



PHOSPHONIUM-BASED IONIC LIQUIDS AND THEIR APPLICATION IN SEPARATION OF DYE FROM AQUEOUS SOLUTION

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ABSTRACT

In this study, phosphonium-based hydrophobic ionic liquids were synthesized and confirm their structures by NMR, FT-IR and CHNS. Their thermal stability was studied by thermo gravimetric analysis (TGA) and shows excellent thermal stability as compare to other ILs. Comparatively phosphonium-based ILs are less elaborated for many applications. Although in separation technology the ILs applications are still in their early stages, the academic interest is increasing in ILs. Dyes are the substantial source of pollution as a wastewater. These ILs were applied as adsorbent for the removal of methylene blue (MB) dye from aqueous media and the selected IL on laboratory scale shows good performance with the stripping efficiency of 84.95%. The kinetics study expressed that the adsorption of MB on IL fitted in the pseudo-second order kinetics models with correlation coefficient value (R^2) of 0.999. The study proved that ionic liquids are an effective and environmentally benign adsorbent for MB removal from aqueous solution.

Keywords: phosphonium, ionic liquids, methylene blue, kinetic study.

INTRODUCTION

Ionic liquids are entirely consist of ions and considered as unique solvents (Hecke and Meervelt, 2010). Today ILs are under increasing study because of their peculiar characteristics including low vapour pressure, flame retardancy and high ion concentration, ability to dissolve organic, inorganic, polymeric materials and high thermal stability (Chiappe and Pieraccini, 2005; Ullah, 2015; Ullah and Bustam, 2015). The ionic liquids distinctive properties have generated incredible amount of interest in both of their chemistry and prospective applications (Del Sesto *et al.*, 2009).

Apart from imidazolium based ionic liquids have been frequently used, phosphonium based ILs have been investigated to explore their general scope and their inimitable capabilities. Phosphonium based ILs production on an industrial scale is less expensive, and are also an efficient and recyclable media (Sowmiah *et al.*, 2009). Compared to nitrogen based ILs, phosphonium based ILs present further advantages, such as less toxic and more thermally stable (Almeida *et al.*, 2013). In spite of a large number of studies concerning imidazolium based ionic liquids, phosphonium based fluids are still poorly characterized. The interest in phosphonium based ILs during the past decade, expanding to include diverse applications such as Catalysis, separations, electrochemistry, electrodeposition, photochemistry, liquid crystals, CO₂ capture, desulfurization of fuel, enzymatic syntheses, lubrication, rocket propulsion, and thermal storage devices (Bradaric *et al.*, 2003; Ullah *et al.*, 2014). A number of phosphonium cation-based ILs are also available and have a range of useful properties, but have been much less studied. Early reports regarding phosphonium ILs were published in the 1970s by Parshall using stannite and germinate salts (Fraser and Macfarlane, 2009).

The ILs vary in ions size and can be either hydrophilic or hydrophobic (Ziyada *et al.*, 2011). Hydrophobic ILs is estimated to be effective in various applications. These are unsuited to conventional hydrophobic liquids, containing hydrophobic ILs which includes OTf, NTf₂, PF₆, BF₄ or their derivatives. Generally hydrophobic ILs are obtained when the cation or anion has a long alkyl chain, or fluorinated the anion, as in hexafluorophosphate [PF₆], bis (trifluoromethane) sulfonylimide [Tf₂N], and so on (Fukumoto and Ohno, 2006).

Dyes are widely used for different applications in industries, such as textile, paper, printing, food, cosmetics, leather tanning etc (Harrelkas *et al.*, 2009; Amini *et al.* 2011; Charumathi and Das, 2012). (Ferreira *et al.*, 2014) reported that worldwide 1 million tons of dyes are produced, and 10-15% of them are discharged by the textile industry. Finally they are the substantial source of pollution as a wastewater. However, these dyes and their metabolites are mostly toxic and highly carcinogenic in nature. The aquatic life is highly affected from them Charumathi and Das 2012; Khan *et al.*, 2014). Hence the removal of these dyes from aqueous effluents is very necessary. There are different methods used to remove dyes from aqueous solution, such as flotation, chemical coagulation, membrane filtration, ion exchange, biological and chemical oxidation, and adsorption. However, most of these methods have some major deficiencies, such as the high concentration of dye, high price, insufficient dye removal, and high energy requirements (Robinson *et al.*, 2001, Ferreira *et al.*, 2014, Coutinho *et al.*, 2014, Nasrullah *et al.*, 2015). Presently ionic liquids which are thermally stable, have high boiling point, low vapour pressure and environmentally friendly proved to be promising alternative for removal of dyes from aqueous media. In literature some imidazolium based ionic liquids



such as $[\text{C}_4\text{MIM}][\text{PF}_6]$, $[\text{C}_6\text{MIM}][\text{PF}_6]$, $[\text{C}_8\text{MIM}][\text{PF}_6]$, $[\text{C}_6\text{MIM}][\text{BF}_4]$, and $[\text{C}_8\text{MIM}][\text{BF}_4]$ have been successfully used for separation of different dyes from aqueous media (Pei *et al.*, 2012). In the present study, phosphonium based hydrophobic ILs with fluorine anions were synthesized and tested for the removal of methylene blue (dye) from aqueous media.

EXPERIMENTAL

All the chemicals were obtained from Sigma-Aldrich, and all these chemicals were used as received.

The ILs were synthesized by metathesis reaction process (Figure-1) in room temperature. Take tetra butyl phosphonium bromide in water and then added a stoichiometric amount of Lithium trifluoromethanesulfonate, Bis (trifluoromethane) sulfonimide lithium salt, lithium hexa fluoro phosphate and lithium tetra fluoro borate. The reaction was very fast and run approximately for three hours and then washed with distilled water to remove the impurities and tested with silver nitrate (AgNO_3) solution to completely remove the halogens and then dried.

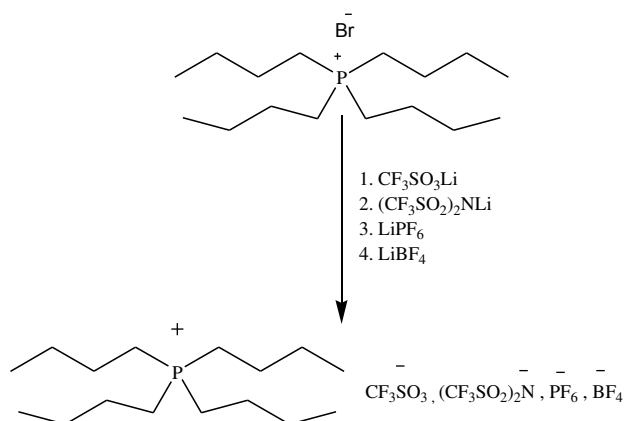


Figure-1. General Synthetic pathway of phosphonium based ionic liquids.

Characterization

Four ILs were synthesized with tetrabutylphosphonium cation and with four different anions, all these ILs final yields was in white solid form. The ILs structures were confirmed by NMR (Bruker Avance 500 MHz spectrometer), FTIR (Perkin Elmer-FTIR, spectrum one 54841) and elemental analysis (CE Instruments EA-1110).

Thermal study

The thermal properties of the synthesized ionic liquids were measured by Perkin-Elmer thermogravimetric analysis (TGA), Pyris V-3.81 to investigate their thermal stability. A sample weight of 2-5 mg held in a TGA pan and heated from 50-600°C at a heating rate of 10°C/min in the presence of nitrogen flow. The experimental decomposition temperatures are presented in term of weight loss (%) and TG (°C).

Batch experiments

Phosphonium based ILs with fluorine anions were prepared and used for removal of methylene blue (MB) from aqueous solution. The experiment was conducted by adding 0.5 g of IL to 20 ppm aqueous solution of MB dye in 250 mL flask and stirrer at 400 rpm. Initially each IL was tested for better removal. After specific interval of time, sample aliquots were withdrawn and filter to separate the dye-loaded IL from dye solution. The remaining concentration of MB was measured spectrophotometrically by measuring the absorbance of the supernatant (dye solution) left after filtration. To find the optimum experimental conditions for MB removal, IL with PF_6^- anion, the effect of time (30-240 min), dye concentration (10 ppm, 20 ppm, 40 ppm), IL loading (0.5g) and shaking velocity (500 rpm) were thoroughly studied.

The color removal efficiency (R) and adsorption capacity (q) of IL was measured by applying the following Equations (1) and (2), respectively.

$$(R\%) = \left(\frac{C_0 - C_t}{C_0} \right) 100 \quad (1)$$

$$q_t = (C_0 - C_t)V/m \quad (2)$$

Where q_t (mg/g) are the amount of MB adsorbed at time t; C_0 and C_t (mg/L) are concentration of MB at initial at time t_0 and time t, respectively; V is the solution volume and m (g) is the mass of IL.

Optimization of physico-chemical parameters

The adsorption of methylene blue on the surface of IL depends upon chemical structure and properties of MB and also on chemistry and morphology of IL surface. Various parameters which affect the adsorption capacity of MB dye on IL were studied and optimized as follows.

Effect of time

To study the equilibrium time required for the IL to bind to the dye molecules, was studied by adding 0.5 g of IL and specified concentration of dye solution (10 ppm, 20 ppm, 40 ppm) into the 250 mL round bottom flask. Solution was stir for the varying period of time (30, 60, 120, 180, 90 and 240 min) at 500 rpm. After evolution of specific contact time, the supernatant was analyzed for the determination of the concentration of MB in the solution.

Effect of initial dye concentration

To study the effect of initial concentration on MB adsorption by IL, 10 ppm, 20 ppm, and 40 ppm of MB solutions were selected. The dose of IL, contact time, and stirring speed were maintained constant throughout the experimental work unless otherwise specified.



Kinetics study

To study the adsorption mechanism of MB on IL pseudo-first and pseudo-second order kinetic models were used.

The pseudo-first-order equation

The pseudo-first-order kinetic model or Lagergren kinetic equation is generally expressed as follows:

$$\log(q_e - q_t) = \log q_1 - \frac{K_1 t}{2.303} \quad (3)$$

where, q_e is the amounts adsorbed (mg/g) at equilibrium, q_t is the amounts adsorbed (mg/g) at any time and k_1 is the adsorption rate constant for pseudo-first order (s^{-1}).

The pseudo-second order model

If the rate of sorption is a second order mechanism, the pseudo-second-order kinetic rate equation is used and it is expressed as:

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \quad (4)$$

$$\frac{dq_t}{(q_2 - q_t)^2} = k_2 dt \quad (5)$$

By integration of Equation (5) for the boundary conditions when $t = 0$ and $q_t = q_i$

$$\frac{1}{(q_2 - q_t)} = \frac{1}{q_2} + k_2 dt \quad (6)$$

Where k_2 (g/mg. min) is the rate constant of pseudo second order.

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \quad (7)$$

If $\frac{t}{q_t}$ is plotted against t , it gives a straight line, which means that the adsorption follow pseudo-second order kinetics. This model is based upon the assumption that if the rate limiting step may be chemisorption which involve valence forces resulting from electron sharing or electron exchange between the adsorbent and adsorbate.

RESULTS AND DISCUSSIONS

The NMR, CHNS and FTIR results are discussed as under, while the results of NMR, FTIR and elemental analysis confirmed the structure of the respective ionic liquids.

NMR and CHNS analysis

Tetrabutylphosphonium
[TBP][OTf]

Trifluoromethanesulfonate

^1H NMR(500 MHz, DMSO): δ = 1.007-1.036 (t, CH_2CH_3), 1.488-1.593 (m, CH_2CH_3), 2.248-2.308 (m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.60-2.609 (t, P- CH_2).

^{13}C NMR(500 MHz, DMSO): 13.722, 17.631, 23.099, 23.773.

CHNS elemental analysis for $\text{C}_{17}\text{H}_{36}\text{F}_3\text{O}_3\text{PS}$, Found (%): C: 50.02, H: 9.01, N: 0, S: 7.95. Calculated (%): C: 49.93, H: 8.89, N: 0, S: 7.83.

Tetrabutylphosphonium Bis((trifluoromethylsulfonyl)imide [TBP][NTf₂])

^1H NMR(500 MHz, DMSO): δ = 0.913-0.942 (t, CH_2CH_3), 1.395-1.499 (m, CH_2CH_3), 2.152-2.211 (m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.508-2.515 (t, P- CH_2).

^{13}C NMR(500 MHz, DMSO): 13.685, 17.633, 23.093, 23.761.

CHNS elemental analysis for $\text{C}_{18}\text{H}_{36}\text{F}_6\text{NO}_4\text{PS}_2$, Found (%): C: 40.07, H: 6.77, N: 2.43, S: 11.99. Calculated (%): C: 40.11, H: 6.71, N: 2.62, S: 11.87.

Tetrabutylphosphonium Hexafluorophosphate [TBP][PF₆]

^1H NMR(500 MHz, DMSO): δ = 0.913-0.941 (t, CH_2CH_3), 1.393-1.497 (m, CH_2CH_3), 2.149-2.209 (m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.507-2.515 (t, P- CH_2).

^{13}C NMR(500 MHz, DMSO): 13.725, 17.626, 23.092, 23.772.

CHNS elemental analysis for $\text{C}_{16}\text{H}_{36}\text{F}_6\text{P}_2$ Found (%): C: 47.47, H: 9.10, N: 0, S: 0. Calculated (%): C: 47.52, H: 8.97, N: 0, S: 0.

Tetrabutylphosphonium Tetrafluoroborate [TBP][BF₄]

^1H NMR(500 MHz, DMSO): δ = 0.913-0.941 (t, CH_2CH_3), 1.408-1.482 (m, CH_2CH_3), 2.149-2.209 (m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.507-2.515 (t, P- CH_2).

^{13}C NMR(500 MHz, DMSO): 13.349, 18.277, 23.577, 23.950.

CHNS elemental analysis for $\text{C}_{16}\text{H}_{36}\text{BF}_4$, Found (%): C: 55.47, H: 10.50, N: 0, S: 0. Calculated (%): C: 55.50, H: 10.48, N: 0, S: 0.

FTIR analysis

The FTIR spectra of the phosphonium based ionic liquids were recorded in the range of 450-4000 cm^{-1} . In the Figure-2, the peaks at 2875, 2937, or 2961 cm^{-1} are assign to the C-H stretching or (CH_3 stretching) and at 1383, 1467 cm^{-1} are attributed to (C-H bending) and (CH_3 bending) (Warner et al, 2012). The medium peaks at 722-755 cm^{-1} and peaks at 1200-1300 are corresponding to P\C stretching and P- CH_2 -R deformation band respectively. The t-butyl groups doublet stretching is overlaid in the same region and a related peak reported in literature (Dharaskar et al, 2014). The broad peak at 1258 cm^{-1} is due to CF_3SO_3 , and the broad peaks at 1193, 1353 cm^{-1} are attributed to CF_3 and SO_3 (Zein El Abedin et al, 2012). The peaks at 557 cm^{-1} is due to F-P-F and at 838 cm^{-1} is due to P-F respectively. The characteristic frequency at 521 and 1059 cm^{-1} are assign to BF_4 (Warner et al, 2012).

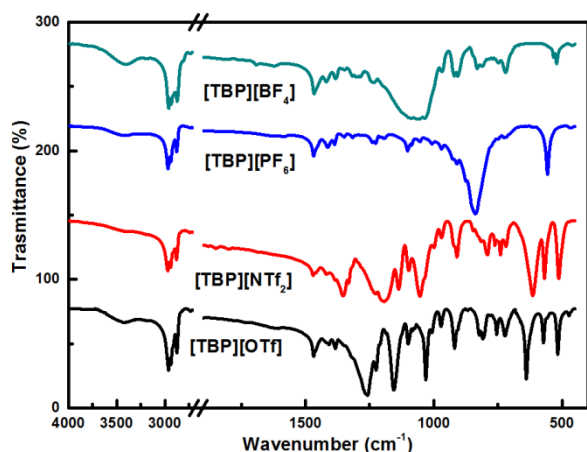


Figure-2. FTIR spectra of Phosphonium based ionic liquids.

Thermal stability

The phosphonium based ionic liquids thermal stability was studied by thermogravimetric analysis (TGA) in the nitrogen atmosphere as shown in the Figure-3. These ionic liquids shows high thermal stability, weight loss started and a change of slope of the TGA curve is found and calculated by the instrumental software Pyris V-3.81, and the onset decomposition temperature was appeared at 402.27, 369.18, 374.03, 389.41°C for [TBP] [OTf], [TBP] [NTf₂], [TBP] [PF₆], and [TBP] [BF₄]. All these ionic liquids are completely decompose at a very high temperature like 463-589°C. All the ionic liquids shows very high decomposition temperature as earlier stated about phosphonium base ionic liquids that thermally very stable (Almeida *et al*, 2013). The decomposition difference is due to anion because all the ILs has same cation, and the anion CF₃SO₃⁻ abbreviated with (OTf) shows high thermal stability as compare to other anions due to extremely stable anion (Ziyada *et al*, 2011).

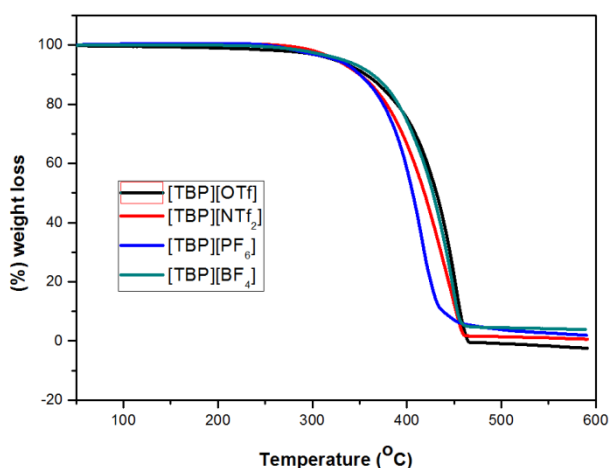


Figure-3. Thermogravimetric analysis (TG) of phosphonium based ionic liquids.

Solubility

The synthesized ILs solubility property was studied in various common solvents, and the Table-1 shows their miscible and immiscible nature with the following common solvents.

Initial screening

Initially the synthesized four ILs were tested for the removal of methylene blue for aqueous media at a fixed parameters and IL with PF₆⁻ anion was selected as better one for further study comparatively as shown in Figure-4. The same anion in different ILs is reported in literature for the cationic dye like MB (Pei *et al*, 2012) and for many more extraction purposes (Han and Row, 2010).

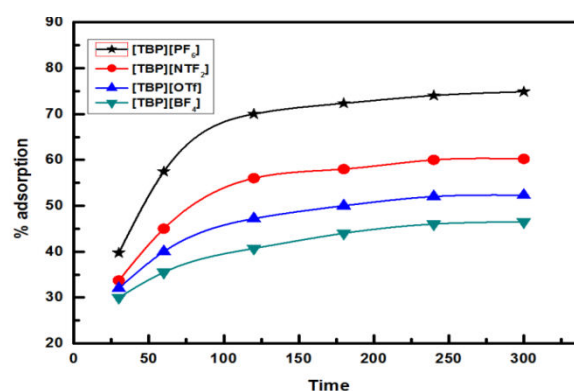


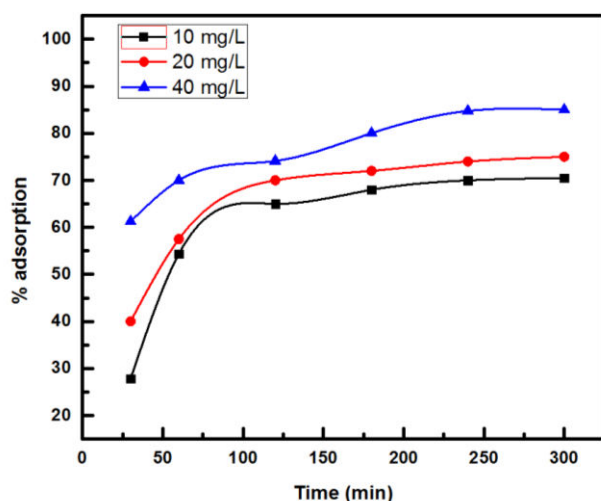
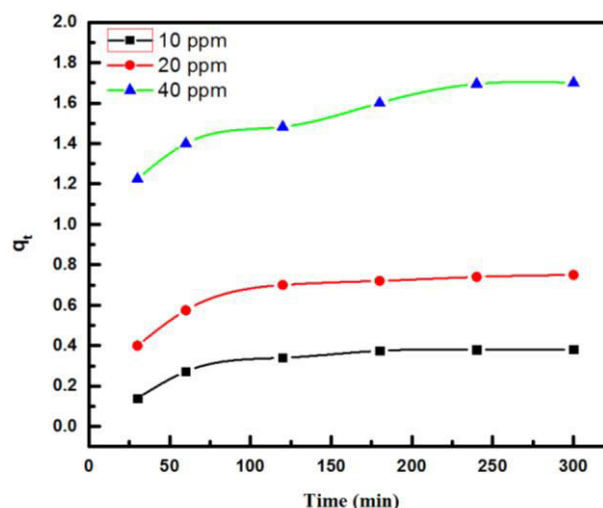
Figure-4. Effect of the four ILs on 20 ppm solution of MB dye.

Effect of time and dye concentration on adsorption of dyes

Adsorption of MB on IL is affect by time and concentration. Figure-5 and Figure-6, shows the % adsorption and adsorption capacity as a function of initial concentration of dye and time, respectively. Result shows that with the increase of contact time between MB and IL the %adsorption and adsorption capacity both increases and attained equilibrium at 120 min. The increase in contact time beyond 120 min cannot enhance the considerable dye adsorption. The initial dye adsorption is very high because of the abundant availability of binding sites on IL. After 120 min most of the active sites is covered by the MB molecules and further adsorption of MB becomes difficult. The time of contact between the dye and adsorbent, and also the concentration of dye can affect the adsorption process. The result shows that the equilibrium time is independent of initial concentration of MB, for all initial concentration equilibrium reached in same time. It was found that with increase of MB concentration from 10 to 40 mg/L the % removal and adsorption capacity increases. It is very common exercise that with increase of initial concentration of dyes the capacity of adsorption increases because of strong driving force and transfers of more dye molecules from aqueous phase to ILs (Han *et al*, 2011).

**Table-1.** Miscibility and immiscibility of the synthesized ILs with common solvents.

Solvents	[TBP][OTf]	[TBP][NTf ₂]	[TBP][PF ₆]	[TBP][BF ₄]
Ethyl Acetate	Soluble	Soluble	Soluble	Soluble
Acetone	Soluble	Soluble	Soluble	Soluble
Acetonitrile	Soluble	Soluble	Soluble	Insoluble
Diethyl Ether	Soluble	Soluble	Insoluble	Insoluble
Ethanol	Soluble	Soluble	Soluble	Insoluble
Methanol	Soluble	Soluble	Soluble	Soluble
Toluene	Soluble	Soluble	Insoluble	Insoluble
Hexane	Insoluble	Insoluble	Insoluble	Insoluble
Chloroform	Soluble	Soluble	Soluble	Insoluble
DMSO	Soluble	Soluble	Soluble	Soluble
Dichloromethane	Soluble	Soluble	Soluble	Insoluble
Water	Insoluble	Insoluble	Insoluble	Insoluble

**Figure-5.** Effect of time on (%) adsorption of dye concentration.**Figure-6.** Effect of contact time on the adsorption of methylene blue.

Kinetics of adsorption and model fittings

In order to evaluate the mechanism process of MB adsorption on IL, pseudo-first order and pseudo second order kinetic models were used (Ho *et al*, 2000). The result indicated that (Figure-7) the adsorption of MB on IL fitted in the pseudo-second order kinetics models with regression coefficient (R^2) 0.99.

Intraparticle and liquid film diffusion model

The intraparticle and liquid film diffusion models are represented by equation 8.

$$q_t = K_i \cdot dt^{0.5} \quad (8)$$



Figure-8 shows the intraparticle diffusion model fitting for the adsorption of various concentration of MB. The result shows that the plot of q_t vs $t^{0.5}$ is not very linear for whole time and can be divided into two regions. The multi-linearity of the plot for MB adsorption shows the multistage adsorption of MB on IL.

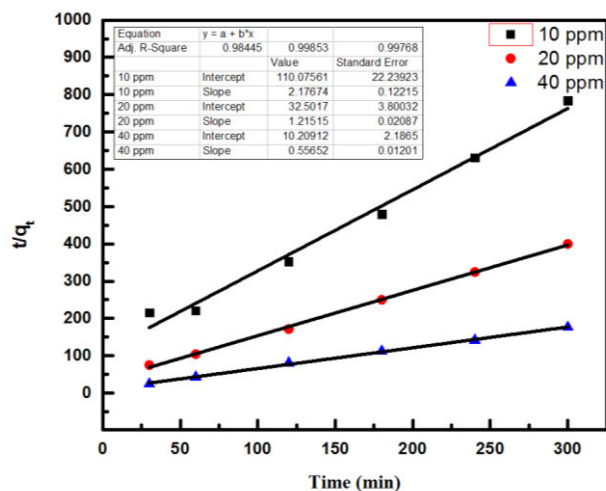


Figure-7. Pseudo-second-order kinetics plot for adsorption of MB on ILs.

Normally if the plot of q_t vs $t^{0.5}$ is pass through origin this indicate the intraparticle diffusion is only the rate-limiting step. However in this study it is clear that the plot of q_t vs $t^{0.5}$ is not passing through the origin, which shows that the intra-particle diffusion is not involved in the adsorption process; therefore it is not a sole rate controlling step. This result confirms that the adsorption process is followed by two or more than two phases (Roy *et al*, 2013; Gupta *et al*, 2014).

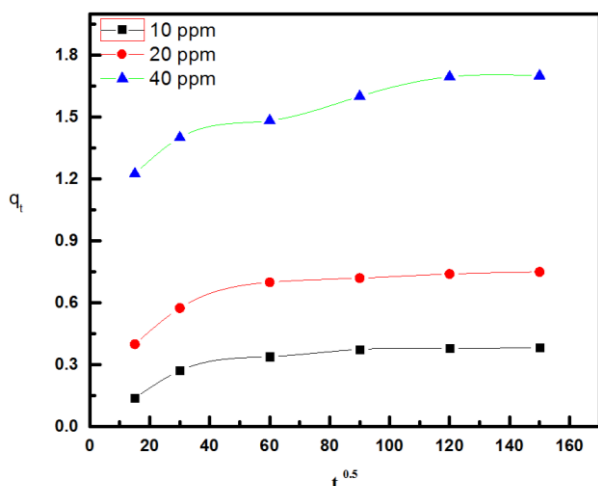


Figure-8. Intraparticle diffusion model for MB adsorption by ionic liquids.

CONCLUSIONS

Ionic liquids used in this study contained the phosphonium cation with the anions CF_3SO_3^- , $(\text{CF}_3\text{SO}_3)_2\text{N}^-$, PF_6^- and BF_4^- , were synthesized and their final product was white solid. Their results show that their hydrophobicity is not too much effective in this study on extraction of dye. The study shows that IL with PF_6^- anion did better removal of MB comparatively. In future their detail study is required, to study the effect of different parameters effecting the removal of dyes and to study this anion with different cations.

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