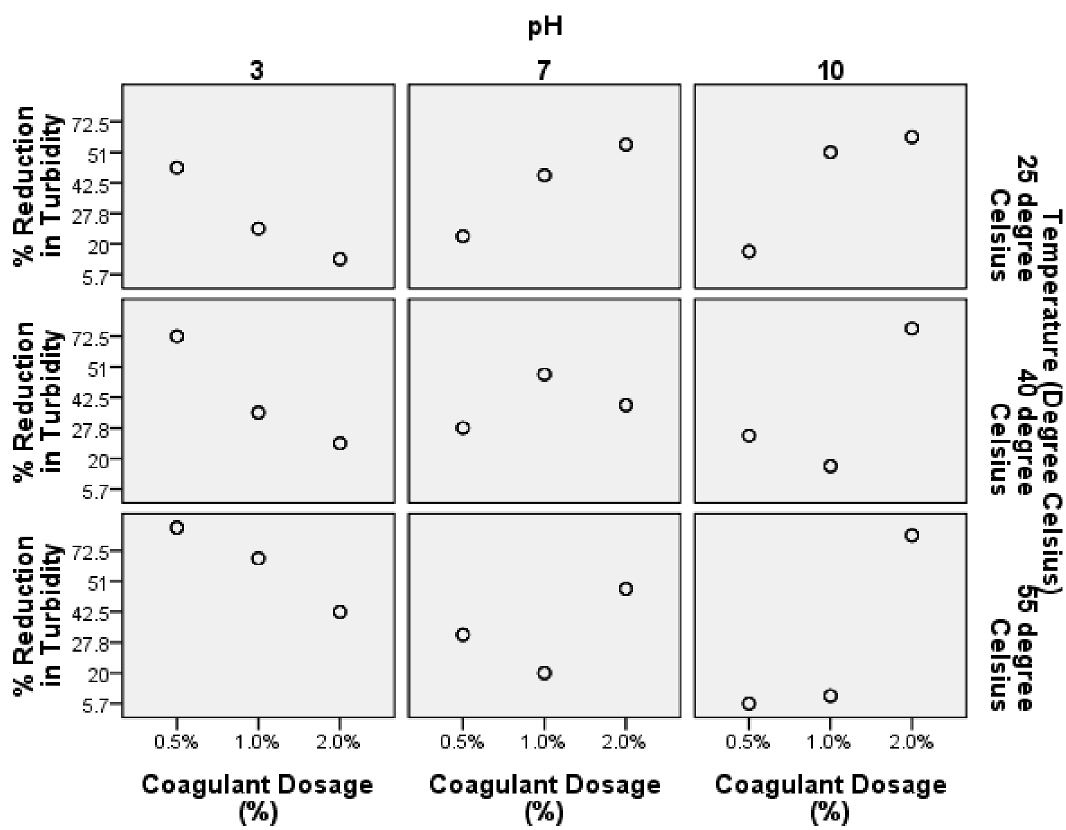

Figure 3: Effect of coagulant dosage, pH and coagulation temperature on percentage turbidity reduction

3.1.1 Effect of dosage in acidic Region

The effect of coagulant dosage on the percentage reduction can be perceived, see figure 3, that at low dosage of potato starch the turbidity reduction is high as compared to that of high coagulant dosage at low pH. Furthermore, it has been reported that, at low pH, most of the functional groups present on the surface of biopolymer, i.e. potato starch, becomes protonate. As a consequence, biopolymer is positively charged and behaved like a cationic polyelectrolyte [21]. It leads to the deduction that with the increment of the biopolymer, the percentage reduction of the dye may increase. But the experimental results contradict the aforementioned argument. It is due to the fact that, at low pH, electrostatic forces between the polyelectrolyte molecules dominate. Therefore, an excess polymer dosage results in the production of re-stabilized colloids which, due to low pH, becomes positively charged and cause the electrostatic repulsion among the suspended solids [22]. As a consequence, the dye removal increases at low coagulant dosage.

3.1.2 Effect of dosage in basic region

In contrary to the previous section, as the coagulant dosage increases the percentage dye removal also increases at a certain value of temperature when pH was kept at 10. It is due to the fact that, at high pH, negative charges appear on the coagulant surface. These negatively charged sites interact with the positive functional groups of dye. It can be noticed (Figure 3) that increasing the dosage of coagulant increases the dye removal. It may be due to the adsorption nature of coagulant, i.e. potato starch. As the concentration of potato starch increases the number of dye adsorption sites also increases that leads to high percentage removal of dye component. [22]. Therefore, this signifies the rapid destabilization of the particles. Further, textile effluent from dye section is almost at pH = 10 and treating the waste at the same pH is more economical and cost effective

3.1.3 Effect of dosage in neutral region

It can be deduced from Figure 3 that the effect of coagulant dosage on percentage dye removal is unpredictable. It can be due to hydrogen bonding, i.e. potato starch contains active hydroxyl group which involve in hydrogen bonding. As a consequence, polymer coiling may occur that can reduce the availability of active site which interact the dye molecules [8].

3.1.4 Effect of Temperature

The effect of temperature at specific value of coagulant dosage has been depicted in figure 3. It can be deduced that as the coagulation temperature increases the percentage turbidity removal also increases at particular dosage of potato starch. The reason may lies in the specific structure of potato starch. It has been reported that there are 11 hydrogen ion acceptor and 8 hydrogen ion donor sites are available on the potato starch surface . So, in acidic region, low pH further empowers the hydrogen ion donors, which results in the significant removal of dye at room temperature. Moreover, with the increment in the value of temperature leads to the breakage of polymer chain. As a consequence, a large number of sites are available on the potato starch to interact with dye. Therefore, at high temperature, percentage reduction in turbidity increases at particular coagulant dosage [18].

3.2 Effect on TDS

The percentage reduction in total dissolved solids (TDS) has also been considered as a supporting parameter with the residual turbidity. The percentage reduction in turbidity is expected to be correlated to TDS as the statistical analysis revealed a strong positive Pearson correlation coefficient (equation 3) of 0.956. Figure 4 depicts the effects of different parameters on the percentage reduction of TDS levels. Almost similar trends for the reduction in TDS were observed.

$$R = \frac{\sum \frac{(X - Mx)}{(Y - My)}}{\sqrt{(SSx)(SSy)}} \quad (3)$$

Where R is the Person correlation factor. X and Y are the percentage reduction in turbidity and TDS respectively. M_X and M_Y are mean of X and Y. SS_X and SS_Y are the sum of squares of X and Y. So, $X\text{-}M_X$ and $Y\text{-}M_y$ are the deviation scores. The effect of Coagulation conditions and coagulant dosage on the TDS has been reported graphically in Figure 5. As the TDS increases with the increment in the percentage recovery of turbidity see figure 4. Consequently, the effect of temperature, pH and percentage dosage of potato starch show similar trend as percentage turbidity reduction.

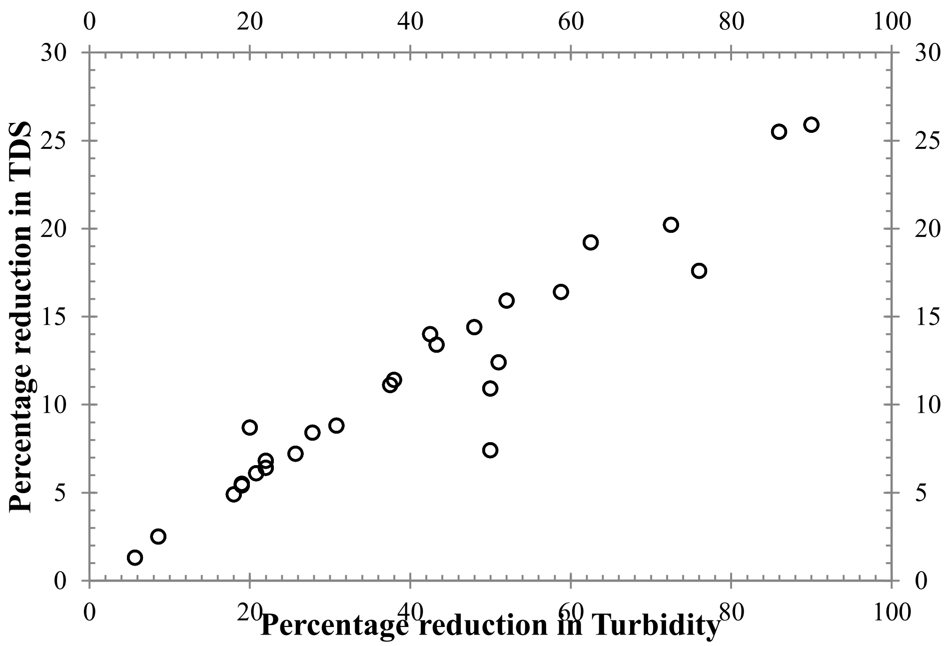

Figure 4: Graphical Co-relation between percentage turbidity reduction and percentage TDS reduction

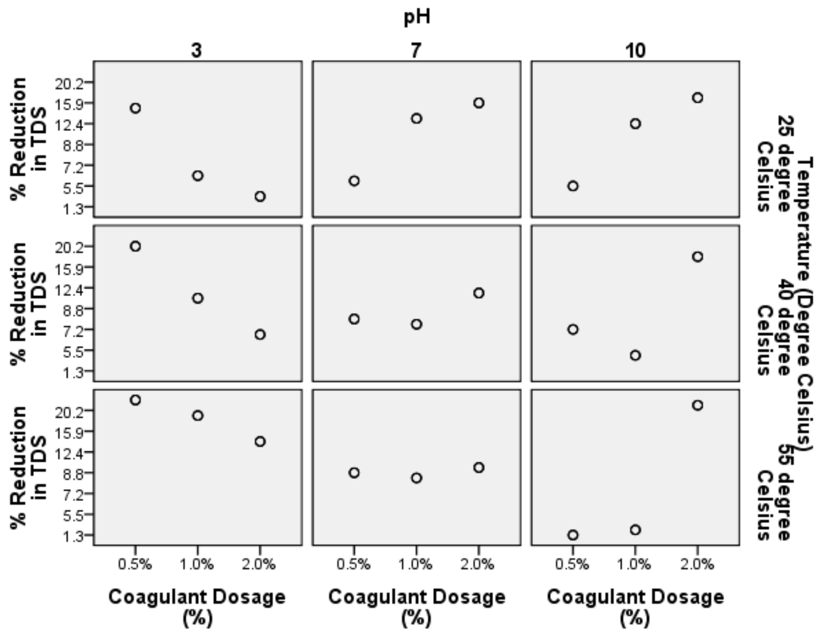

Figure 5: Effect of coagulant dosage, pH and coagulation temperature on total dissolved solid (TDS)

3.3 Effect on Sludge formation

The Figure 6 deflects the effect of coagulation parameters on the formation of sludge by sludge volume index (SVI). In combination with Figure 3, it can be deduced that the values of SVI were higher at those parameters where percentage turbidity was adequate in neutral and basic regions, i.e. high coagulant dosage produced high SVI value. In contrary, at acidic region, it can be observed that there were relatively high values of SVI at low coagulant dosage. As explained in previous section, it may be due to the fact that low coagulant dosage was favorable for percentage reduction in turbidity, consequently, the amount of SVI increased. Moreover, at low pH, excess amount of coagulant can produce restabilized colloids which may cause electrostatic repulsion among the suspended solids. So, the value of SVI decreased in acid region at high coagulant dosage.

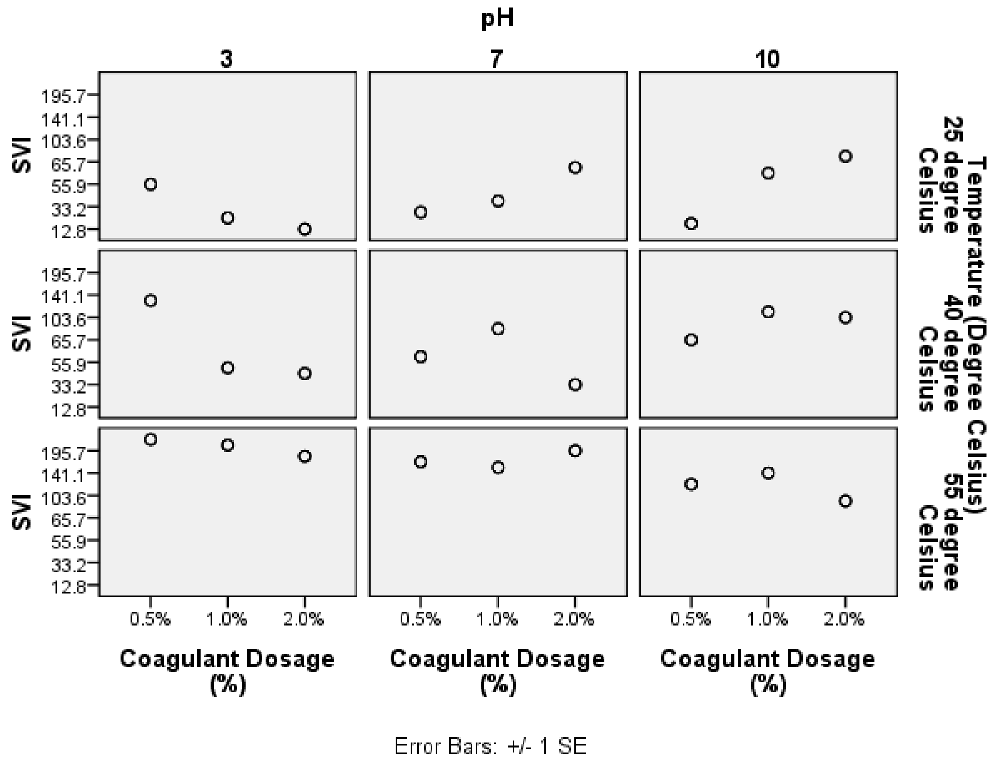

Figure 6: Effect of coagulant dosage, pH and coagulation temperature on sludge volume index (SVI)

Conclusions

The present experimental investigations composed of removal of the spent dye from synthetic textile waste water through coagulation/flocculation process. Potato starch, a biodegradable and environmental friendly polymer, was utilized as coagulant. Further, the impact of coagulation parameters, like coagulant dosage, temperature and pH, were investigated on percentage turbidity reduction, SVI and TDS. It can be concluded that:

- Low coagulant dosage favors the percentage turbidity reduction of the solution, i.e. higher dye removal when the pH of the solution lies in acidic region. In contrary, the dye removal was observed to be better at high coagulant dosage at basic region. Moreover, the pH of the textile effluent is already within basic region. Therefore it is more economical to treat dye solution at high pH. The effect of coagulant dosage within neutral region was not straightforward and further experimental investigations would be required to explain the facts. Increasing temperature resulted high dye removal as compared to low temperature. It is because the polymer chain of coagulant, i.e. potato starch, breaks at elevated temperature. So, more sites may be available to react with the dye molecule. Consequently, the percentage reduction in turbidity, i.e. dye removal increases.
- There is a strong Pearson correlation coefficient, i.e. 0.956, between percentage reduction in TDS and percentage reduction in turbidity. So, as the dye removal increases the TDS in the treated solution also decreases.

- Sludge volume index (SVI) can be related with coagulant dosage. High coagulant dosage results in the high value of SVI in basic and neutral region. While, at low pH, low coagulant dosage resulted in high SVI as compared to that of high coagulant dosage. It is due to the formation of restabilized colloids at high coagulant dosage, consequently, the SVI value decreases.

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