Nanoparticle for the Removal of DR from Aqueous Solution: Adsorption Equilibrium Studies.

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Abstract: - Abstract- Discharge of dye bearing waste-waters from industries viz, textile paper, printing etc, into natural receiving bodies is resulting in pollution of receiving water bodies. Dyes and their degradation products are highly carcinogenic. The need of the day is the disposal of these waste-waters after proper treatment. Even though many traditional treatment techniques are in use, adsorption is found to be more effective and cheap method for treating waste-waters containing dyes. Further nano-technology and nano-particles are applied successfully in these days to treat dye bearing waste-waters efficiently. In the present paper the findings of bench scale studies to evaluate DR by nano-particles under varied experimental conditions are presented. The adsorption equilibrium and kinetic models with co-relation co-efficients are also presented in this paper. The results showed that NIPVP is able to adsorb 98.2% of DR from aqueous solution under optimum conditions of experimentations. The adsorption studies indicates both Langmuir and Freundlich isotherm models well fits with the adsorption data. Also the kinetic studies demonstrated that the colour adsorption on nanoparticles is in good accordance with the pseudo second order kinetic model.

Keywords*: Direct Red, Nano-particles, batch studies, Adsorption kinetics, Isotherms, Adsorbent dosage (Cd), stirring time (t).*

1. Introduction

In recent years, the water bodies are becoming polluted due to disposal of untreated industrial waste-waters into these water bodies. Of the various pollutants contained in industrial waste-waters, colour is considered to be very important from the point of aesthetics as it is a visible pollutant, and thus make the water bodies unacceptable for various uses. The researchers have reported conventional treatment techniques to treat dye bearing waste waters employing various physical, chemical & biological methods. These methods are found to suffer from one or another limitation and they are unsatisfactory interms of efficiency and economy. Thus in recent time alternative method for the removal of dyes from waste-waters with the use of various low cost adsorbent has been investigated. (Bharathi and Ramesh: 2013, Kharat: 2015, George et al: 2013, Geethakarthi and Panikumar:2011).

Currently nano technology has been extensively studied by researchers. Nano particles have very high adsorbing, interacting and reacting capabilities due to their small size with high proportion of atoms at surface. Nano-particles can achieve energy conservation. Various nano materials tried in recent past include nano adsorbents, nano catalysts, nano particles, nano structured catalytic membranes etc. (Dharmendra et al: 2008, Pankaj et al: 2012, Gayatri et al:) However application of nanoparticles is colour specific & depends upon the various variables.

2. LITERATURE REVIEW

The application of nano-materials in removing colors from wastewaters, as studied and reported by various researchers are discussed/presented by George et al (2013) in their paper titled "the change from past to future for adsorbent materials for treatment of Dyeing wastewaters. Wenquian et al (2019) in their review paper, made an attempt to review the various colour removal by nano-adsorbents. Nidhi et al (2016) reported that, Zero valent iron nanoparticles were found to be capable of decolourizing various types of dyes such as disperse, reactive, sulphur and vat dyes. Further batch experiments were carried out in the laboratory under varied experimental conditions (pH, Stirring time, Adsorbent dosage) to investigate the use of stochiometrically synthesized Cuo nanoparticle for colour removal from textile wastewaters (Anitha et al:2015). However, the authors opine that, the literature is silent on removal of direct red by NIPVP nano particles.

In the present paper experimental findings carried out to evaluate adsorption potential of nanoparticle namely NIPVP in adsorbing direct red colour under varied experimental conditions is presented, discussed along with inferences and conclusions. The experimental conditions such as pH, stirring time, concentration of dye and dosage of adsorbent has been optimized. Isothermic models are also evaluated. The kinetic data was analyzed to study the adsorption mechanism and different models are applied to fit the experimental data.

3. MATERIALS AND METHODOLOGY

3.1 Preparation of synthetic coloured samples.

Commercially available dye (DR) was procured from colortex. Stock solution was prepared by dissolving one gm of dye in thousand ml of double distilled water to make a stock solution of thousand mg/l. further working solutions/concentrations are prepared by diluting calculated quantity of stock solution using double distilled water.

3.2 Adjustment of pH

pH of synthetic coloured samples were adjusted by using H_2SO_4 or NaoH as applicable.

3.3 Experimental variables

Initial dye concentrations of C_o-15, 30, 45 & 60mg/l. pH of 5, 7, 9 stirring time of 20, 40, 60, 80 & 100 minutes, and adsorbent dosages of 30, 50, 70, 90 mg were tried.

3.4 Synthesis of Nanoparticles

The nanoparticle selected for present study namely NIPVP was synthesized as per procedure published by researcher and is documented below.

Procedure given by Ravendra and Prerana (2018). 3.3 mM solution of $NiCl_2$-$6H_2O$ was prepared in 200ml ethanol. To this solution 0.125g of PVP was added and was stirred until complete dissolution of PVP. Further Hydrazine hydrate was added and 1M NaoH was added under constant magnetic stirring. The solution was heated at 60^oc with stirring until the solution turned black. The solution was then cooled and to this cooled solution acetone was added to precipitate out the nanoparticles. Further the solution was vaccum filtered followed by repeated washing with chloroform-methonol (1:1) solution.

3.5 Batch Studies

The batch studies were conducted in an open atmosphere at room temperature. 100 ml aqueous coloured sample of particular color concentration was taken in clean dry 250 ml stoppered conical flask. pH of the sample was adjusted, adding acid or alkali. Pre decided adsorbant dosage was added to the flask. The contents of the flask were initially stirred by using the glass rod. Then the contents were shaken at 140 rpm in a shaker for a selected (varying) stirring time. Subsequently the dye solutions were centrifuged for 5 min at 3000 rpm. The clear solution was then pipetted out and the rate of decolourisation was measured by the adsorbance at a optimum wavelength for a particular colour using spectrophotometer. The percentage of dye decolourisation was found out from calibration curve of the dye solution. The studies were repeated for all the colour intensities, pH, stirring time and adsorbent dosages. The percentage removal of dye/colours was calculated. Further kinetics of adsorption were determined.

3.6 Measurement of decolourization

The treated coloured samples of batch and continuous column studies were analysed by using spectrophotometer. Using spectrophotometer the percentage adsorptions for known concentrations of colours at defined wavelength for a particular color. For color considered for present research work namely DR, the optimum wavelength was 507 nm. Based on this data calibration curve (color intensity vs percentage adsorption) were drawn. The samples to be analysed were kept in spectrophotometer and percentage adsorption was recorded. Corresponding to the percentage adsorption recorded the color intensity was read from calibration curve. Further the removal efficiency was calculated by knowing influent and effluent concentrations.

4. **RESULTS AND DISCUSSIONS**

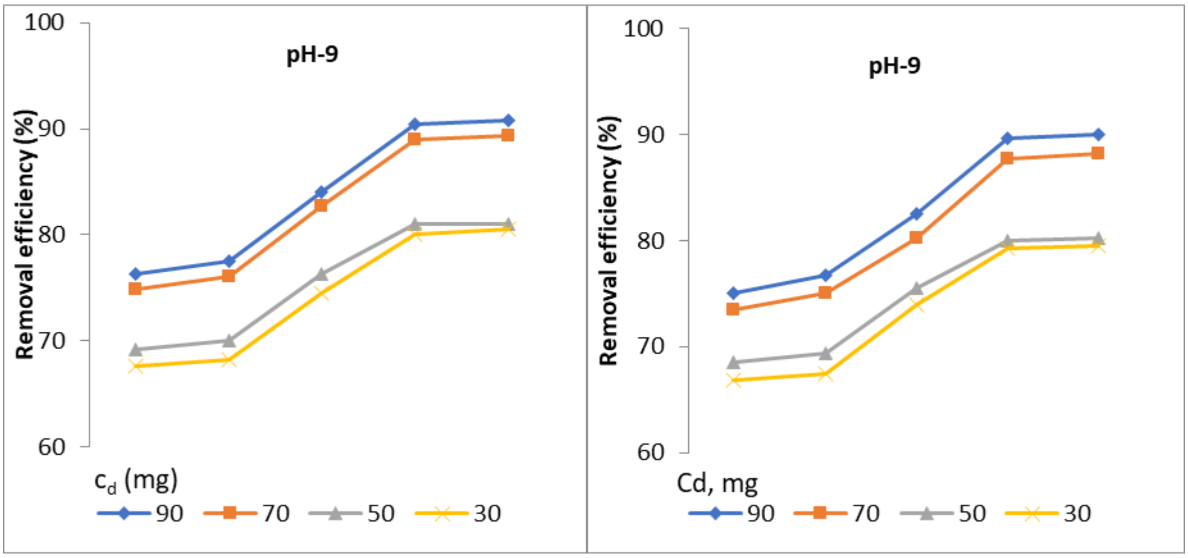
Effect of stirring time on percentage removal of DR by NIPVP under varied experimental conditions are presented in figure-1 and 2. Further based on the analysis of results the discussions are made as under.

3.7.1 Effect of pH

Variation in pH is one of the most significant factors which affects the extentof decolorization. For a given conditions of experimentation, the maximum removal efficiency was recorded at pH-5. Further at higher pH values decrease in removal efficiency has been recorded. The decrease in removal at the higher pH values may be attributed to decrease in reducing power of nano-particles due to covering of nano-particles with corrosion products. Also there may be a change in the charge of nanoparticles surface from positive to negative at alkaline pH which causes a repulsion force between dye & nano-particles. [PHENRAT et al: 2007]

3.7.2 Effect Of Adsorbent Dosage

The results of experimentations on effect of adsorbent dosage on removal efficiency of c olour revealed, the increase in removal efficiency, with increase in nanoparticles dosage. This may be attributed to the availability of more surface sites for reaction with reactive dye at higher dosage which accelerated the removal of colour.



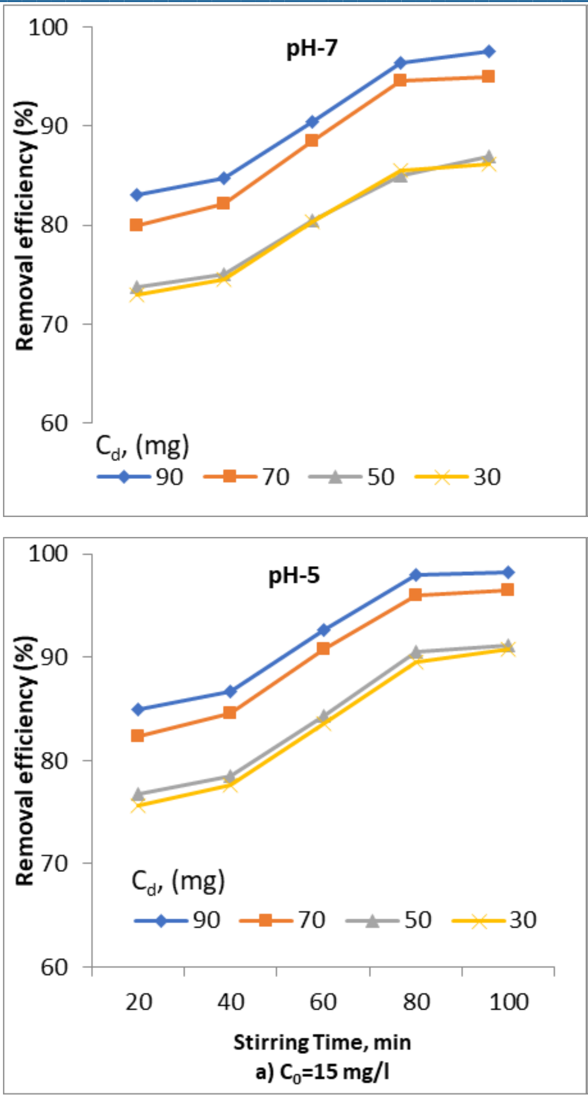


Fig 1: Effect of Stirring Time on removal of DR by NIPVP.

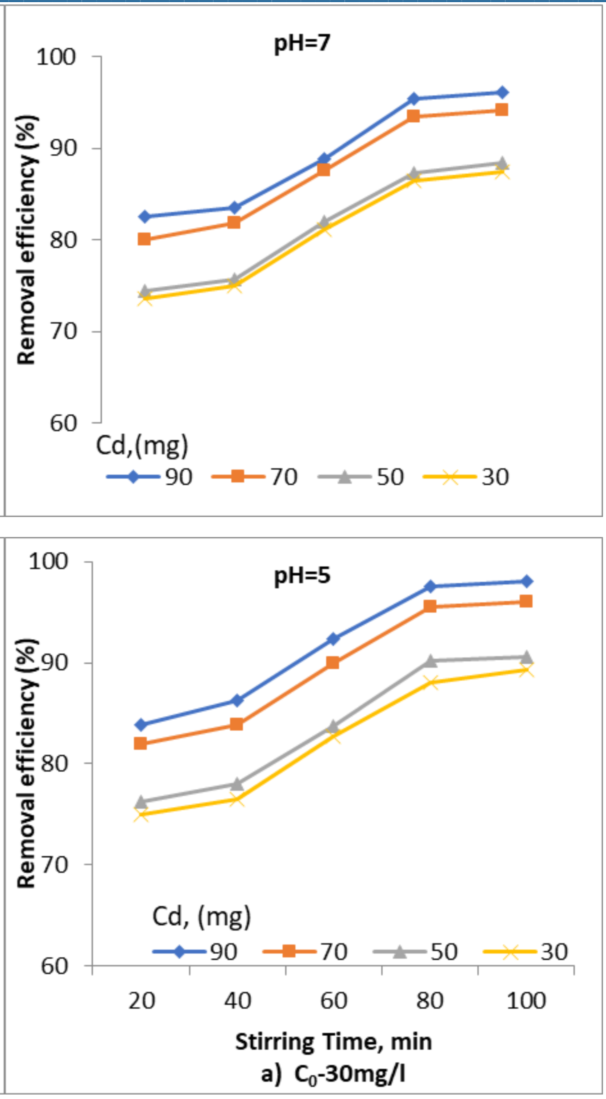
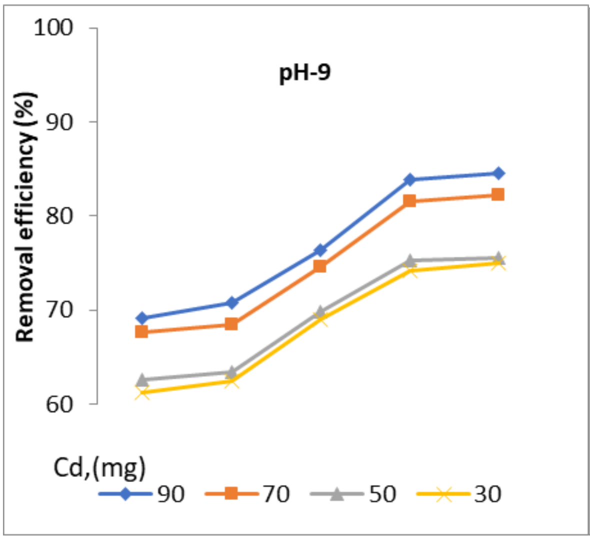
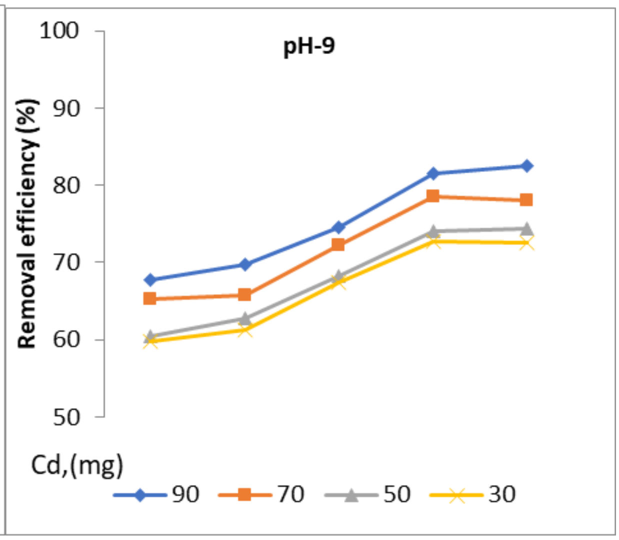


Fig 2: Effect of Stirring Time on removal of DR by NIPVP.





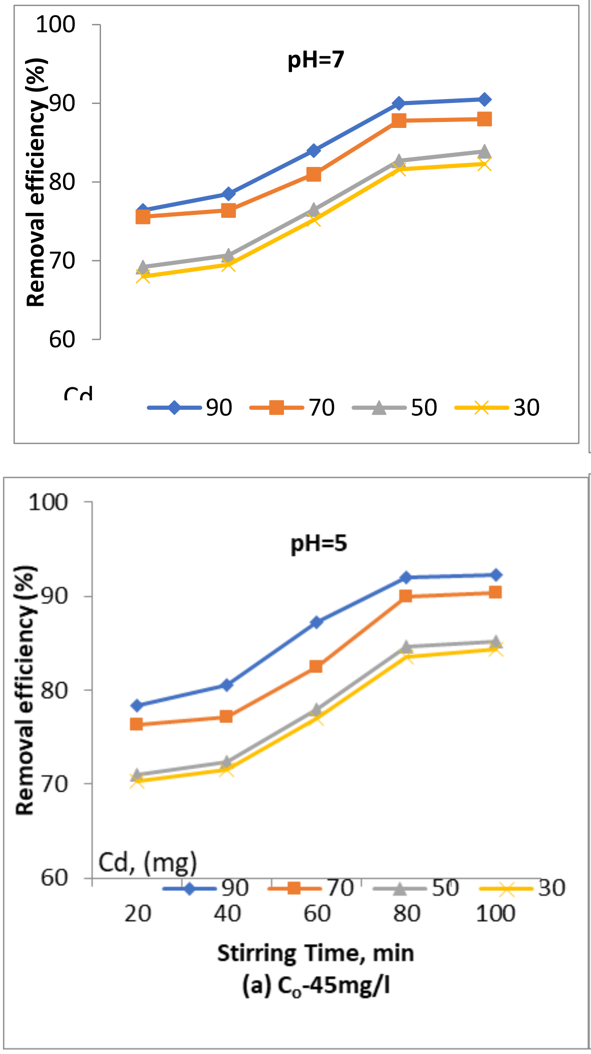


Fig3: Effect of Stirring Time on removal of DR by NIPVP.

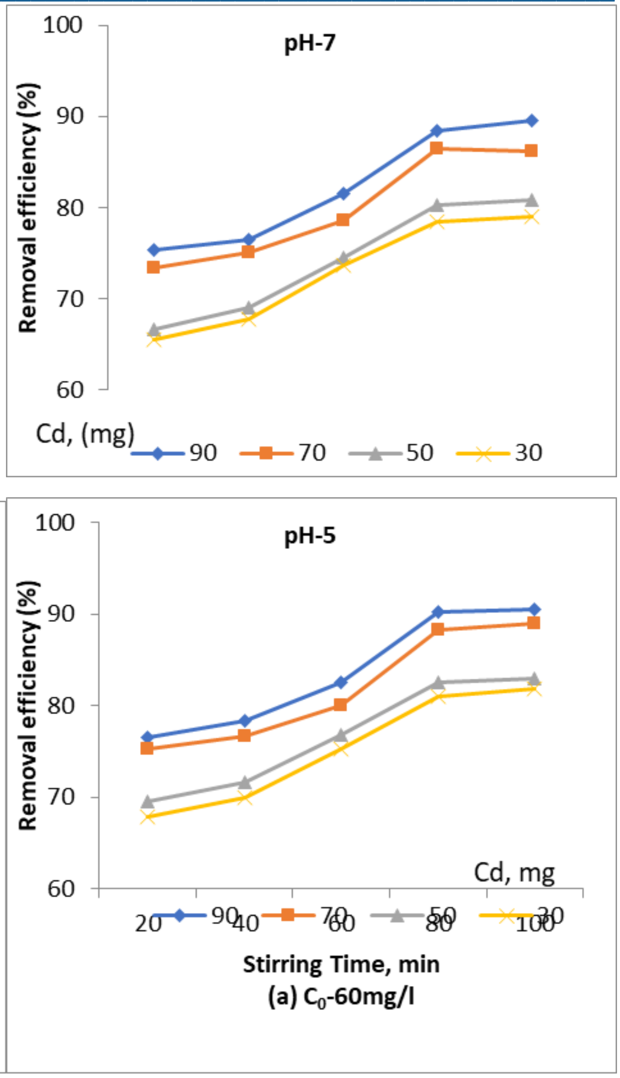


Fig4: Effect Of Stirring Time On Removal Of DR By NIPVP.

3.7.3 Effect of Contact Time

The co-relation between contact time and dye removal efficiency was also examined. Gradual increase in dye uptake by the nanoparticle with increase in contact time upto 120 min has been noticed. The rate of percentage removal slowly increases in the initial stage of the adsorption process and gradually increases later with increase in contact time then it becomes almost constant with increase in contact time from 80 to 100 min. It is basically due to saturation of the active sight which doesn't allow further adsorption.

3.7.4 Effect Of Initial Dye Concentration (C_o)

The studies were carried out to assess the effect of dye concentration on removal efficiency by varying C_o from 15 to 60 mg/l. Inverse relationship between removal efficiency and C_o has been observed. Thus decrease in the percentage removal of dye with increase in the dye concentration has been recorded. The decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more adsorbate available in the solution. At lower concentrations almost all the adsorbate present in the solutions could interact with the binding sites and thus percentage adsorption was higher than those at initial concentrations. At higher concentrations lower adsorption sights yield is due to the saturation of adsorption sights.

3.7.5 Summary Of Results

Under the optimum conditions of batch studies (C_o=15mg/l, t=100mis. pH-5 and C_d-90 mg) the maximum removal of colour DR by NIPVP was found to be 98.2%. Accordingly the minimum removal percentage recorded was found to be 59.8%. (C_o-60 mg/l, t-20 min, pH-9, and C_d-30mg)

3.8 Adsorption Isotherm

The two adsorption isotherms namely Langmuir and Freundlich were tried & presented in this paper. These isotherms helps to discover the co-relation between the amount of adsorbed species & remaining concentration in the solution under the equilibrium conditions. The theory & concepts of these isotherms, graphical representation of data calculation of isotherm constants & their ranges to validate the isotherms also the significance co-relation, co-efficient R^2 are discussed elsewhere in the literature. (Salman et al: 2011, Ajmal : 2006, Desta :2013, Daniel and shoba :2015)

3.8.1 Langmuir Isotherm

The Langmuir isotherm plot C_e/q_e vs C_e is shown in the figure 3. The maximum adsorption capacity (q_{max}) and energy of adsorption (b) are determined by slope & intercept of isotherm plots. Further to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameters (R_L) is defined and is given by $R_L=1/(1+bC_o)$ where

C_o= Initial Concentration of adsorbate, (mg/l)

The value of R_L ($0<R_L<1$) indicates the isotherm is favorable. Also if the plot of C_e/q_e vs C_e yield a straight line, the Langmuir adsorption is said to be obeyed by adsorption equilibrium.

R_L=0.057 and b=1.163 (l/mg) were calculated from the graph, C_o=15mg/l being the initial concentration. R^2 was found to be 0.9730 and are tabulated in Table-1. Thus the values obtained from the experimental outcome and the plots thereby confirmed that the adsorption followed the Langmuir isotherm model.

3.8.2 Freundlich Isotherm

Figure 4 plot of $\log q_e$ vs $\log C_e$ depicts the Freundlich isotherm. From the intercept and slope of the straight line $\log K_f$ and 1/n are calculated. Where K_f is the freundlich constant (sorbent capacity of sorbent) & 1/n is the freundlich intensity parameter which indicates the deviation of the adsorption isotherm from linearity, and its value less than one (1/n<1) indicates the adsorption is favourable. From the graph 1/n and R^2 values were observed and were found to be 0.3734 and 0.9107 respectively (Table-1). Also sorption capacity of sorbent

(K_f) was found to be 2.250 mg/g. thus it is inferred that, the adsorption of DR onto NIPVP is favourable at studied condition

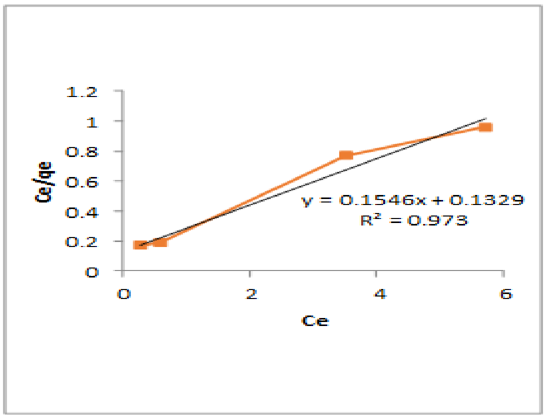


Fig 3: Langmuir Isotherm plots for DR

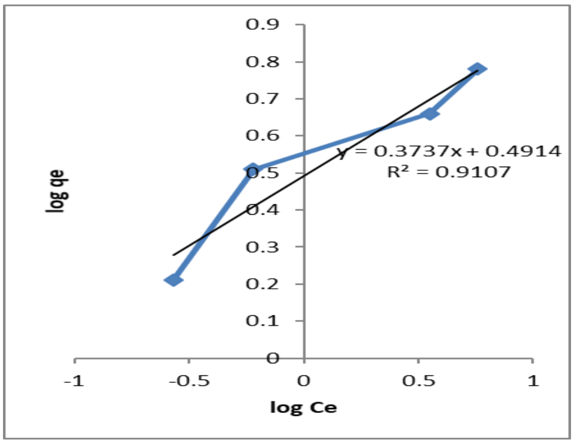


Fig 4: Freundlich Isotherm plots for DR

Table 1: Isotherm Constants for DR

Isotherm	q_{max}	b(l/mg)	R_L	K_f(mg/g)	1/n	R^2
Langmuir	6.47	1.163	0.057	-	-	0.9730
Freundlich	-	-	-	2.250	0.3734	0.9107

The constant/parameters and coefficients calculated further confirmed the fitment of experimental data into both the isotherms.

3.9 Adsorption Kinetics

Kinetic studies help to understand reaction pathways and sorption interaction mechanism. Also kinetic defines the solute uptake rate and these rate controls the residence time of adsorbate uptake at the solid-solution interface. Kinetics can be evaluated using reaction and diffusion based models.

Amongst the many models available, pseudo first and second order models are popularly used. Fundamentals and significance of these kinetics, graphical representation of experimental findings, comparision of adsorption capacities and the validation of these kinetics are widely published and discussed by the researchers. (Daniel & Shoba : 2015, Davoud et al : 2015).

Findings of the research work to validate the kinetics are further presented and discussed in this paper. The graph of log(q_e-q_t) verses stirring time (t) and t/q_t verses t corresponding to pseudo first and second order kinetics are presented in figure 5 and 6 respectively. q_e and q_t indicate the adsorption capacity at equilibrium (mg/g) and at time 't'. Rate constants k_1 and k_2 and q_e obtained from slope and intercept of corresponding graphs along with values obtained from experimentation are summarized in Table 2

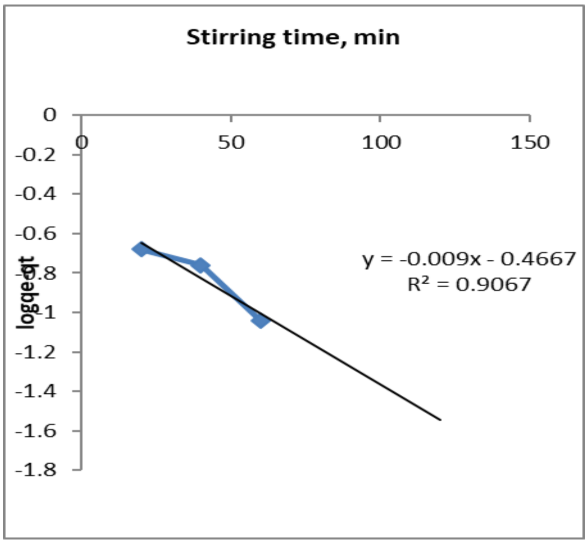


Fig 5: Pseudo first order plots for DR

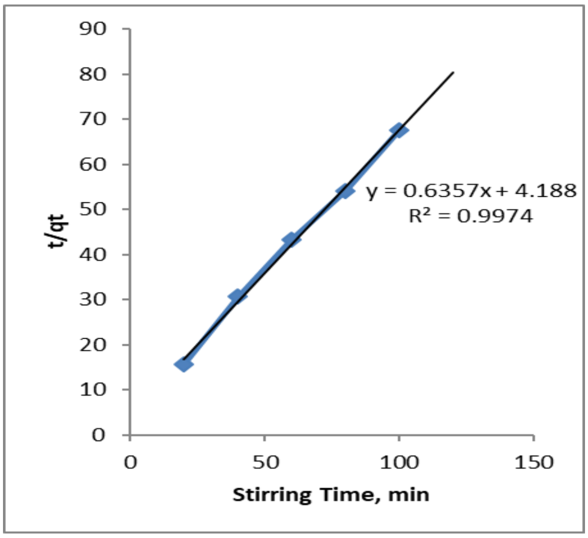


Fig 6: Pseudo Second order plots for DR

Table 2: Kinetic Constants

Kinetic	K_1	K_2	q_e(mg/g)		R^2
			From Graph	Experimental	
Pseudo First order	0.415	-	0.341	1.540	0.9067
Pseudo second order	-	0.097	1.573	1.540	0.9974

The comparison of q_e values as listed in the table 2 for pseudo first and second order kinetics revealed that, the pseudo first order model does not fit, whereas for pseudo second order kinetic model, the uptake capacities agreed very well with the experimental data. Further for pseudo second order kinetic, R^2 value is also found to be very high compared to R^2 values of pseudo first order kinetics. Thus it can be inferred that, the adsorption of colour by NIPVP followed pseudo second order kinetics. Therefore it is further inferred that, chemisorption might be the rate limiting step in the sorption process.

5. Conclusions

Findings of batch studies carried out to investigate the equilibrium and the dynamics of the adsorption of Direct Red on to NIPVP nano particle has been presented in this paper. The adsorption capacity of the adsorbent is considerably affected by initial concentration of the colour, adsorbent dose, stirring time and pH of the colour. The results suggested, increase in the adsorption capacity with increase in stirring time and adsorption dosage but at lower initial concentration of colour. The Langmuir and Freundlich models are used for the mathematical description of the adsorption equilibrium. The experimental data fitted very well with both the isotherms. Further adsorption data modelled using the first and second order kinetic equations revealed that the second order kinetic equation could best describe the sorption kinetics. Under the optimum conditions of experimentations (C_o=15mg/l, t=100min, pH-5 and C_d-90 mg) NIPVP will be able to adsorb maximum of 98.2% of direct Red. Thus it is concluded that the NIPVP Nano particles could be employed for the removal of Direct Red from the aqueous solution

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