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Orange II removal from aqueous solution by a cellulose acetate biopolymer incorporated with zinc oxide nanoparticles

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Zinc oxide nanoparticles and cellulose acetate composite have been synthesized using the in-situ co-precipitation technique and characterized using Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) analyses. The nanocomposite has been used as the adsorbent for the removal of Orange II dye from aqueous solution through adsorptive mechanism. The effect of concentration, *p*H, time contact, adsorbent dosage and temperature are investigated, and maximum percentage removal of the dye is calculated to be 83%. The Langmuir and Freundlich isotherm model gave a positive result with the adsorption experimental data with value of b and n equal to 0.075 and 1.197 respectively while regression coefficient R^2 equal to 0.839 and 0.859 in each case. The thermodynamics studies of the adsorption show that the adsorption reaction is exothermic and the process follows a pseudo second order kinetic model.

Keywords: Composite, Cellulose acetate, Adsorbent, Adsorbate, Zinc oxide

Metal particles at nano level have gained more attention in the field of electronic and medical research due to their structural, thermal and electronic properties[1] and are of high scientific applications as catalysts, sensors, and photo-electronic devices[2]. The unique structure and electronic properties of some nanoparticles have been exploited in their use as adsorbents and biosorbents for the removal of pollutants that are difficult to remove by particles at bulk level[3-]. Chemically modified nanomaterial have also attracted a lot of attention especially nanoporous materials due to their exceptionally high surface area for adsorption and catalysis[3].

Zinc oxide (ZnO) nanoparticles are in the centre of attention due to their fascinating properties and extensive application. Zinc oxide (ZnO) is a wide band gap semiconductor with an energy gap of 3.37eV at room temperature and has been used considerably for its catalytic, electrical, optoelectronic, and photochemical properties[2]. Their aforementioned interesting properties and enormous application potential has led to numerous methods being developed for synthesis of nanoparticles of various shapes and sizes[4].

Many methods have been described in the literature for the production of ZnO nanostructures such as lase ablation, hydrothermal methods, electrochemical depositions, sol–gel method, chemical vapour deposition, thermal decomposition, and combustion method[1]. Recently, ZnO nanoparticles were prepared by ultrasound, microwave-assisted combustion method, two-step mechanochemical-thermal synthesis, anodization, co-precipitation, and electrophoretic deposition[2].

Various chemical, physical and biological treatment methods have developed for the removal of dyes from aqueous solutions, including precipitation, coagulation–flocculation, reverse osmosis, oxidation with ozone, chlorine or hydrogen peroxide, use of anion exchange membranes and bacterial cells[5]. Adsorption has proven to be a reliable treatment methodology due to its low capital investment cost, simplicity of design, ease of operation and insensitivity to toxic substances, but its application is limited by the high price of some adsorbents and the large amounts of colour solution normally involved[6].

The aim of this work is to synthesize and characterize zinc oxide nanoparticles and cellulose acetate composite and to estimate its adsorption capacity in the removal of commercial Orange II dye.

Experimental Section

Reagents

Sodium hydroxide pellets, zinc acetate dihydrate, glacial acetic acid, acetic anhydride acid, conc. sulphuric acid, hydrogen peroxide, hydrochloric acid and ethanol were obtained from Sigma Aldrich, USA and BDH Analar, England.

Synthesis of zinc oxide nanoparticles

The procedure of Awodugba, *et.al* (2013) was adopted. ZnO nanoparticle was synthesized using 1 mM zinc acetate dihydrate salt and 0.01 M sodium hydroxide as the precursor. The solution of sodium hydroxide was added to the solution of zinc acetate dihydrate in drops. The precipitate was obtained and the *p*H of the resultant mixture was adjusted to 11 using 0.1M of HCl and NaOH. The solution then filtered using nano-filter pump. The precipitate obtained washed for three times using ethanol after which it was taken to oven to dry at 80°C for 6 h.

Cellulose isolation from saw dust

According to the procedure used by Lukmanul (2013), 50 g of the saw-dust sample collected was firstly suspended in distilled water for 2 h and then filtered out. The residue was dried under room temperature and later suspended in 12% NaOH and heated for 2 h. The mixture was then filtered and the residue washed until it was no longer soapy and free of NaOH. 30% solution of glacial acetic acid added to the residue and heated under water bath for 2 h and 200 mL of 30% H_2O_2 was added to the residue and heated in water bath till the white fibre of cellulose was isolated. The pure white cellulose obtained washed with ethanol three times and dry at room temperature.

Synthesis of cellulose acetate

The procedure used by Atanu (2006) was modified. 25 g of Cellulose synthesized was dispersed in 100 mL of glacial acetic acid and kept in water bath at 55°C for 1h with frequent stirring. Acetylation mixture of 0.8 mL of conc. H_2S0_4 and 50 mL of acetic anhydride was added to the glacial acetic acid mixture gradually. The resulting solution kept on water bath and heated for 2 h with occasional stirring at 55°C. A clear colloidal solution was obtained and transferred into 1L of distilled water and filtered. The residue obtained was oven dried at 60°C.

Impregnation of zinc oxide into cellulose acetate

The procedure used by Susan (2014) was modified. 15 g of cellulose acetate synthesized was suspended in water for 1 h. 1M solution of Sodium hydroxide was prepared separately in a conical flask. 6 g of zinc acetate dehydrate salt was prepared in 100 mL of ethanol and the residue of cellulose acetate dispersed in the solution of zinc acetate dehydrate. 1M NaOH solution was added to the solution in drop wise at 85°C under water bath with constant stirring for 90 min. The colloidal solution obtained was filtered and the white residue obtained was dried at ambient temperature for 4 days. The result product then sent for both SEM and FTIR analysis.

Adsorption studies

Batch adsorption of Orange II dye was carried out in aqueous solutions using zinc oxide-cellulose acetate nanocomposite as adsorbent and the effect of *p*H, temperature, amount of adsorbent, initial adsorbate concentration, and contact time was carried out. Adsorption isotherms were recorded at equilibrium conditions for concentration of dyes over the range 5-100 ppm at a fixed *p*H (11.0) and temperature (308 K).

Adsorption study was made in a mechanically agitated 100 mL Erlenmeyer flask filled with 60 mL of dye solution of desired concentration along with a known amount of adsorbent. The supernatant was carefully filtered through Whatmann filter paper and analyzed spectrophotometrically at λ_{max} of 485 nm after equilibrium. Stock solution of the dye was diluted to the required volume and concentration. The experiments were performed in duplicate and the average results were reported. The amount of dye adsorbed at time t, q_t (mg/g), was obtained by calculating the difference between the initial and the final Orange II dye concentration as shown in equation below:

$$q_e = \frac{(C_o - C_e)V}{W}$$

where qe (mg/g) is the amount of dyes adsorbed, and C_0 (mg/L) is the initial dye concentration, while Ce (mg/l) is the concentration of dye in solution at equilibrium, V (mL) is the volume, and W (g) is the weight of adsorbent. The percentage removal of the dye was computed using the following equation:

$$dye\ removal\ efficiency\ (\%) = \frac{(C_i - C_f)}{C_i} \times 100$$

C_i and C_f represent the initial and final (after adsorption) dye concentrations respectively and the amount of dye adsorbed onto nanoparticles at equilibrium, qe (mg g^{-1}), was calculated by the relationship[13].

Thermodynamic studies

Linearized Van't Hoff equations, were used to calculate the thermodynamic parameters such as

Gibbs's free energy change (ΔG_o), enthalpy change (ΔH_o) and entropy change (ΔS_o) during the process. The equations are shown below:

$$\log K_c = \Delta S^{\mathbf{0}}/_{2.303\,R} - \Delta \mathrm{H}^{\mathbf{0}}/_{2.303\,RT}$$

$$G^0 = -RT \log K_c$$

Kc is equilibrium constant and it is the amount of adsorbate in adsorbent/amount of adsorbate in solution.

Kinetic studies

Kinetic studies were carried out in batch at 60 mg/L of initial dye concentration with a fixed dose of adsorbent dose of 0.5 g at 308 K and *p*H 11.0. After a fixed time interval the adsorbent was separated by filtration and the filtrate thus obtained was analyzed spectrophotometrically to determine the equilibrium concentration of the dye. The study of kinetics of adsorption describes the solute uptake rate at the solid-solution interface.

Results and Discussion

The peaks at 3390, 2903 and 2113 cm^{-1} are attributed to O-H, C-H and bound water stretching vibrations within the cellulose molecules. 1640 cm^{-1}, 1427 cm^{-1} are the peaks for end group carbonyl stretch and C-H bending vibrations. The other C-H bending vibrations for asymmetrical and symmetrical CH_2 are attributable to the peaks at 1367 and 1315 cm^{-1}. The deep trough at 1054 cm^{-1} is significant for the C-O-C of glucopyranoside in cellulose biopolymer.

The peaks at 3740, 3440, 2937, 2124, 2318, 2027 cm^{-1} which corresponds to free and bound hydroxyl, C-H stretch and bound water have been greatly reduced when compared with the corresponding peaks on native cellulose IR patterns. The deep trough at 1725 cm^{-1} shows the presence of C=O of acetate while the peak at 1636 cm^{-1} confirms the presence of end group carbonyl on the cellulose acetate synthesized.1423, 1222, 1155 and 1028 cm^{-1} are the peaks for C-H, CH_2, O-H bending vibrations and C-O-C pyranoside of cellulose acetate.

The peaks at 894 and 700 cm^{-1} represents the Zn-O and Zn-C bonds respectively. The spectra reveal that the other various significant peaks at the functional group region for ordinary cellulose acetate and Zno have been greatly reduced.

The SEM micrographs of the cellulose acetate, zinc oxide and the composite of the two are presented in Fig 1. From the overall view of the images, the morphology of the fibre changed with respect to the

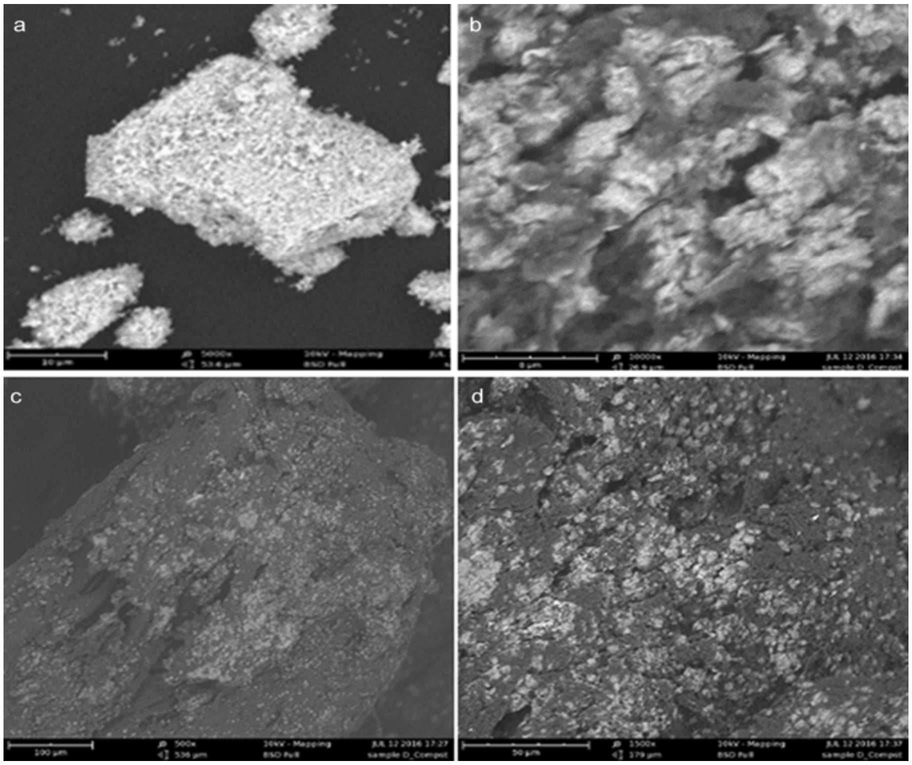

Fig. 1 — SEM images of (a) cellulose acetate (b) zinc oxide (c) and (d) cellulose acetate-zinc oxide composite at different magnification.

treatments. The cellulose acetate synthesized is an aggregated mass with a well distributed rough-like and spong-like surface.

The occurrence of the ZnO nanoparticles was observed by SEM analysis in Fig. 1 c and d. The SEM image reveals that the ZnO nanoparticles incorporate well into the cavities of the cellulose acetate. It also shows specific pores that affirms the adsorbent properties of the compound. These pores enhance the interactions of zinc ions with the ester and hydroxyl groups of cellulose acetate. The average crystallite size of the composite is found to be 8 µm.

The XRD pattern of the zinc oxide and cellulose acetate composite incorporate the two sets of diffraction peaks for ZnO and Cellulose acetate. The composite shows the characteristic pattern of an amorphous phase with typical low intensity at 2θ of 23° with couple of peaks before 20° showing cellulose acetate impregnation. The XRD pattern further reveals peaks of ZnO-CA at 2θ values of 29.5, 32.3, 36.4, 44.6°. The diffraction peaks at 2θ= 19.5° and 29° corresponds to the 100 and 101 plane respectively and the XRD pattern reveals a crystalline ZnO well dispersed within the cellulose acetate phase. The characteristic peaks of cellulose actetae were found at 13, 23.8, 29.3, 39.5° while the ZnO nanoparticles matched the ICPD card number 36-1451 with peaks at 24, 31, 36° respectively (Fig. 2).

Adsorption studies

The initial concentration determines the measure of mass transfer resistance of Orange II dye particles in the aqueous phase and the adsorbent solid phase. The Figure. 3 indicates that equilibrium concentration is found at 75 ppm.

The *p*H affects the surface charge of adsorbent, degree of ionization and speciation of adsorbate species which affect the sorption capacity, kinetics and equilibrium properties of adsorption process. The adsorbed amount increases rapidly with *p*H from *p*H of 8 to 11. Hence, a basic condition is needed to adsorb Orange II dye particles (Fig. 4).

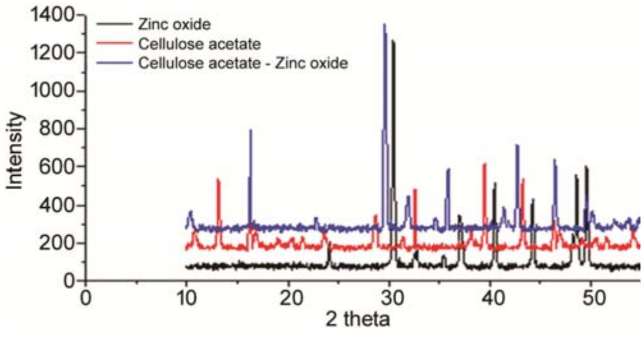

Fig. 2 — XRD pattern of ZnO-Cellulose acetate nanocomposite

The contact time determines the equilibrium time for adsorption process. Large amount of Orange II dye particles were removed in the first 50 min and equilibrium was reached in the 60th min with maximum percentage removal of 80%. After the equilibrium, adsorption uptake was not increased significantly. The curve representing the effect of adsorbent dosage shows that equilibrium is reached when 0.6 g of the adsorbent is used with percentage removal of 80%[12] (Figs. 5 and 6). The fig. 7 above shows that equilibrium is reach at 35°C with the highest percentage removal efficiency of 83.5%.

Adsorption isotherm

Langmuir isotherm is based on the assumption that maximum adsorption corresponds a saturated monolayer of solute on homogenous adsorbent surface. It comprised of a finite number of identical sites with homogeneous adsorption energy. A basic assumption states takes sorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no further

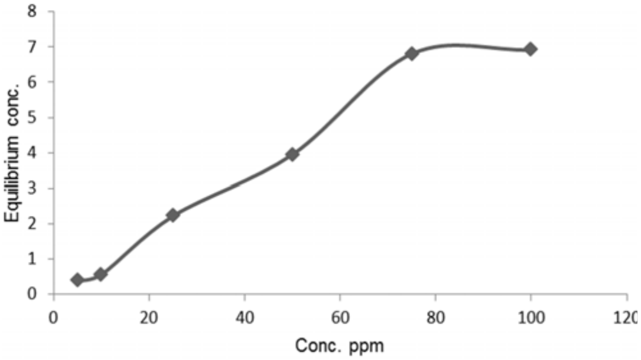

Fig. 3 — Effect of initial concentration

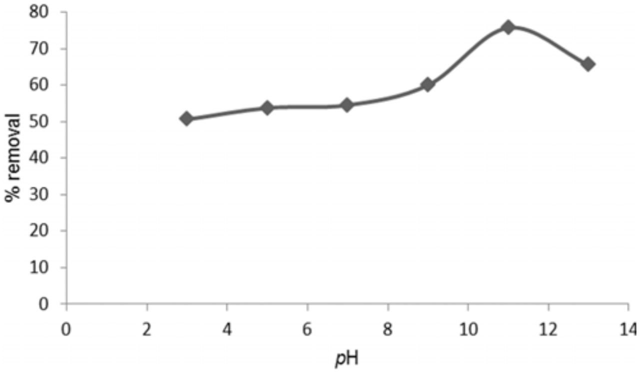

Fig. 4 — Effect of *p*H

transmigration can take place at the same site. The total monolayer capacity of the adsorbent is equal to Q_o, a Langmuir constant. The rearranged Langmuir isotherm is represented by following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

C_e is the equilibrium concentration of dye (mg/L), qe is the amount of dye adsorbed at equilibrium (mg/g), Q_o is the monolayer adsorption capacity (mg/g), and b is the constant related to the free energy of adsorption. Hence, a plot of C_e/q_e versus C_e yields a straight line with Q_o calculated from the slope and the value of b as its intercept (Fig. 8).

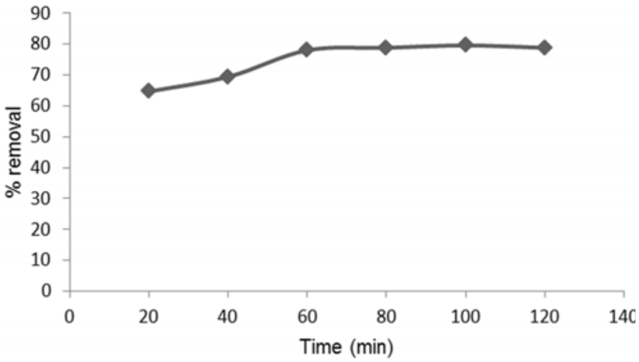

Fig. 5 — Effect of contact time

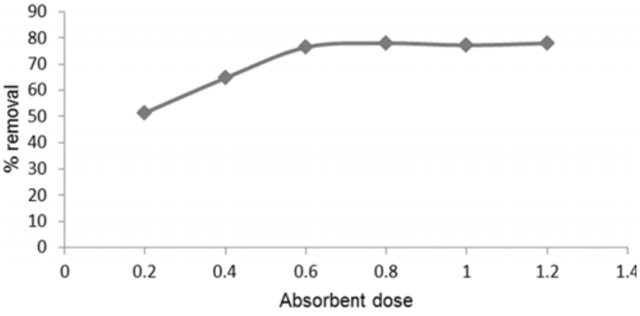

Fig. 6 — Effect of adsorbent dose

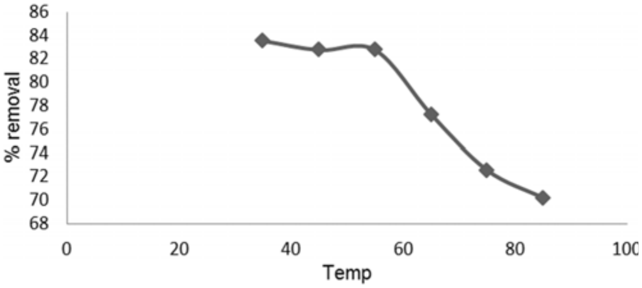

Fig. 7 — Effect of temperature

Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface or surface supporting sites of varied affinities it. Due to variation of interactions between the adsorbed molecules sites with of stronger affinity are occupied first, and in this way multilayer setting of adsorbate molecules takes place. The validity of the Freundlich isotherm model was proved by using following relation: Freundlich isotherm is an exponential equation and can be written as:

$$q_e = K_f Ce^{1/n}$$
$$\log Q_{eq} = \log k_f + 1/n \log C_{eq}$$

where K_f is the Freundlich adsorption equilibrium constant which is an indicator of the adsorption capacity and n is a characteristic coefficient relating to adsorption intensity. The plot of log Q_{eq} versus log C_{eq} gives a straight line. K_F and 1/n were determined from the intercept and slope of the plot (log Q_{eq}) versus (log C_{eq})^5 (Fig. 9).

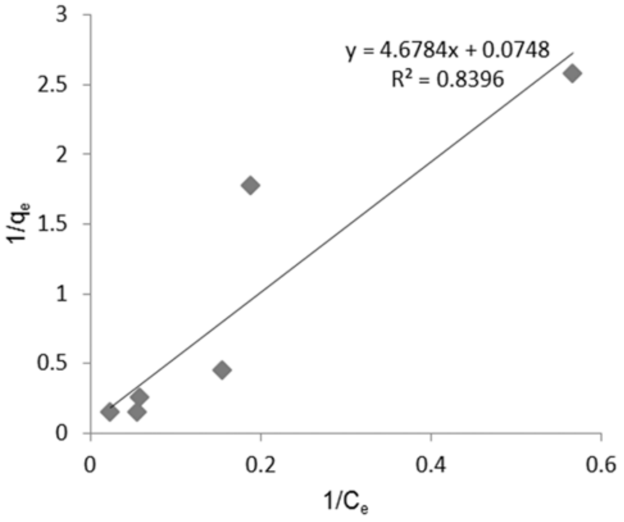

Fig. 8 — Langmuir isotherm

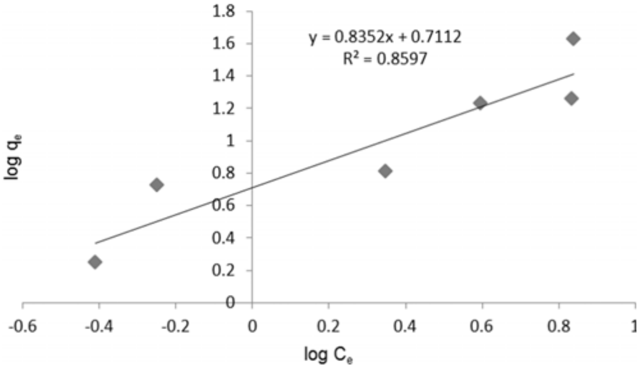

Fig. 9 — Freundlich isotherm

The value of $n > 1$ indicates that the adsorption is a favourable physical process and if $n < 1$, the adsorption is chemically favourable[13] and the closeness of the value of regression coefficient of Freundlich plot also indicates that the line is well fit with Freundlich isotherm[5].

The results indicated in Table 1 shows that the Freundlich isotherm display a minimal deviation from rhe fitted equation as indicated by its highest R^2 value 0f 0.859. The linear plot of Freundlich gave the value of n to be 1.197 which also indicates the adsorption to be favourably heterogenous.

Thermodynamics studies

The negative values of ΔG and ΔS^o are indicative of feasible, exothermic and spontaneous nature of the process along with free diffusion of adsorbate molecules through bulk phase (Fig. 10).

The change in Gibbs free energy which is -22.099 kj/mole verifies that the biosorption of orange II onto the nanocomposite was spontaneous and thermodynamically favourable. The negative values indicate the measure of the driving force of adsorption. The change in entropy of -0.9815 KJ/mole/K reveals that the degrees of freedom decreased at the solid-liquid interface during the adsorption. The change in enthalpy of -72.006 KJ/mole/K shows that the biosorption of the dye is exothermic and the adsorption rate decreases as the temperature increases. The adsorption can be classified as physisorption since the magnitude of the change in enthalpy is less than 84 KJ/mol[13].

Table 1 — Isotherm parameters

Isotherm type	Parameters	ZnO-CA nanocomposite
Langmuir	q_{max} (mg/g)	4.678
	b	0.075
	R^2	0.839
Freundlich	k_f	5.140
	n	1.197
	R^2	0.859

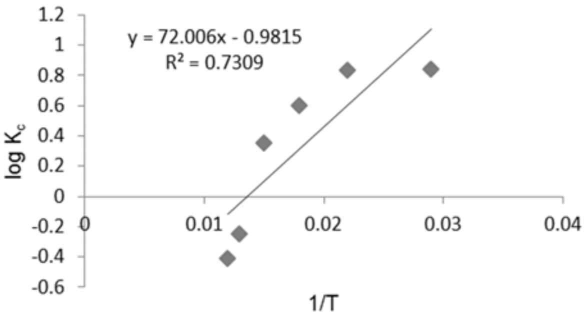

Fig. 10 — Thermodynamics plot

Adsorption kinetics

In order to analyze the adsorption kinetics of orange II dye on cellulose acetate-zinc oxide nanocomposite, the pseudo first and second order kinetic models were used to analyze the experimental data. After definite integration, the Lagergren equation, a pseudo first-order equation describes the kinetics of the adsorption process as follows:

$$Log\ (q_e - q_t) = Log\ q_e - {k_1 t}/{2.303}$$

A straight line of log (q_e-q_t) versus t suggests the applicability of this kinetic model to fit the experimental data. The first order rate constant k_1 and equilibrium adsorption density q_e were calculated from the slope and intercept of this line **(**Fig. 11**).**

After definite integration, the pseudo second order kinetic model based on adsorption equilibrium capacity is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

The experimental data showed a good compliance with the pseudo second order equation with R^2 value of 0.9983 which is greater than the 0.3386 of pseudo first order equation at 75ppm[5] (Fig. 12).

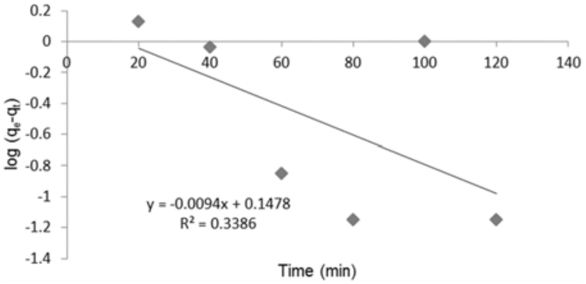

Fig. 11 — Pseudo-first order plot

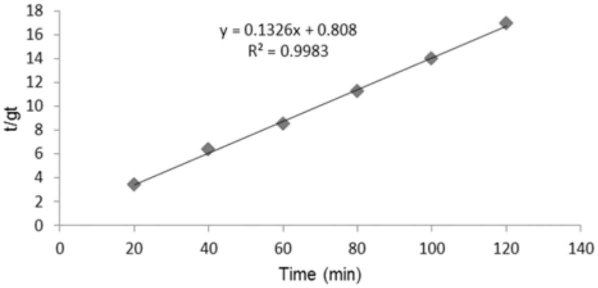

Fig. 12 — Pseudo-second order plot

A Q_e(exp) of 7.18 mg/g and k_2 of 0.808 was obtained for the pseudo second order plot.

Conclusion

In this work, ZnO nanoparticle is successfully synthesised via co-precipitation method using zinc acetate dihydrate and Sodium hydroxide as precursors. The SEM image of the product reveals a smooth surface morphological appearance suitable for adsorption processes. From the SEM image of ZnO-Cellulose acetate composite, it is revealed that the compound has a very large pore size, and ZnO nanoparticles are uniformly distributed. The modification of the ZnO nanoparticle is achieved by composing it with cellulose acetate which was synthesized from the native cellulose using acetylation method. The composite subjected to the adsorption process where it used as an adsorbent for removal of colorant from solution of Orange II dye. The thermodynamic studies of the process reveal that the rate of adsorption is spontaneous, thus, ZnO-Cellulose acetate composite appeared to be a good adsorbent for removal of colorant from aqueous colour solution.

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