



Adsorption removal of carcinogenic acid violet19 dye from aqueous solution by polyaniline-Fe₂O₃ magnetic nano-composite

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Received 26 Mar 2014, Revised 30 Sept 2014, Accepted 30 Sept 2014.

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Abstract

The present work deals with the development of a novel method for the removal of dyes from aqueous solution by using Polyaniline (PANI)-Fe₂O₃ nano-composite. It is successfully synthesised in situ through self polymerisation of monomer aniline. Adsorptive removal studies are carried out for water-soluble carcinogenic acid violet 19 (acid fuchsine) dye by using PANI-Fe₂O₃ nano-composite in aqueous solution. Different parameters like dose of adsorbent, contact time and pH have been studied to optimise reaction condition. It is observed that adsorptive removal by PANI-Fe₂O₃ nano-composite is more effective and faster mode of removing Acid violet 19 dye from aqueous solution than work done before. The optimum conditions for the removal of the dye are initial concentration 20 mg l⁻¹, adsorbent dose 10 gm l⁻¹, pH 8. The adsorption capacity is found 7.7 mg g⁻¹. The EDS technique gives elemental composition of synthesised PANI-Fe₂O₃. The SEM and XRD studies are carried for morphological feature characteristics of PANI-Fe₂O₃ nano-composite. Besides the above kinetics and isotherm studies have also been carried out.

Keywords- Adsorptive removal, Acid violet 19 dye, PANI-Fe₂O₃ nano-composites, SEM, EDS, XRD.

1. Introduction

Environmental pollution due to industrial effluent is a major concern because of its toxicity and threats for human beings. The environmental pollution control is one of the prime concerns of the society in today's context. The presence of these dyes in water even at very low concentration is highly visible and undesirable. A wide range of methods have been developed for the removal of synthetic dyes from water and wastewater to decrease its impact on environment. Over 70,000 tons of approximately 10,000 types of dyes and pigments are produced annually world wide of which about 20 – 30% are wasted in industrial effluents during the textile dyeing and finishing processes [1]. Adsorption is one of the method, which is obtaining more attention because of its easy operations and versatility.

Adsorption is an affordable and effective technique for the removal of dyes and colored pollutants from wastewater [2]. Nano-adsorbents can be readily integrated into existing treatment processes in slurry reactors. Applied in the powder form, nano-adsorbents in slurry reactors can be highly efficient since all surfaces of the adsorbents are utilized and the mixing greatly facilitates the mass transfer [3]. Removal of hazardous, carcinogenic compounds from industrial wastewater is one of the growing needs in the present time. Many dyes and pigments are toxic in nature, with carcinogenic and mutagenic effects [4]. Use of cellulose based waste materials for adsorption of dyes from aqueous solution [5]. Activated carbon is the most widely used adsorbent for the removal of color from textile effluents. It is so because it has a high capacity for organic matter, but its use is limited due to its high cost [6]. Removal of textile dyes from aqueous solution with eco-friendly bio-adsorbent [7], a low cost agro waste material [8], Adsorption of dye on to rice husk [9], Adsorption of dye on shale oil ash [10], have been searched. Use of fibrous mass is a recent method for the removal of hazardous and carcinogenic effect having dyes [11]. Acid dyes are organic sulphonic acids, the commercially available forms are usually sodium salts, which exhibit good water solubility.[12]. Several researchers have also tried for the treatment of various dye wastewater by adsorption over low cost materials [13]. Adsorption of hazardous dye on low cost adsorbent [14-18].

In recent years, composites containing PANI and magnetic oxides exhibiting different nanostructures, such as nano-tubes, nano-rods or core shell nano-structures, have been extensively studied [19-22]. Clays can be modified to improve their sorption ability, one of the modification method is coating of magnetic nano-particles

[23,24]. Many authors have been used magnetic particle in nano-scale [25]. Fast removal and recovery of congo-red by modified iron oxide magnetic nano-particles [26].

The present work of investigation is a novel, simple and fast method for removal and recovery of Acid violet 19 dye by conducting PANI-Fe₂O₃ nano-composites as adsorbent. Adsorption experiment is carried out and also studied the adsorption kinetics for adsorption of Acid violet 19 on PANI-Fe₂O₃ nano-composites.

2. Experimental;

2.1. Materials and methods

Acid violet 19, Fe(NO₃)₃·9H₂O, FeS, NH₄OH, monomer Aniline, distilled Water, Ammonium per-sulphate [(NH₄)₂S₂O₈]. The water soluble Acid violet 19 dye which has M.F.C₂₀H₁₇N₃O₉S₃Na₂, M.W. 585.54 gm and PANI-Fe₂O₃ nano-composite is used as adsorbent. All chemicals and reagents were of analytical grade purity. The structure of dye presented in the fig-1. The stock solution 50 mg/l of acid violet 19 dye is prepared in double distilled water. In 50 ml of dye solution of the desired concentration, of different adsorbent dose is added and stirred with magnetic stirrer. At specific time interval suitable aliquot of the sample is withdrawn and analyse after centrifugation. The changes in dye concentration are determined by UV-Visible double beam spectro-photometer (systronics model-2203) at λ max 545 nm in our laboratory.

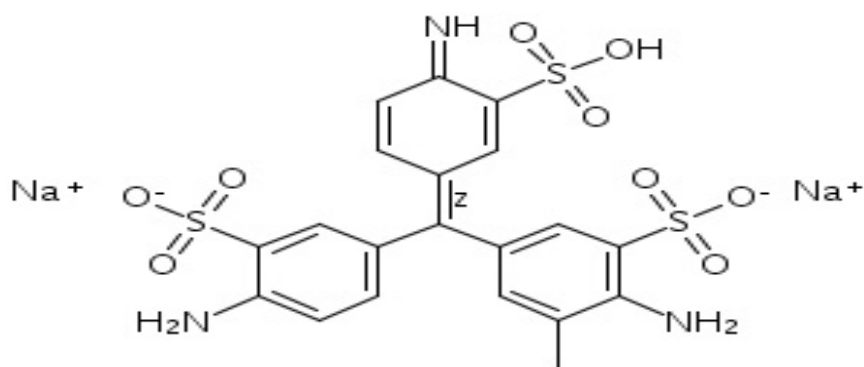


Fig-1. Structure of acid violet 19 dye

2.2. Preparation of Ferric Oxide nanoparticles

The 100 ml solution of Ferric nitrate [Fe(NO₃)₃·9H₂O](0.1M) was prepared in distilled water, it was then gelled by using 800 ml of monohydrated citric acid solution (0.1M) as ligand molecules. The Ferric nitrate solution was added to the citric acid solution drop-wise with vigorous stirring. The solution was then heated to a temperature of 80C⁰, while maintaining vigorous stirring until the gel was formed and the contained water was evaporated. Then nano-particles of Fe₂O₃ was yielded.

2.3. Preparation of PANI-Fe₂O₃ nano-composite

The solution of Fe₂O₃ nano-particle, monomer aniline, and ammonium per-sulphate ((NH₄)₂S₂O₈) was prepared in distilled water with vigorous stirring at R.T. The amount of Fe₂O₃ & monomer aniline was taken in 1:2 ratio. The pH value was controlled during the entire experiment to pH-11. A black precipitate of PANI-Fe₂O₃ was observed after 10 hour. The resulting polymer nano-composite was poured into water and filtered. Each wash step is carried out until the filtrate become clear and colourless. Finally, the polymer composite is washed with distilled water, ethanol, then dried.

3. Results and Discussion

3.1. Characterisation and Analysis:

3.1.1. SEM Analysis-

Scanning electron microscopy is widely used to study the morphological features and surface characteristics of adsorbent materials. The PANI-Fe₂O₃ nano-composites is analysed by SEM before fig-2(a) and after adsorption of Acid violet 19 dye as shown in the fig-2(b). It show SEM micrographs of PANI-Fe₂O₃ and PANI-Fe₂O₃ dyed by Acid violet 19. They shows surface texture and porosity of PANI-Fe₂O₃. The PANI-Fe₂O₃ has heterogeneous surface, micro-pores and meso-pores as seen from its surface micrographs.

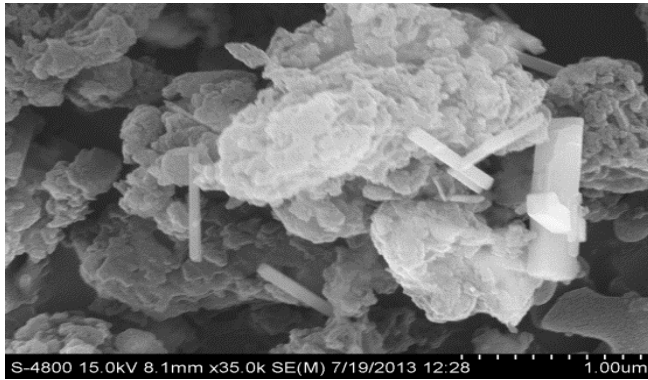


Fig-2(a). SEM images of Prepared PANI- Fe₂O₃ nano-composites.

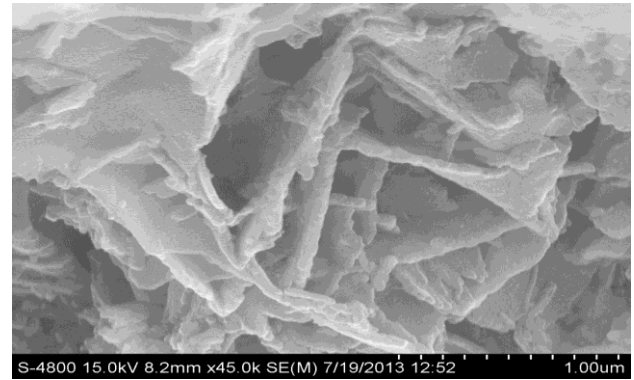


Fig-2(b). SEM images of adsorption of acid violet 19 dye on PANI-Fe₂O₃ nano-composites.

3.1.2. Electron Dispersive X-Ray Spectroscopy(EDS) Analysis-

Interaction of electron beam with a sample target produces a variety of emissions. An energy-dispersive (EDS) detector is used to separate the characteristic x-rays of different elements into an energy spectrum, and EDS system software is used to analyze the energy spectrum in order to determine the abundance of specific elements. EDS can be used to find the chemical composition of materials down to a spot size of a few microns, and to create element composition maps over a much broader raster area. Together, these capabilities provide fundamental compositional information for a wide variety of materials. From the analysis, comes to know that PANI-Fe₂O₃ nano-composite consist of exact elemental composition of specific element like Fe, O, C, N etc. is as shown in the(fig.3).The observed elemental composition is Fe=2.39%,O=16.68%,C=67%,N=12.21%.As PANI-Fe₂O₃ is conducting material therefore it needs to coat with gold(Au) metal.

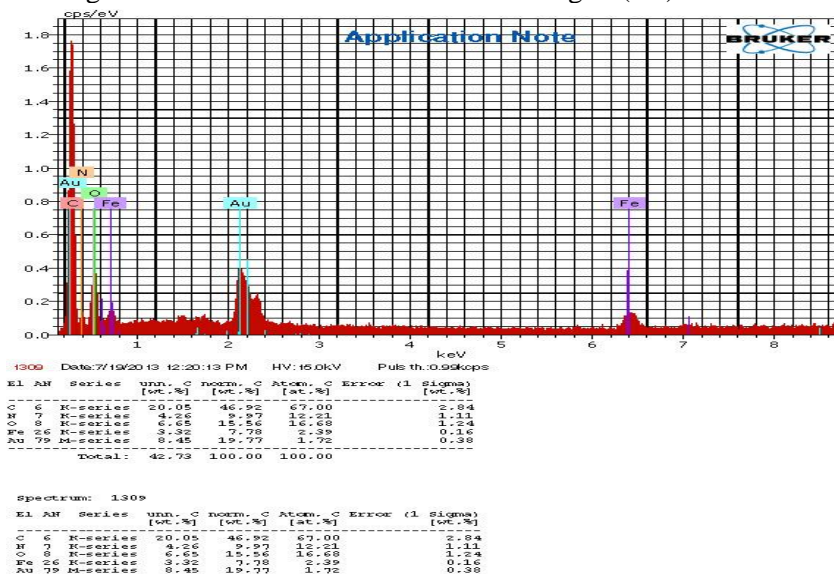


Fig- 3. EDS image of gold coated (Au) PANI-Fe₂O₃ nano-composites

3.1.3. XRD Analysis-

The XRD diagram of PANI-Fe₂O₃ is as shown in Fig-4.It shows the main peak spectrum 2θ of 33° and 2° peak of 2θ of 35° and 63° respectively. The high intensity of peaks indicates the crystalline nature of PANI-Fe₂O₃. By Scherer, formula is 20 nm estimated the average crystalline size of PANI-Fe₂O₃ particles.

3.2. Parametric studies-

The adsorptive removal of Acid violet 19 is studied at λ max 545 nm. The optimum condition for removal of dyes is 20 mg/ Lt, pH 8, PANI-Fe₂O₃ 10gm/lit. The results obtained during this study are as shown in the figs (5-7).

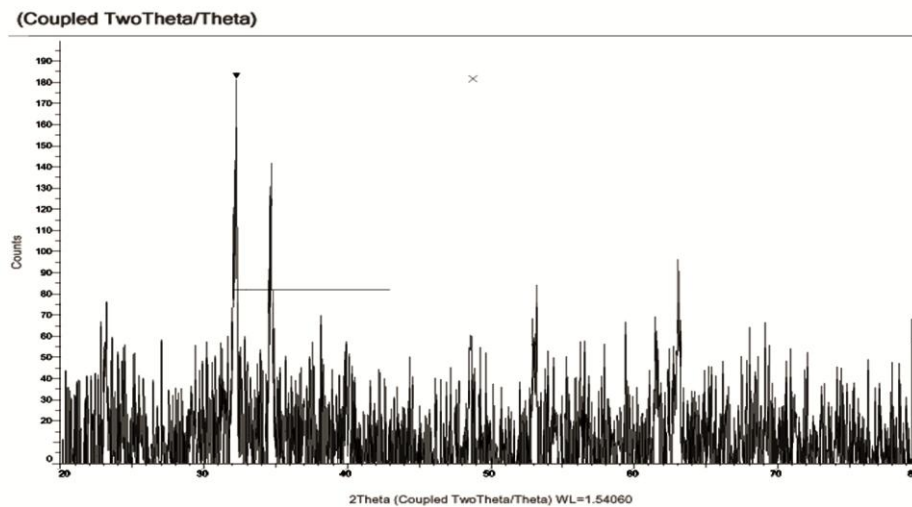


Fig-4 the XRD diagram of prepared PANI-Fe₂O₃.

3.2.1. Effect of adsorbent dose-

The effect of adsorbent dose on the removal of acid violet 19 dye is investigated. The % removal of acid violet 19 dye by PANI-Fe₂O₃ nano-composite at different adsorbent doses 2 to 10gm/lt for 20 to 80 mg/lt of dye conc. was studied as shown in the (fig-5). Adsorptive removal of Acid violet 19 increases rapidly from 55-98.5% with an increasing amount from 2-10gm/lt of PANI-Fe₂O₃ nano-composite. As the number of active sites for the adsorption increases, removal of acid violet 19 also increases as shown in the (fig 5). It is also observed that, as the conc. of dye increases from 20 -80 mg/lt, % removal of dye decreases from 98.5-90 % for adsorbent dose 10 gm/lt.

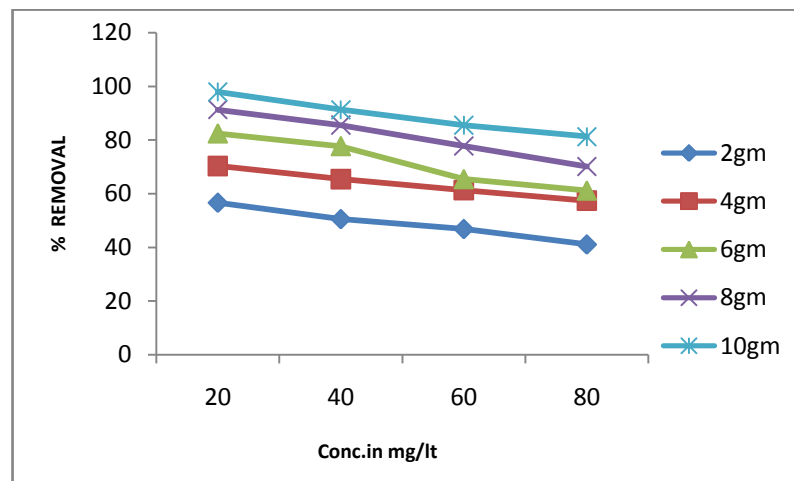


Fig-5: Effect of adsorbent dose on % removal of acid violet 19 dye for different initial dye conc. With contact time 90min, pH 8.

3.2.2. Effect of pH-

The adsorptive removal of dye was studied at different pH values as it is an important parameter for reaction taking place on the particular surface. The role of pH on the adsorptive removal of acid violet 19 was studied in the pH range 0-10 at dye concentration 20 mg/lit and PANI-Fe₂O₃ concentration 10gm/lt. It was observed that the rate of adsorption increases with an increase in pH up to 8 as shown in the (fig-6). As the pH increases, no. of acid anions increased. These acid anions form a bond with PANI-Fe₂O₃ nano-composite. This adsorption is based on Intraparticle diffusion model. When the pH increases onwards 8.5, the repulsion of the dye anions by negatively charged PANI-Fe₂O₃, therefore surface would result in reduction in efficiency of adsorption of Acid violet 19 dye. At low pH acid anions of dye does not formed hence observed % removal of dye is minimum.

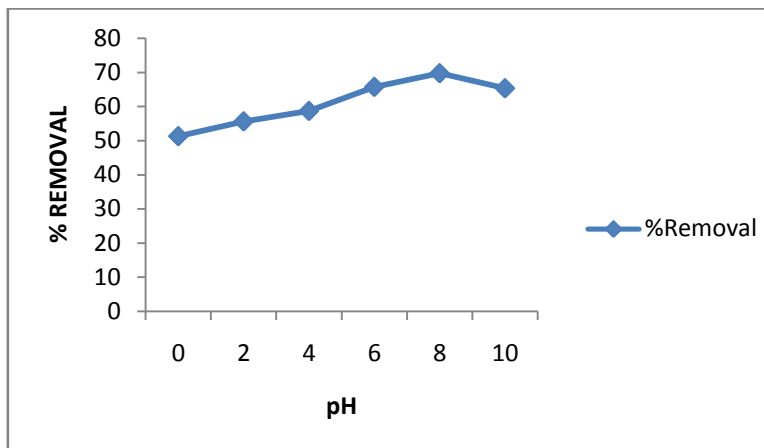


Fig 6. Effect of pH on removal of acid violet 19 dye by PANI-Fe₂O₃ adsorbent dose 10g/l at 20mg/l.

3.2.3. Effect of contact time-

The effect of contact time for the removal of acid violet 19 dye by PANI-Fe₂O₃ nano-composite is as shown in fig-7. It is observed that the dye is rapidly adsorbed in the first 40 min up to 80% and then adsorption rate decreased gradually and reached equilibrium in about 90 min up to 98.5%. At the beginning adsorption rate is faster as the dye ions are adsorbed by the exterior surface of the PANI-Fe₂O₃ nano-composite. When the adsorption of the exterior surface reaches saturation, the ions exerted onto the pores of the adsorbent PANI-Fe₂O₃ and are adsorbed by the interior surface of particle. This phenomenon takes relatively long contact time.

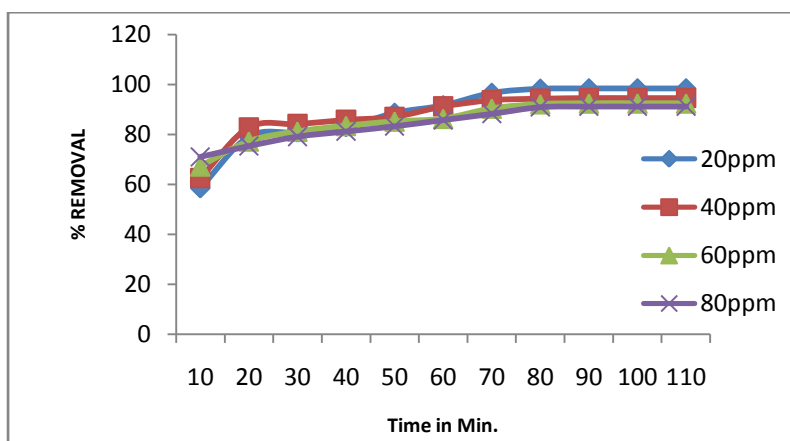


Fig-7. Effect of contact time of acid violet 19 on % removal adsorbent dose 10g/l at pH 8 (where-1 ppm = 1mg/l)

4. Adsorption kinetics study-

The adsorption kinetics gives the idea about mechanism of adsorption, from which efficiency of process estimated.

4.1. Pseudo 1st Order-

The integrated form of equation is

$$\log(q_e - qt) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad (2)$$

Where q_e & qt are the amounts of dye adsorbed (mg/g) on PANI-Fe₂O₃ at equilibrium & at time t (min) respectively, while K_1 is the rate constant obtained from the slope of the plot $\log(q_e - qt)$ Vs time is as shown in (fig-8&fig-9). The linear relationship of the plot for 20,40,60,80 mg/l dye concentration indicates validity of equation. These calculated K_1 and correlation coefficient r^2 values are shown in Table 1. The correlation coefficient r^2 for the plots are >0.866 , the calculated q_e values from 1st order kinetics plots are too small as compared to experimental q_e values (as shown in Table 1). This shows that the Pseudo 1st order kinetic model is not applicable to predict the adsorption kinetics of acid violet 19 on PANI-Fe₂O₃ nano-composite.

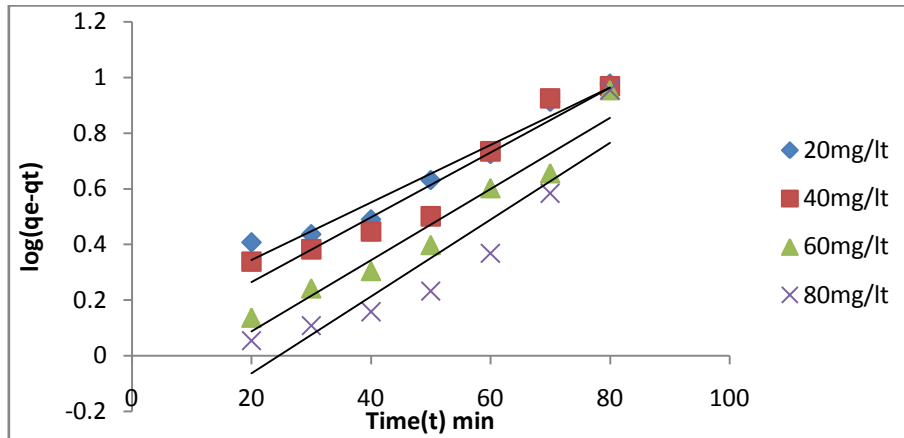


Fig-8. Pseudo 1st order kinetics of acid violet 19 dye with adsorbent(PANI-Fe₂O₃) dose 10gm/ Lt.

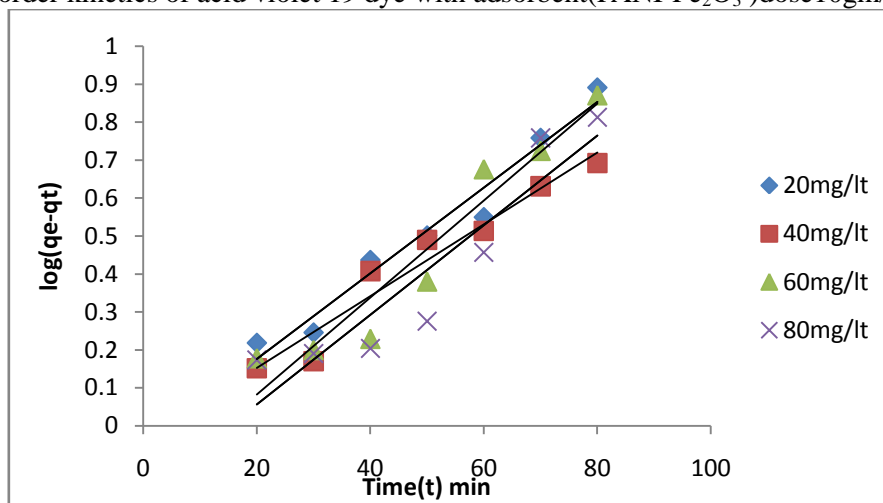


Fig-9. Pseudo 1st order kinetics of acid violet 19 dye with adsorbent(PANI-Fe₂O₃) dose 6 gm/Lt.

4.2. Pseudo 2nd Order-

Adsorption kinetics were explained by 2nd order model is represented by equation.

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where K_2 is rate constant for 2nd order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), while k_2 and q_e are determined from slope and intercept of plot t/qt Vs t (fig-10 and fig-11). The linear plot with correlation coefficient (r^2) 0.985 to 0.999 (as shown in table 1) shows a good agreement to the experimental q_e . It shows that adsorption belongs to the 2nd order kinetics model.

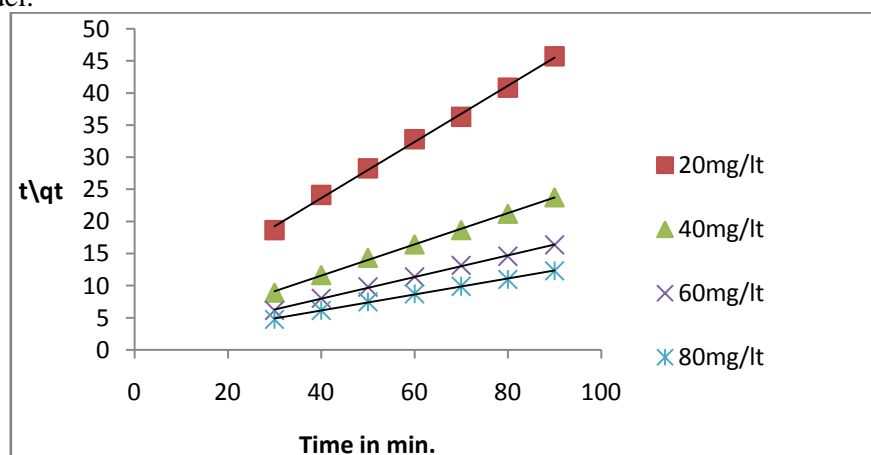


Fig-10. Pseudo 2nd order kinetics of acid violet 19 dye with adsorbent(PANI-Fe₂O₃) dose 10gm/ Lt.

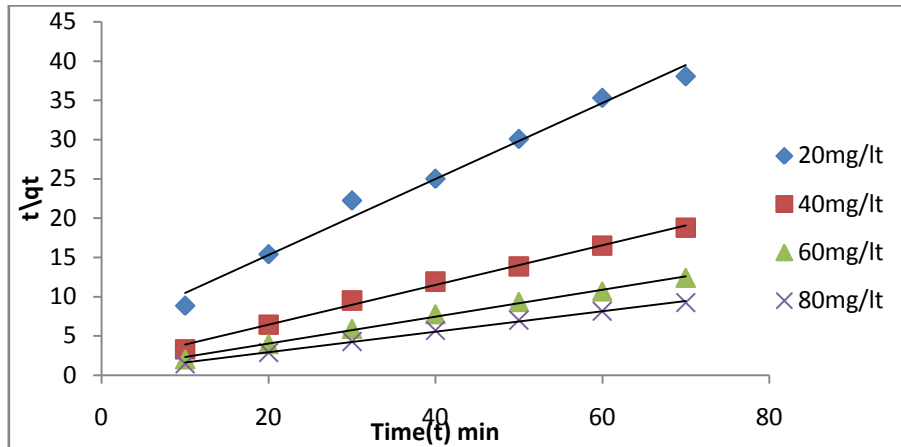


Fig-11. Pseudo 2nd order kinetics of acid violet 19 dye with adsorbent(PANI-Fe₂O₃) dose 6 gm/ Lt.

Table: 1 comparisons of the pseudo first order and pseudo second order adsorption rate constants and Calculated and experiments q_e values for different initial concentrations

Pseudo first order					
adsorbent dose(g/Lt)	initial conc.(mg/Lt)	q_e (exp)(mg/g)	q_e (cal)(mg/g)	K_1 (min ⁻¹)	R ²
6	20	1.17	0.98	0.026	0.965
6	40	3.78	0.99	0.02	0.952
6	60	5.5	0.67	0.0294	0.927
6	80	7.3	0.66	0.027	0.866
10	20	1.96	1.37	0.023	0.96
10	40	3.92	1.07	0.002	0.933
10	60	5.78	0.67	0.025	0.948
10	80	7.7	0.45	0.031	0.863

Pseudo second order					
adsorbent dose(g/Lt)	initial conc.(mg/Lt)	q_e (exp)(mg/g)	q_e (cal)(mg/g)	K_1 (min ⁻¹)	R ²
6	20	1.17	2.06	0.041	0.985
6	40	3.78	3.95	0.047	0.994
6	60	5.5	5.83	0.05	0.996
6	80	7.3	7.67	0.052	0.997
10	20	1.96	2.28	0.031	0.997
10	40	3.92	4.11	0.032	0.998
10	60	5.78	5.93	0.022	0.999
10	80	7.7	8.03	0.013	0.998

4.3. Intraparticle diffusion-

In the batch mode adsorption process, initial adsorption occurs on the surface of the adsorbent. In addition, there is a possibility of the adsorbate to diffuse into the interior pores of the adsorbent. Weber and Morris suggest the following kinetic model to investigate the adsorption is intra particle diffusion or not. The relationship may be given as equation (4)

$$qt = \frac{k_p t^{1/2}}{2} \quad (4)$$

Adsorption is a multilayer process, involving transport of solute particle from the aqueous phase to the surface of the solid adsorbent followed by diffusion into the interior of the pores. The possibility of intraparticle diffusion is tested by plotting a graph between the amount of dye adsorbed & the time $t^{1/2}$ at different time intervals. Where K_p is intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{0.5}$). The plot of qt Vs $t^{1/2}$ is linear indicates occurrence of intraparticle diffusion as shown in fig (12 and 13). The K_p has values 0.1153 to 0.2621 ($\text{mg g}^{-1} \text{min}^{0.5}$) for 20,40,60,80 mg/Lt dye conc. and 10 g/Lt adsorbent dose.

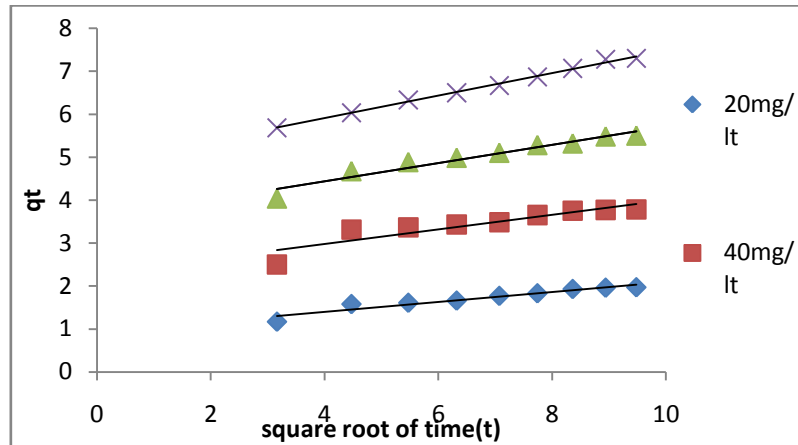


Fig-12. Intraparticle diffusion model of acid violet 19 dye with adsorbent(PANI-Fe₂O₃)dose 10 gm/ lt.

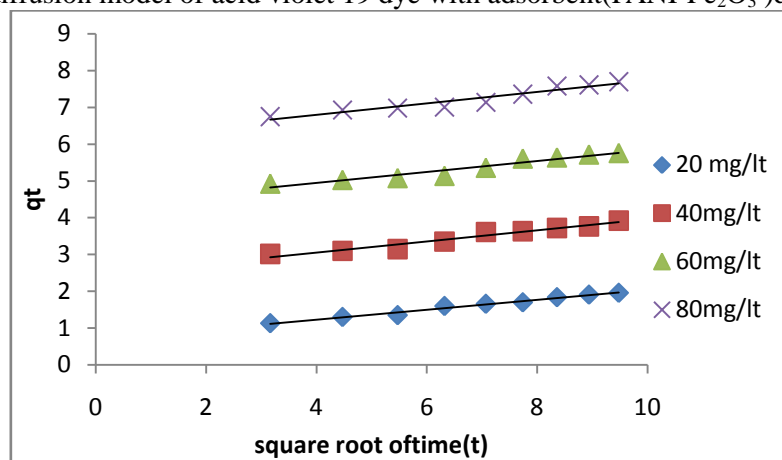


Fig-13. Intraparticle diffusion model of acid violet 19 dye with adsorbent(PANI-Fe₂O₃)dose 6 gm/ lt.

4.4 Elovich-

The Elovich equation is mainly applicable for chemisorption process. The equation is often valid for systems in which the adsorbing surface is heterogeneous [27]. The equation is given as follow

$$qt = \left(\frac{1}{\beta}\right) \ln \alpha \beta + \left(\frac{1}{\beta}\right) \ln t \quad (5)$$

Where α and β are constants during any experiment. α is the initial adsorption rate (mg/g min) and β the desorption constant (g/mg) during any one experiment. The constant can be obtained from the slope and intercept of the plot of qt versus $\ln t$ (fig-14&15).The value of β decreases from 2.88 to 1.31 (g/mg) for 10 gm/lt of adsorbent dose .The β value increases from 2.54 to 2.88 (g/mg) as adsorbent dose increased from 6 to 10 g/lt for 20 mg/lt of dye conc. (Table-2).

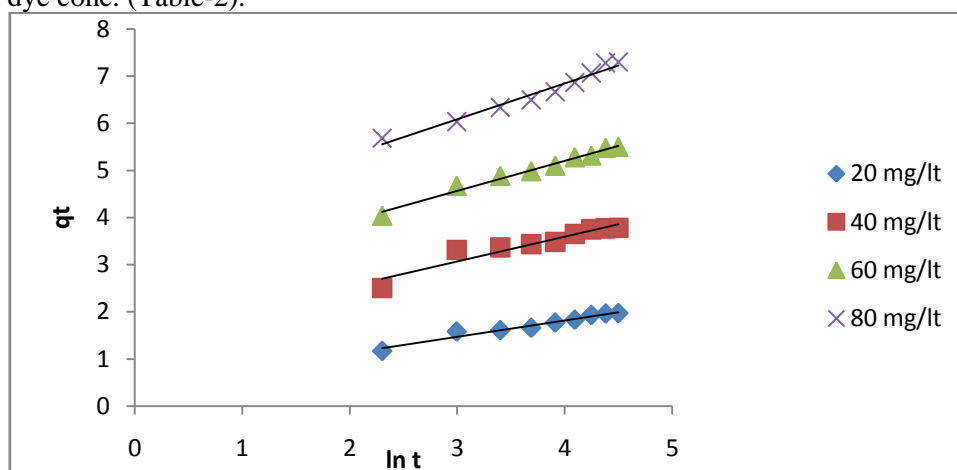


Fig-14. Elvoich adsorption model of acid violet 19 dye with adsorbent(PANI-Fe₂O₃)dose 10 gm/ lt.

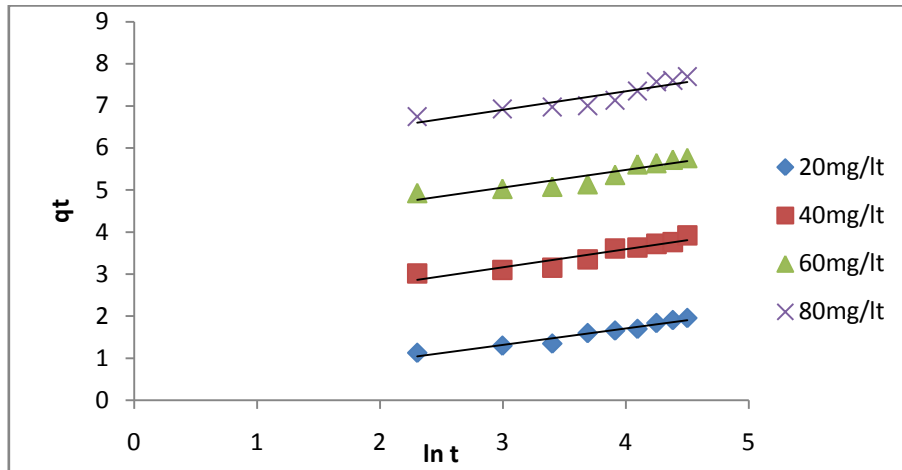


Fig-15. Elvoich adsorption model of acid violet 19 dye with adsorbent(PANI-Fe₂O₃)dose 6 gm/ lt.

Table-2. Coefficients of Intraprticle diffusion model and Elvoich model

Intraprticle diffusion model				Elvoich model			
adsorbent dose(mg/lt)	initial conc.(mg/lt)	Kp(int)	R ²	qt	α	β	R ²
6	20	0.1355	0.982	0.6947	0.269	2.54	0.951
6	40	0.1508	0.954	2.753	3.2X10 ⁴	2.32	0.895
6	60	0.1487	0.93	4.626	1.5X10 ²	2.38	0.855
6	80	0.1563	0.927	6.168	7.9X10 ¹¹	2.27	0.846
10	20	0.1153	0.922	0.863	1.51	2.88	0.961
10	40	0.1706	0.825	2.53	1.5X10 ²	1.9	0.905
10	60	0.2118	0.939	3.559	5.1X10 ³	1.56	0.982
10	80	0.2621	0.994	4.214	5.2X10 ⁴	1.31	0.969

4.5 Freundlich isotherm-

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems can be expressed in its logarithmic form as equation (6).The Freundlich adsorption isotherm equation is applied for acid fuchsin dye.

$$\log q_e = \log k_f + \left(\frac{1}{n}\right) \log C_e \quad (6)$$

where q_e is the amount of dye adsorbed (mg/g) and C_e is the equilibrium concentration of dye in solution(mg l⁻¹).The K_f and n are the constants incorporating and factors affecting adsorption process.The linear plot of $\log q_e$ vs $\log c_e$ shows Freundlich adsorption.In adsorption K_f value increases the quantity of dye adsorbed onto the surface of PANI-Fe₂O₃ also increases (fig-16).The slope $1/n$ ranging between 0 and 1 is the measure of adsorption extent or surface becomes heterogeneous as its value gets closer to zero [28]. The values of $1/n$ is between 0.775 to 0.621 for 20 to 60 mg/lt dye conc.and adsorbent dose 10 gm/lt. It indicates chemisorption.The calculated K_f and $1/n$ values are presented in Table-3.

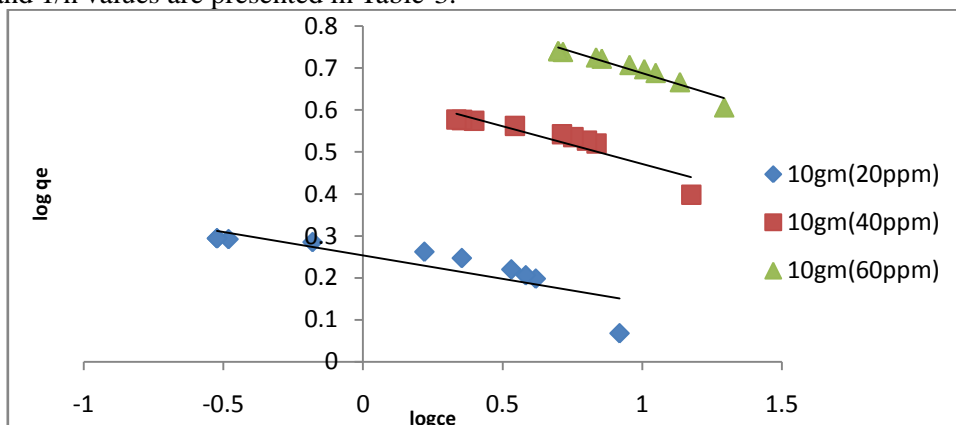


Fig-16. Freundlich adsorption isotherm for acid violet 19 dye at pH 8.(Where- 1ppm=1mg/lt)

4.6 Langmuir isotherm-

Langmuir isotherm is a test on the assumption that adsorption occurs at specific homogenous sites within the adsorbent. Once an adsorbate molecule occupies a site, no further adsorption can take place. Thus, adsorption reaches to an equilibrium value. The saturated monolayer curve can be express in the equation given below. It has been successful for the explanation of monolayer adsorption. The linear form of Langmuir equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (7)$$

Where C_e is the equilibrium concentration (mg/L), q_e amount of dye adsorbed at equilibrium (mg/g) and Q_0 (mg/g) is the monolayer coverage capacity, b is Langmuir isotherm constants(l/mg). The values of Q_0 and b are determined from the slope and intercepts of the linear plots of C_e/q_e Vs C_e . It is shown in the (fig- 18) .calculated Q_0 and b values are presented in Table-3. The Langmuir adsorption suggest the monolayer coverage of dye on PANI-Fe₂O₃ nano-composite. The essential characteristics of the Langmuir isotherm can be expressed by dimensionless constant called equilibrium parameter.

$$RL = \frac{1}{1+bC_i} \quad (8)$$

where b is the Langmuir constant, C_i is the initial dye concentration (mg/lt). According to the rule of RL. $RL \geq 1$ Unfavorable, $RL=1$ linear, $1 \geq RL \geq 0$ Favorable, $RL=0$ Irreversible. When the rule $1 \geq RL \geq 0$ is obeyed, Langmuir isotherm becomes favorable. The correlation coefficient of r^2 values for Langmuir and Freundlich isotherm are shown in Table-3. Both the isotherms are found to fit well to experimental data and agree with literature [29-31].

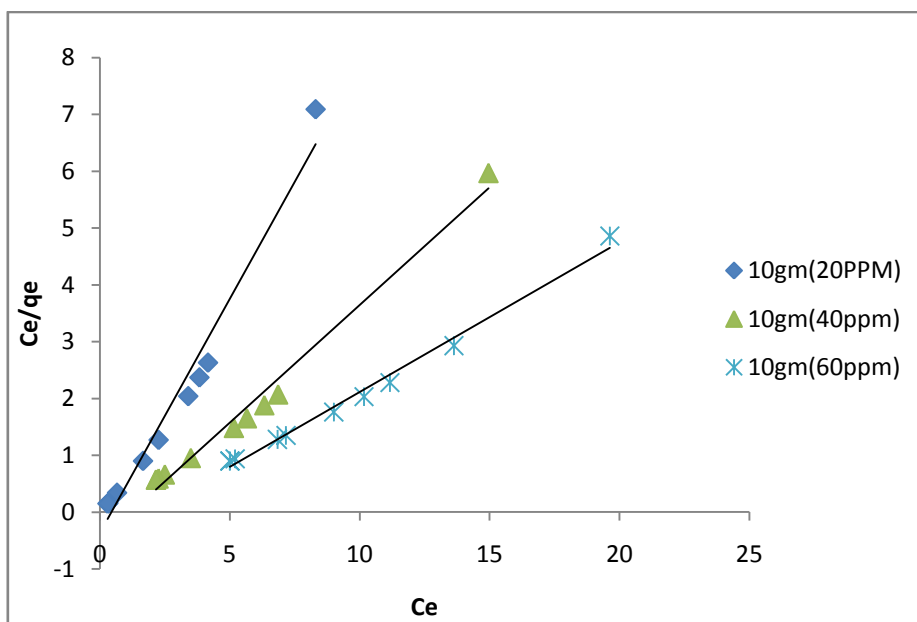


Fig-17. Langmuir adsorption isotherm for acid violet 19 dye at pH 8. .(Where- 1ppm=1mg/lt

Table-3. Freundlich and Langmuir coefficients for adsorption of acid violet 19 dye on PANI-Fe₂O₃ for different dye concentration at pH 8.

Freundlich coefficients						Langmuir coefficients			
adsorbent dose (mg/lt)	initial conc.(mg/lt)	Kf(l/g)	n	1/n	R ²	Q ₀ (mg/g)	b	RL	R ²
6	20	35.48	0.95	1.052	0.799	0.977	1.89	0.025	0.977
6	40	17.78	1.35	0.74	0.935	0.995	2.37	0.01	0.995
6	60	14.45	1.21	0.826	0.951	0.798	0.5	0.032	0.798
10	20	1.79	1.29	0.775	0.7443	0.97	2.27	0.0211	0.97
10	40	4.47	1.51	0.662	0.853	0.984	0.835	0.029	0.984
10	60	7.76	1.61	0.621	0.931	0.99	0.507	0.046	0.99

Conclusions

1. PANI-Fe₂O₃ nano-composite is successfully synthesised in situ through self polymerisation of monomer aniline.
2. Adsorptive removal of acid violet 19 dye by using adsorbent dose (PANI-Fe₂O₃) is successfully applied. The adsorption rate increased significantly by increasing amount of adsorption dose, while with an increasing dye concentration adsorption rate decreases. Basic pH condition is found, which significantly affect the dye adsorption efficiency of acid violet 19 dye is 98.5% and after elution the concentration of dye is 20 mg/lit.
3. The present study shows that conducting PANI-Fe₂O₃ can be used adsorbent for the removal of acid violet 19 dye from aqueous solution.
4. The amount of adsorbed dye is found from 1.7 to 7.7(mg/g) increased with an increase contact time and increase in initial dye concentration with an increasing adsorbent dose.
5. The rate of adsorption is found to confirm the pseudo second order kinetics with good correlation with R² values.
6. It is found that Elvoich model has good correlation with R² values, which indicates chemisorptions.
7. Adsorption isotherms are described by Langmuir isotherm and Freundlich isotherm models. Freundlich isotherm model is found to fit with experimental data due to higher 1/n and K_F values.

Acknowledgement-Authors are gratefully acknowledged to the Director UDCT, Jalgaon (M.S) for SEM, EDS &XRD studies. Authors are also thankful to the Principal of G.T. Patil College, Nandurbar for providing necessary laboratory facilities.

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