PREPARATION OF CROSSLINKED POLYVINYLPYRROLIDONE NANOCOMPOSITES AND INVESTIGATION OF THEIR ADSORPTION KINETICS

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Abstract

In the study, nanocomposites of cross-linked polyvinylpyrrolidone (PVPPNC) was chosen to analyze the adsorption properties. For this purpose, nanofiller sodium montmorillonite with two types of cation exchange capacity (CEC) values of 92.6 and 145 meq/100 g were used and modified into organoclay (OC) with octadecyl ammonium chloride. Monomer, initiator, and crosslinker with (or without) OC (w/w, 5% or 10 %) in the specified reaction conditions were mixed together and purified to prepare PVPPNC. The synthesized samples were structurally identified by performing the FTIR, DSC, and TGA characterizations. In the adsorption experiments, methylene blue (MB) adsorption from its solution onto the PVPPNC were carried out and the adsorption capacities were determined as functions of dye solution concentration, amount of adsorbent, and temperature. Adsorption capacity increased with increasing temperature, with increasing MB concentration, and decreased with increasing amount of adsorbent depending on the percentage of OC and its CEC.

1 Introduction

Among the various decolorizing methods in textile, metal plating, packaging, and paper industry's wastewater, namely biological, electrochemical, oxidation, adsorption, and coagulation/flocculation, adsorption is one of the most effective ways of treatment [1, 2]. Adsorption is one of the most widely applied techniques for environmental remediation. Its kinetics are of great importance to evaluate the performance of adsorption capacity of the adsorbent. Formerly, activated carbon was the most commonly used adsorbent, but today its use is very limited because of its high cost and high energy requirement for its regeneration [3]. A good alternative to activated carbon is surface modified clay minerals. Since clay is abundant, it has lower cost compared to activated carbon [4,5]. On the other hand, the regeneration of the adsorbent is also important for industrial usage. Therefore polymeric structure containing clay minerals become more important.

In this study, water soluble polyvinylpyrrolidone (PVP) which is commonly used in the industry was cross-linked (PVPP) to analyze its adsorption property. The adsorption capacity of cross-linked polyvinylpyrrolidone was increased by preparing polyvinylpolypyrrolidone nanocomposites (PVPPNC). For this purpose, a layered mineral sodium montmorillonite (Na-

MMT) was chosen as nanofiller for the synthesis of PVPPNC. The structural characterization and the adsorption properties of PVPPNC samples were investigated in detail.

2 Materials and testing methods

2.1 Materials

Two types of Na-MMT with cation exchange capacity (CEC) values of 92.6 meq/100 g (from Nanocor PGW) and 145 meq/100 g (from Southern Clay Products) were used and modified into organoclay (OC) with octadecyl ammonium chloride (from Merck A.G.). Monomer N-vinyl pyrrolidone (from Fluka A.G.), crosslinker divinylbenzene (DVB) (from Sigma-Aldrich), initiator azobisisobutyronitrile (AIBN) (from Sigma-Aldrich), cationic dye methylene blue (MB) (from Sigma-aldrich) and all other reagents (from Merck) were used without further purification.

2.2 Preparation methods

Modification of clays: Octadecyl ammonium chloride (ODA) (50 mmol) was dissolved in 100 mL of distilled water in an acidic medium and heated up to 80°C. The solution was mixed with a suspension composed of 20 g clay in 400 mL hot water. The mixture was vigorously stirred for 1 h at 80°C. The white powder OC was formed, and then filtered. The precipitate OC was washed with fresh hot water. After stirring for one more hour, the filtration and washing process was repeated once more. The final precipitate was dried in an oven at 60^0C and then grinded. [6].

Preparation of PVPPNC: In a typical polymerization, AIBN, ethanol, and OC were mixed together at room temperature. The amount of OC was selected 5 % and 10 % for each Na-MMT. Then desired amount of DVB and the monomer added to this mixture under reflux at 80 ^{0}C. After the gelation occurring in 2 hours, more hot ethanol was added and the reaction was carried out for 4 more hours. The reaction mixture was cooled, washed with water, and then filtered. This purification was repeated twice. The powdered PVPPNC was obtained. This was repeated without OC to obtain PVPP to compare the results.

2.3 Characterization methods

Infrared spectra of samples were recorded on a ATRP equipped FTIR spectrophotometer (Perkin Elmer Spectrum 100). The glass transition temperatures (T_g) were determined by DSC instrument (Perkin Elmer DSC 4000) at a heating rate of 10 ^{o}C.min^{-1} under a nitrogen flow of 20 mL.min^{-1} between -10 ^{0}C and 300 ^{0}C. Termogravimetric analyses were carried out in a thermogravimetric analyzer (EXSTAR) under a nitrogen atmosphere (200 mL.min^{-1}) at a heating rate of 10 ^{o}C.min^{-1} between 25 ^{0}C and 900 ^{0}C. Adsorption experiment results were recorded by UV-VIS spectrophotometer (PG T80).

2.4 Adsorption experiments

The determined wavelength corresponding to maximum adsorption of MB was found as 664 nm in UV-VIS spectrophotometer. Then the calibration curve between absorbance and MB concentration at this wavelength was obtained. For adsorption experiments, aqueous solutions having MB concentrations of 40, 80, and 120 mg.L^{-1} were prepared. All experiments were conducted at a pH of 5.40.

In adsorption experiments, discontinuous equilibrium method was followed. In each experiment, 0.05 g adsorbent was put into 100 mL of methylene blue solution of known concentration and the mixture was stirred at 1000 rpm while keeping the temperature

constant. Samples were taken within pre-determined time intervals and the adsorbent in each sample was precipitated by centrifuging the sample at 2500 rpm.
Adjusting the wavelength to 664 nm, concentration of MB remaining in the solution (C_e) was determined by absorbance measurements obtained from UV-VIS spectrophotometer. The amount of MB adsorbed for each sample (C_a) was calculated by subtracting the amount of MB in the final solution from that in the initial solution. From the ratio of the mass, in mg, of MB adsorbed at various times, to mass, in g, of adsorbent, adsorption capacities (q_t) were calculated as $mg.g^{-1}$. Experiments were conducted until a constant value of adsorption capacity was obtained.
The influence of temperature on adsorption characteristics were determined by obtaining adsorption isotherms at 30, 40, and 50˚C.

3 Results and discussion

In this study, there are 2 PVPP samples and 4 PVPPNC samples from 2 types of OC by using two ratios were prepared.

3.1 Characterization Results

FTIR analysis results: The FTIR Spectra analysis results of the samples summarized in Table 1. It was given for the comparison of the preparation steps of PVPPNC samples.

Sample No	Sample Name	Chemical Bond Type	Wavenumber, cm^{-1}
1	Na-MMT (CEC=92.6)	-Si-O-	991.26
2	Na-MMT (CEC=145)	-Si-O-	988.24
3	OC (CEC=92.6)	-Si-O- $-CH_2-CH_2-CH_2-$	1001.76 2924.72 – 2850.71
4	OC (CEC=145)	-Si-O- $-CH_2-CH_2-CH_2-$	999.12 2920.21 – 2850.37
5	ODA	-C-H $-CH_2-CH_2-CH_2-$	2955.10 2916.27 – 2848.45
6	PVP	-C-H -N-C=O	2956.83 1645.86
7	PVPP	-C-H -N-C=O	2921.09 1667.08
8	PVPPNC (5% OC) (CEC=92.6)	-C-H -N-C=O	2922.33 1667.08
9	PVPPNC (10% OC) (CEC=92.6)	-C-H -N-C=O	2922.77 1660.99
10	PVPPNC (5% OC) (CEC=145)	-C-H -N-C=O	2924.35 1686.22
11	PVPPNC (10% OC) (CEC=145)	-C-H -N-C=O	2922.76 1659.70

Table 1. FTIR results of all samples

DSC analysis results: The T_g values were obtained for the polymeric samples (Table 2).

Sample No	Sample Name	T_g, ^{0}C
7	PVPP	132.0
8	PVPPNC (5% OC) (CEC=92.6)	131.0
9	PVPPNC (10% OC) (CEC=92.6)	131.1
10	PVPPNC (5% OC) (CEC=145)	130.8
11	PVPPNC (10% OC) (CEC=145)	130.4

Table 2. DSC results of polymeric samples

TGA analysis results: Percent weight loss of the nanocomposites and their degradation temperatures were given in Table 3 and Figure 1. The weight loss percent of the nanocomposites showed the inorganic parts of the prepared samples. The results were found as compatible.

Sample No	Sample Name	Degradation starting temperature, ^{0}C	Percent weight loss
7	PVPP	830	--
8	PVPPNC (5% OC) (CEC=92.6)	840	4.6
9	PVPPNC (10% OC) (CEC=92.6)	836	9.2
10	PVPPNC (5% OC) (CEC=145)	837	4.1
11	PVPPNC (10% OC) (CEC=145)	840	8.5

Table 3. TGA results of polymeric samples

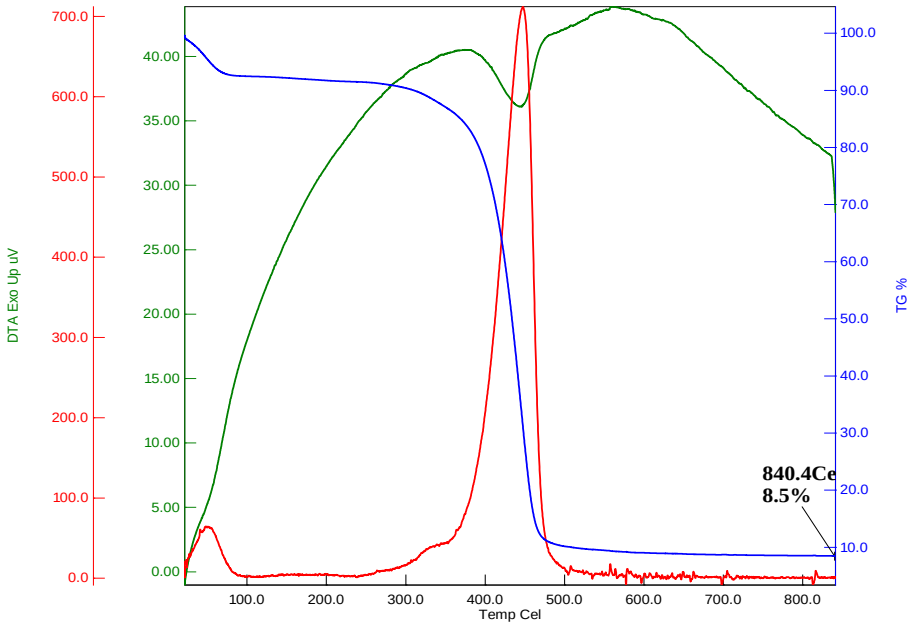

Figure 1. TGA Thermogram of Sample No 11.

3.2 Results of Adsorption Experiments

Adsorption capacities of the prepared nanocomposites were given in Figures 2 and 3.

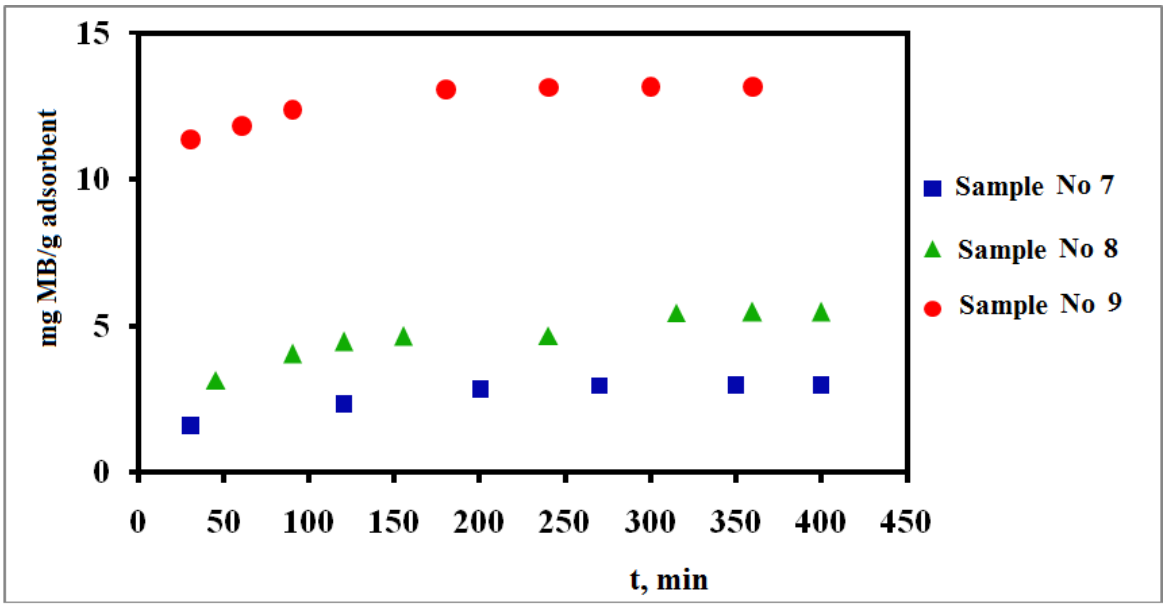

Figure 2. Variation of adsorption capacities with time for Samples No.7, 8, and 9. (Initial MB concentration = 40 mg.L^{-1}, amount of adsorbent=0.05 g, T = 30 °C, pH = 5.40)

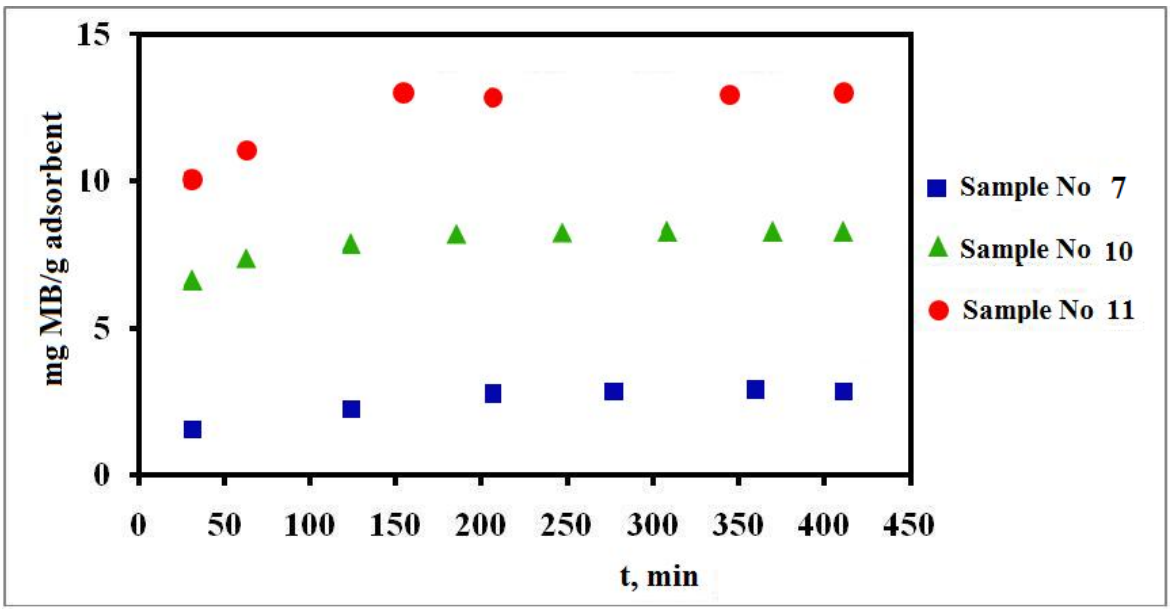

Figure 3. Variation of adsorption capacities with time for Samples No.7, 10, and 11. (Initial MB concentration = 40 mg.L^{-1}, amount of adsorbent=0.05 g, T = 30 °C, pH = 5.40)

The applicability of the results of adsorption experiments to pseudo-first-order and pseudo-second-order kinetic models have been investigated. The results fitted linearized form of pseudo-second-order kinetic model given by Ho ve McKay is as follows [7,8]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2.q_e^2}\right) + \frac{t}{q_e} \qquad (1)$$

where q_t and q_e are the amounts of dye adsorbed per gram of adsorbent ($mg.g^{-1}$) at time t and at equilibrium, respectively and k_2 is the second-order rate constant ($g.mg^{-1}\ min^{-1}$).

Results of adsorption experiments at 30 ^{0}C with the initial MB concentration 40 $mg.L^{-1}$ and mass of adsorbent of 0.05 g were plotted as t/q_t – t in Figures 4 and 5 and the calculated k_2, q_e ve R^2 values were tabulated in Tables 4 and 5.

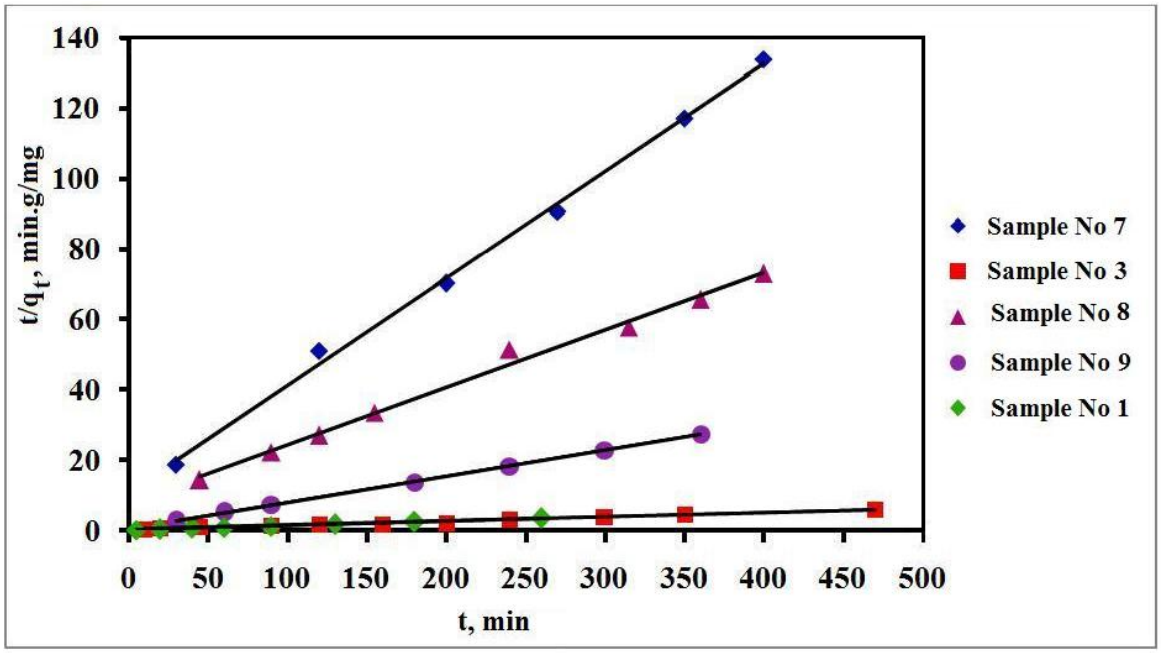

Figure 4. Pseudo-second order sorption kinetics of MB onto Samples No 7, 3, 8, 9, and 1. (Initial MB concentration = 40 $mg.L^{-1}$, amount of adsorbent=0.05 g, T = 30 °C, pH = 5.40)

Sample No	Sample Name	k_2, $g.mg^{-1}\ min^{-1}$	q_e, $mg.g^{-1}$	R^2
1	Na-MMT (CEC=92.6)	$15.6x10^{-3}$	79.4	0.999
3	OC (CEC=92.6)	$0.513x10^{-3}$	79.3	0.998
7	PVPP	$8.63x10^{-3}$	3.3	0.997
8	PVPPNC (5% OC) (CEC=92.6)	$3.42x10^{-3}$	6.1	0.993
9	PVPPNC (10% OC) (CEC=92.6)	$11.2x10^{-3}$	13.5	0.997

Table 4. Kinetic parameters (k_2 and q_e) for the adsorption of MB (with an initial MB concentration of 40 $mg.L^{-1}$) on three different modified clays at 30 °C.

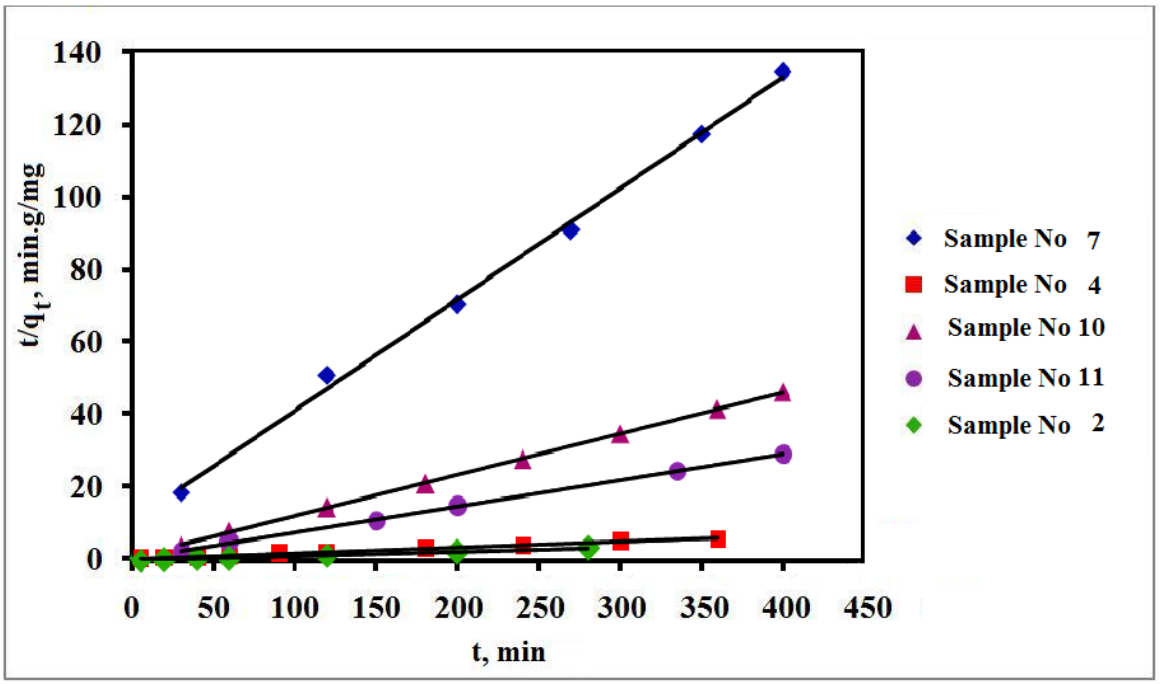

Figure 5. Pseudo-second order sorption kinetics of MB onto Samples No 7, 4, 10, 11, and 2. (Initial MB concentration = 40 mg.L^{-1}, amount of adsorbent=0.05 g, T = 30 °C, pH = 5.40)

Sample No	Sample Name	k_2, g.mg^{-1} min^{-1}	q_e, mg.g^{-1}	R^2
2	Na-MMT (CEC=145)	391x10^{-3}	80.0	0.999
4	OC (CEC=145)	0.43x10^{-3}	64.1	0.999
7	PVPP	8.63x10^{-3}	3.3	0.997
10	PVPPNC (5% OC) (CEC=145)	14.0x10^{-3}	8.9	0.999
11	PVPPNC (10% OC) (CEC=145)	8.16x10^{-3}	14.0	0.999

Table 5. Kinetic parameters (k_2 and q_e) for the adsorption of MB (with an initial MB concentration of 40 mg.L^{-1}) on three different modified clays at 30 °C.

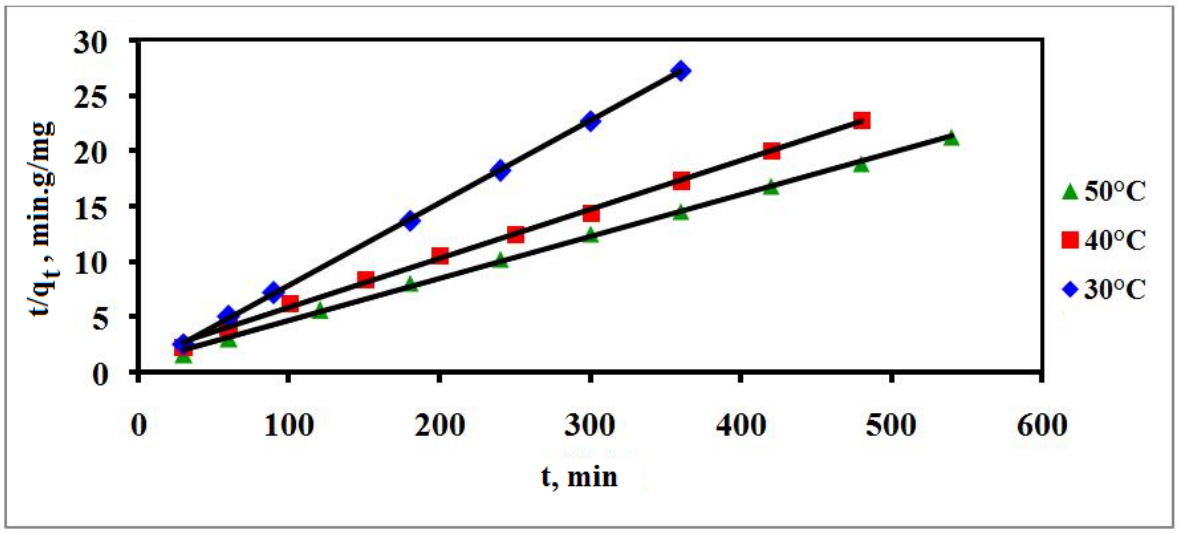

Figure 6. Pseudo-second order sorption kinetics of MB onto Samples No 9 at different temperatures. (Initial MB concentration = 40 mg.L^{-1}, amount of adsorbent=0.05 g, pH = 5.40)

The effect of temperature on the kinetic parameters was investigated for the adsorption of MB on Sample No 9. The results of adsorption experiments at three different temperatures (30 °C, 40 °C, and 50 °C) were applied to obtain t/q_t versus t plots (Figure 6). q_e and k_2 at each temperature were determined from the slope and intercept of each straight line. The kinetic parameters for the adsorption of MB on this sample at three different temperatures are given in Table 6.

T, ^{0}C	k_2, g.mg^{-1} min^{-1}	q_e, mg.g^{-1}	R^2
30	$11.2x10^{-3}$	13.5	0.999
40	$1.32x10^{-3}$	22.6	0.998
50	$1.55x10^{-3}$	26.4	0.999

Table 6. Kinetic parameters (k_2 and q_e) for the adsorption of MB at different temperatures (Initial MB concentration = 40 mg.L^{-1}, amount of adsorbent=0.05 g, pH = 5.40)

Applying the data in Table 6 to Arrhenius equation gives E_a =81.54 kJ.mol^{-1} for the adsorption of MB on the sample 9. This value corresponds to a high potential energy barrier indicating that adsorption has a chemical nature. Thermodynamic parameters were calculated by application of Van't Hoff equation. A ΔH^0 value of 35.1 kJ.mol^{-1} indicates that the adsorption process is endothermic. The experimental data is consistent with Freundlich isotherm model which gave the best results on heterogeneous surfaces.

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