Kinetics of Adsorption of Reactive Red 120 Using Bentonite Modified by CTAB and Study the Effect of Salts

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ABSTRACT

Commercial bentonite was activated by aluminium hydroxide and then modified by cetyl trimethyl ammonium bromide (CTAB). The properties of modified bentonite were diagnosed using FTIR, X-ray diffraction and SEM. The adsorption of Reactive Red 120 (RR120) onto supported bentonite (B.A.CTAB) was investigated. The influence of various experimental parameters, such as temperature, initial concentration of dye, adsorbent dosages, initial pH and inorganic salts on RR120 removal was studied. The results showed that the optimum conditions for dye adsorption on modified bentonite are: temperature = 303K, pH = 3.5, contact time = 10 min, adsorbent dosage = 0.1 g and RR120 concentration 96 mg.L⁻¹, it achieved a removal efficiency of 91%. The pseudo-second-order version yields a higher fit to the experimental facts than the pseudo-first-order model. The consequences revealed that Langmuir version turned into extra appropriate to explain RR120 adsorption than the Freundlich model. Also, the thermodynamic function such as ΔG°, ΔH° and ΔS° was evaluated. The consequences of various inorganic anions (which included Cl⁻, SO₄²⁻, CO₃²⁻, and so forth.) on the removal activity of RR 120 adsorption on modified bentonite was examined.

INTRODUCTION

The rapid development in the field of industry with the increasing discharge of industrial wastewater has become a major problem in the pollution of the environment (Zhang & Qiu 2019). Azo dyes are commonly used in the textile industry. These dyes are highly poisonous and difficult to decompose and their presence in wastewater leads to high organic pollution content, deep colour and significant effluence on microorganisms (Qiu 2019). There are significant challenges to getting rid of this pollution to obtain high quality water. In recent years, many wastewater treatment technologies have evolved from textile industries including adsorption, advanced oxidation, electrochemical methods, coagulation, etc. (Suba & Rathika 2016); but prefer the method of adsorption because it is a low cost, easy to operate and highly efficient in dealing with various organic and inorganic pollutants (Fan et al. 2015). Many of the adsorbent materials are economically or easy to access and have been verified in many research studies such as ferric hydroxide (Konicki et al. 2015), blast furnace slag (Zhang et al. 2013), palygorskite (Giustetto & Wahyudi 2011), palm ash (Hameed et al. 2007), zeolite (Engin et al. 2008), and oxide tailings (Giri et al. 2011). Bentonite is clay, in particular, constituted by way of the clay mineral montmorillonite (Lim et al. 2013). Montmorillonite surface is hydrophilic and has low affinity for no polar liquids (Orucoglu & Haciyakupoglu 2015). The positive inorganic cation on the surface of bentonite can be replaced with organic matter that changes the properties of its surface from hydrophilic to hydrophobic bentonite to obtain a highly efficient rate of adsorption of organic pollutants such as dyes, phenols and other environmental contaminants (Yan et al. 2015). Cetyl trimethyl ammonium bromide (CTAB) is an organic material that can control the size and shape of alkaline particles and their properties and can reduce the surface tension of nanoparticles (Caglar et al. 2016). In this study, CTAB was chosen as a modified material for the bentonite surface to remove the dye solution. The factors influencing adsorption of a dye such as adsorbent dosage, solution pH, initial concentration of dye solution and temperature have been evaluated. Meanwhile, kinetics, adsorption isotherms, and thermodynamics were also investigated to explore the adsorption mechanism of RR120 onto B-A-CTAB. Also, the effects of various inorganic anions (such as Cl⁻, SO₄²⁻, CO₃²⁻, NO₃⁻¹, HPO₃⁻³) on the decolourisation efficiency were studied.
MATERIALS AND METHODS

Materials

Reactive red 120 (RR 120) was obtained from Ciba uniqueness chemical compounds and used with none in addition purification. Cetrimonium bromide (CtBr, CTAB) was obtained from Chuchardt (Germany). NaOH and H2SO4 have been used to modify the pH which changed into bought from Appli Chem (GmbH). AlCl3, NaCl, Na2SO4, Na2CO3, Na2HPO4, 5H2O and NaNO3 were obtained from Fluka. The raw bentonite was purchased from China. All solutions were prepared using distilled water.

Preparation of Modified Bentonites

At first, the raw bentonite was purified by dissolved 100 g of it in one litre of distilled water with stirring for 30 minutes. The solution was then left to settle for 20 minutes. After this process, the solid phase was separated by filtration, then washed with deionized water and dried in the oven at 303K. The bentonite was ground to obtain a powder and pure. In the second step, bentonites were activated by the aluminium hydroxide prepared by the following Eq. (1) (Yan et al. 2010).

\[
\text{AlCl}_3 + 3\text{NaOH} \rightarrow \text{Al(OH)}_3 + 3\text{NaCl} \quad \text{...}(1)
\]

Al(OH)3 is added slowly to pure bentonite by a ratio (10 mmol Al/1.0 g bentonite) with a stirring at 303 K for 24 h. Finally, the modified bentonite by CTAB was prepared according to the references reported (Zhu et al. 2009). B-A-CTAB was organized with the aid of including a certain quantity of CTAB solution to a 0.02 aqueous suspension of 20 g of B-Al below moving. The suspension solution was heated for three hours at 313 K, accrued with the aid of filtration, washed, dried at 353 K to constant mass, activated for 1 h at 413 K, saved in a complete airtight plastic vial in a desiccator until addition use.

Batch Experiments

Adsorption of RR120 on modified bentonite turned into done in a batch gadget. A 50 mL RR120 solution (50-150 mg/L) within conical flasks. The aggregate was shaken using thermostatically achieve shaker right away. The shaker velocity worked at one hundred fifty rpm. The samples had been withdrawn (6 mL) at precise time periods (5, 10, 15, 20, 30, 45, 60 min), centrifuged for 10 min to detach the dye solution from the adsorbent, and evaluated for the colouration elimination efficiencies at \( \lambda_{max} = 535 \text{ nm} \) using ultraviolet and visible spectroscopy (Japan; Optima Model SP – 3000; UV / VIS) geared up with a quartz cell of 1.0 cm path duration.

The scanning electron microscope (SEM, Ties can Vega III Czech Republic) was used to study their surface morphology and Fourier transformed infrared spectrophotometer (IR Prestige – 21 Shimadzu) were performed in the range of 4000-500 cm\(^{-1}\) with KBr pellets. The X-ray diffraction (XRD) patterns of the sample were measured with Shimadzu Corporation Lab-X (XRD-6000) and recorded in the range of (3-80) deg with speed 5.0 deg min\(^{-1}\) and preset time 0.6 sec.

RESULTS AND DISCUSSION

Analysis and Calculation

Decolourisation activity was expressed in all optimization study in terms of decolourization efficiency (%), and it was calculated as follows:

Degradation efficiency % = \[ [(C_0 – C_t)/C_0] \times 100\% \] \( \text{...}(2) \)

In which \( C_0 \) (mg L\(^{-1}\)) is the initial concentration of dye and \( C_t \) (mg L\(^{-1}\)) is the concentration of dye of reaction time \( t \) (min).

\[
q_t = (C_0 - C_t) \frac{V}{W} \quad \text{...}(3)
\]

Where \( q_t \) (mg g\(^{-1}\)) is the quantity of RR120 dye adsorbed according to unit mass of adsorbent, \( V \) (L) is the volume of solution, and \( W \) (g) is the mass of the adsorbent.

Adsorption Kinetics

Two kinetic sorts the pseudo-first-order, and the pseudo-second-order have been used to suit into the experimental facts received from the colour removal steps. The Lagergren pseudo-first-order model is given by Eq. (4) (Fang et al. 2019):

\[
\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad \text{...}(4)
\]

Where in \( qt \) (mg g\(^{-1}\)) is the adsorption ability at time \( t \), \( q_e \) (mg g\(^{-1}\)) is the adsorption potential at equilibrium, and \( k_1 \) (min\(^{-1}\)) represents the rate constant of the pseudo-first-order version. Eq. (5) is the pseudo-second-order (Wang & Wu 2006) defined as follows:

\[
t/q_t = 1/k_2 q_e^2 + t/q_e \quad \text{...}(5)
\]

Where \( k_2 \) (L mg\(^{-1}\)min\(^{-1}\)) is the rate constant of the pseudo-second-order model.

Adsorbent Characterization

FTIR spectroscopy is a touchy approach to probe the interaction kind configuration and topical environment of the surfactant cations within the interlamellar vicinity of bentonite (Luo et al. 2019). The comparative FTIR spectra of P-Bent, P-Bent-Al and P-Bent-Al-CTAB are shown in Fig. 1. The band at 3622 cm\(^{-1}\) assigned to stretching vibrations of structural OH groups (Tomic et al. 2015), whereas the bands at 3441 and 1639 cm\(^{-1}\) can be assigned to the O-H deformation
of water (Ayodele & Hameed 2013). The Si-O stretching vibrations are shown at 1088 and 1042 cm\(^{-1}\), respectively (Tomic et al. 2015). The band absorption at 918 cm\(^{-1}\) can be assigned to stretching vibrations of structural OH groups (Tomic et al. 2015), whereas the bands at 3441 and 1636 cm\(^{-1}\) can be attributed to the antisymmetric and symmetric stretching vibration modes of -CH\(_3\) and -CH\(_2\), respectively.

In FTIR spectra of B-Al a considerable growth within the density of the bands at 3410 and 1636 cm\(^{-1}\) of sorbed water molecules, due to the creation of hydroxy-aluminium cations increasing large quantities of water and hydroxyl. However, a considerable reduction in the intensities of these two bands while CTAB cations had been introduced (Ayodele & Hameed 2013).

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![Fig. 1: FTIR spectra of a. P-Bent, b. P-Bent-Al and c. P-Bent-Al-CTAB.](image)

![Fig. 2: XRD modality of behaviour the adsorbent.](image)

![Fig. 3: SEM photos of the adsorbents. (A) Pure Bentonite, and (B) P-B-A-CTAB.](image)
The bands at (2928 and 2855) cm\(^{-1}\) had been observed for B-A-CTAB. They could be indicated to the anti-symmetric and symmetric stretching vibration modes of -CH\(_3\) and -CH\(_2\) similarly, the bending vibration of -CH\(_3\) was observed at 1470 cm\(^{-1}\) in organic intercalator. XRD assessment comes to be done which will pick out the mineralogical shape of the supported bentonite adsorbents and the XR-Diffraction styles are verified in Fig. 2. It may be visible that comparable diffraction peaks attributable to the complicated additives of adsorbents had been detected in those three samples. The principle crystalline phases determined in pure-Ben for SiO\(_2\), located at 20 (Theta) of 6.61°,19.6°, 21.69°,26. 59°, 36.71° and 62.04°, which have been consistent with that of the literature mentioned (Tiwari et al. 2011). The boom of basal wideness from 13.4 A\(^{\circ}\) for pure-Bent to 18.2 A\(^{\circ}\) for B-A-CTAB changed into due to the competing of Al and CTAB molecule into the interlayer distance area of pure-Bent that increased its interlayer spacing and later confirmed RR120 adsorption potential, which changed into, also assured via FTIR. SEM photographs of the adsorbents are given in Fig. 3. Even though it was no longer possible to precisely limit the particle size of the adsorbents, big aggregates of platelets component with small particles, especially among 20 and 50 micrometres in length and have been determined for the pure bent. Under the modification, the average particle size reduces; smell and properly unattached particles can be located, particularly for B-A-CTAB. This commentary advised that some disaggregation of bentonite particles happened for the duration of the modification.

**Effect of Different Factors on the Decolorization Efficiency of RR120**

**Comparison of various adsorbents:** An experiment was performed to compare three adsorbents on the dye solution. Fig. 4 shows the efficiency of colour removal over time. The decolourization efficiency is high for the Bent-Al-CTAB up to 93% in 30 minutes and is higher than pure bentonite and activated by aluminium. Bentonite pure isn’t a powerful adsorbent for the organic compounds in water. These results show that the modified bentonites’ ability to remove the colour of the dye solution has been strongly enhanced after surface modification, as surface properties have changed from hydrophilic to hydrophobic form (Xu et al. 2017). Modified bentonite was used in further studies.

**Effluence of adsorbent dosage:** Fig. 5 shows the effect of changing bentonite modified dose on the decolourization efficiency of dye solution. It was found the efficiency of removal of the colour increases with the increase of the dose.

![Fig. 4: Assessment of the three adsorbent on decolorization performance (adsorbent dosage: 0.1g, temperature: 303K, pH = 6.0, rpm =150 and RR120 concentration: 96 mg.L\(^{-1}\)).](image1)

![Fig. 5: Effect of adsorbent dosage on decolorization efficiency: (temperature 303K, pH = 6, rpm =150, contact time = 60 min and RR120 concentration: 96 mg.L\(^{-1}\)).](image2)
of bentonite modified, but it is not necessary to use a dose greater than 0.1 gm because the decolourization efficiency was not affected greatly. When the dose of B-A-CTAB is 0.1 g, the efficiency of colour removal reached 95%. Thus this amount of the modified bentonite has been used for the next experiments.

**Effect of initial pH on decolorization efficiency** (303K, adsorbent dosage = 0.1g, rpm =150 and RR120 concentration: 96 mg.L⁻¹). Therefore, it is vital to have a look at the effect on the primary dye concentration, and the effects are shown Fig. 7. It indicates elevated colour elimination performance with decreased concentration of dye RR120. As the concentration of dye lowers from 150 mg.L⁻¹ to 50 mg.L⁻¹, the decolourization performance of dye grows from 48% to 93% within 15 min of the adsorption process. The degradation performance of dye reduced as the preliminary concentration increased, this brings about the settlement with proposed whilst the positioned range of susceptible sites, the competitive adsorption might contact the adsorption and degradation of contaminants on the surface of particles, and further reduce the reaction velocity (Jafari et al. 2016).

**Study of adsorption kinetics**: Two kinetic models pseudo-first-order and pseudo-second-order have been used to fit the experimental data points obtained from the decolourization processes. An assessment of the consequences with the precise line is plotted in Figs. 8 and 9 and the kinetic parameters are summarized in Table 1. The \( R^2 \) correlation coefficients of the pseudo-first-order version are lower than the ones of the pseudo-second-order model, and the calculated \( q_e \) adsorption potential at equilibrium appeared to be

![Effect of initial pH on decolorization efficiency](image1)

**Effect of initial pH on decolorization efficiency (303K, adsorbent dosage = 0.1g, rpm =150 and RR120 concentration: 96 mg.L⁻¹).**

![Effect of variations in initial dye concentration on the decolorization efficiency](image2)

**Effect of variations in initial dye concentration on the decolorization efficiency (pH = 6.0, 303K, adsorbent dosage = 0.1g, rpm =150).**
Effect of temperature and adsorption isotherms: The effect of temperature on the adsorption process is an important parameter and should be studied. As can be observed in Fig. 10, the removal rate for RR 120 was enhanced by increasing the temperature from 293 K to 303 K and the colour removal from 60% and 81% respectively was achieved at 15 min of the adsorption process. This increase can be attributed to faster mass transfer in solution and increased collision frequencies between adsorbents and dye molecules. However, removal efficiency decreased as temperature increased further to 313 K and 323 K indicating that the RR120 adsorption on modified bentonite is exothermic by nature and these results are similar in previous reports (Yan et al. 2010).

The Langmuir and Freundlich isotherms were used and expressed by Eqs. (6) and (7) respectively.

Table 1: The kinetic parameters for Reactive red 120 on modified bentonite.

| T (k) | C_o (mg.L^-1) | q_e, exp (mg.L^-1) | Pseudo-first-order model | Pseudo-second-order model | R² | q_e,c (mg.g^-1) | k_2 (g.mg^-1.min^-1) | R² |
|-------|----------------|------------------|--------------------------|--------------------------|----|---------------|---------------------|----|
| 303   | 50             | 25.30            | 1.99                     | 0.0217                   | 0.9858 | 25.38        | 0.0426               | 0.9994 |
| 75    | 26.30          | 2.43             | 0.0596                   | 0.9284                   | 26.50 | 0.0601       | 0.9999               |
| 100   | 46.96          | 29.78            | 0.0744                   | 0.9520                   | 51.81 | 0.0033       | 0.9990               |
| 150   | 46.40          | 12.50            | 0.0380                   | 0.8084                   | 47.62 | 0.0074       | 0.9982               |
| 293   | 96             | 45.13            | 80.50                    | 0.1239                   | 0.8956 | 55.60        | 0.0017               | 0.9890 |
| 313   | 96             | 46.30            | 20.72                    | 0.1078                   | 0.7558 | 52.63        | 0.0040               | 0.9940 |
| 323   | 96             | 38.13            | 42.34                    | 0.0857                   | 0.9493 | 43.84        | 0.0030               | 0.9840 |

Fig. 8: The pseudo-first-order kinetics plots for the adsorption of RR120 onto B-A-CTAB at (A) diverse RR120 preliminary concentrations and (B) various temperatures.

Fig. 9: The pseudo-second-order kinetics draws for the adsorption of RR120 onto B-A-CTAB at (A) many RR120 initial concentrations and (B) various temperatures.
The isotherm parameters for RR120 adsorption on modified bentonite are summarized in Table 2. The correlation coefficients ($R^2$) of Langmuir isotherm had been better than that of Freundlich isotherms, and the monolayer saturation adsorption amount ($q_m$) changed closer to the calculated value ($q_{e,max}$), indicating that the Langmuir isotherm outfitted fine to the experimental information, and the monolayer coverage nature of the adsorbate on the surface of B-A-CTAB (Karaca et al. 2008).

Study thermodynamic of the adsorption process:

$$\frac{C_e}{q_e} = 1 / K_L q_m + \frac{C_e}{q_m}$$ ...

$\ln q_e = \ln K_F + (1/n) \ln C_e$ ...

Where, $q_e$ (mg.g$^{-1}$) and $q_m$ (mg.g$^{-1}$) are the equilibrium adsorption quantity at the adsorbate and the monolayer saturation adsorption quantity on the adsorbent, respectively. $C_e$ (mg.L$^{-1}$) is the equilibrium concentration of adsorbate. $K_L$ and $K_F$ are the Langmuir and Freundlich isotherm constant, respectively. The suitable lines are plotted in Fig. 11 and the isotherm parameters are summarized in Table 2. The correlation coefficients ($R^2$) of Langmuir isotherm had been better than that of Freundlich isotherms, and the monolayer saturation adsorption amount ($q_m$) changed closer to the calculated value ($q_{e,max}$), indicating that the Langmuir isotherm outfitted fine to the experimental information, and the monolayer coverage nature of the adsorbate on the surface of B-A-CTAB (Karaca et al. 2008).

Study thermodynamic of the adsorption process:

Fig. 10: Influence of variations in temperature on the decolorization efficiency ($pH = 6.0$, adsorbent dosage = 0.1g, rpm =150 and RR120 concentration = 96 mg.L$^{-1}$).

$$\frac{C_e}{q_e} = 1 / K_L q_m + \frac{C_e}{q_m}$$ ...

$\ln q_e = \ln K_F + (1/n) \ln C_e$ ...

Where, $q_e$ (mg.g$^{-1}$) and $q_m$ (mg.g$^{-1}$) are the equilibrium adsorption quantity at the adsorbate and the monolayer saturation adsorption quantity on the adsorbent, respectively. $C_e$ (mg.L$^{-1}$) is the equilibrium concentration of adsorbate. $K_L$ and $K_F$ are the Langmuir and Freundlich isotherm constant, respectively. The suitable lines are plotted in Fig. 11 and the isotherm parameters are summarized in Table 2. The correlation coefficients ($R^2$) of Langmuir isotherm had been better than that of Freundlich isotherms, and the monolayer saturation adsorption amount ($q_m$) changed closer to the calculated value ($q_{e,max}$), indicating that the Langmuir isotherm outfitted fine to the experimental information, and the monolayer coverage nature of the adsorbate on the surface of B-A-CTAB (Karaca et al. 2008).

Study thermodynamic of the adsorption process:

Fig. 11: Langmuir and Freundlich isotherms for Reactive red 120 adsorption on modified bentonite.

Table 2: The isotherm parameters for RR120 adsorption on modified bentonite.

| Model     | Parameters | T (K)       |
|-----------|------------|-------------|
|           |            | 293  | 303  | 313  | 323  |
| Langmuir  | $q_m$(mg.g$^{-1}$) | 51.28 | 45.66 | 49.75 | 50.51 |
|           | $K_L$(L.mg$^{-1}$)  | 0.0007 | 0.001 | 0.0008 | 0.0006 |
|           | $R^2$      | 0.9965 | 0.9231 | 0.9987 | 0.9986 |
| Freundlich| $n$        | 5.397  | 11.737 | 5.115  | 5.291  |
|           | $K_F$      | 25.485 | 31.016 | 23.098 | 24.953 |
|           | $R^2$      | 0.8898 | 0.4613 | 0.7690 | 0.7890 |
The effect of the salt on the elimination performance of RR 120 adsorption on modified bentonite become tested through the usage of the extraordinary salts as NaCl, Na$_2$SO$_4$, Na$_2$CO$_3$, NaNO$_3$, and Na$_2$HPO$_3$.5H$_2$O (Fig. 12). The results show that the presence of NaCl and NaNO$_3$ enhances the decolourization efficiency. Whilst the presence of Na$_2$SO$_4$, Na$_2$CO$_3$ and Na$_2$HPO$_3$.5H$_2$O decrease the decolourization effectiveness because SO$_4^{2-}$, CO$_3^{2-}$ and HPO$_3^{2-}$ ions compete with dye molecules and occupy the reactive places on modified bentonite surface (Sribenja & Saikrasun 2015).

**CONCLUSIONS**

The activated bentonite was modified by CTAB then confirmed by techniques FTIR, X-ray diffraction and SEM. The second-order kinetic model can well explain the dye degradation process using B-A-CTAB. The Langmuir isotherm had been better than that of Freundlich isotherms. The presence of NaNO$_3$ and NaCl enhances the decolourization efficiency while the ions SO$_4^{2-}$, CO$_3^{2-}$ and HPO$_3^{2-}$ were inhibiting the process of dye removal.

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