

Article

Polyaspartate-Ionene/Na⁺-Montmorillonite Nanocomposites as Novel Adsorbent for Anionic Dye; Effect of Ionene Structure

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Synthesis of ionene compounds

Synthesis of poly(dimethylene, xylylene ionene) (PDMXI) (I-1): Ionene samples were prepared according to the method described by Rembaum *et al.*. The synthesis of I-1 is typical: a solution of α,α' -dichloro-*p*-xylene (6.13 g, 35 mmol) in DMF (20 mL) was mixed with TMEDA (4.07 g, 35 mmol) and heated to 40 °C, under nitrogen, for 5 days, resulting in 8.96 g of I-1(87%). FT-IR (KBr, cm⁻¹): 3016(alkyl C–H), 3020 (methylene C–H stretch), 3411 and 1480 (ammonium nitrogen). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 3.1 (t, 12H, CH₃), 4.16 (4 H, CH₂), 4.65 (4H, CH₂), 7.68 (4H, phenyl).

Synthesis of poly-2,2-ionene (PI) (I-2): Poly-2,2-ionene (PI) was prepared following the procedure for (PDMXI), using the following quantities: 1,2-dichloroethane (4.02 g, 40 mmol), TMEDA (4.65 g, 40 mmol), in DMF (20 mL) to yield 5.7 g I-2 (65%). FT-IR (KBr, cm⁻¹): 3009 (alkyl C–H stretch), 2969 (methylene C–H stretch), 3480, 1480, and 1404 (ammonium nitrogen). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 3.3 (t, 12H, CH₃), 3.87 (4 H, CH₂), 4.65 (4H, CH₂).

Synthesis of I-3: A solution of benzyl chloride (9.11 g, 72 mmol) in DMF (30 mL) was mixed with TMEDA (4.063 g, 35 mmol) and heated to 40 °C, under nitrogen, for 48 h to yield 8.3 g I-3 (63%). FTIR (KBr, cm⁻¹): 2920 (alkyl C–H stretch), 3020 (methylene C–H stretch), 3475, 3392, and 1487 (ammonium nitrogen). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 3.30 (s, 12H, CH₃), 3.68 (d, 4 H, CH₂), 4.5 (s, 4H, CH₂), 7.6 (m, 10H, benzene).

Table S1. Summary of the amounts used for preparation of ionene-clay (IC-3-5) and nanocomposites (ICP-3-5) and their yield.

| Sample code | Ionene | | | Clay (g) | mole ratio of clay-ionene | Yield (g) |
|-------------|--------------|-------|----------|--------------------------------|---------------------------|-----------|
| | code | g | mmol X/g | | | |
| IC-1 | I-1 | 0.898 | | | | 2.01 |
| IC-2 | I-2 | 0.810 | 3.7 | 2 | 1:2 | 2.03 |
| IC-3 | I-3 | 1.110 | | | | 1.84 |
| Sample code | Ionene -clay | | | poly(succinimide-co-aspartate) | | Yield (g) |
| | code | g | mmol X/g | g | mmol | |
| ICP-1 | IC-1 | | 1.96 | | | 2.20 |
| ICP-2 | IC-2 | 1.5 | 1.52 | 1.42 | 10 | 1.11 |
| ICP-3 | IC-3 | | 3.03 | | | 1.39 |

Table S2. Summary of the amounts used for preparation of ionene-clay (IC-3-5) and nanocomposites (ICP-3-5) and their yield.

| Inonene Code | %C | | %H | | %N | | ammol X/g |
|--------------|-------|-------|-------|-------|-------|-------|-----------|
| | Calc. | Found | Calc. | Found | Calc. | Found | |
| I-1 | 57.73 | 57.73 | 8.25 | 8.96 | 9.62 | 8.14 | 3.31 |
| I-2 | 44.65 | 44.60 | 9.30 | 9.82 | 13.02 | 13.09 | 4.52 |
| I-3 | 65.03 | 58.79 | 8.19 | 8.69 | 7.58 | 7.10 | 2.19 |
| IC-1 | - | 14.20 | - | 2.36 | - | 2.78 | 1.13 |
| IC-2 | - | 7.18 | - | 2.21 | - | 3.52 | 1.01 |
| IC-3 | - | 15.84 | - | 3.15 | - | 3.52 | 2.02 |

^a Determined by Volhard's titration method.

Table S3. Proposed chemical structure of nanocomposites (ICP-3-5).

| Sample | Proposed structure |
|--------|--------------------|
| ICP-1 | |
| ICP-2 | |
| ICP-3 | |

Adsorption studies

Adsorption experiments were carried out in batch equilibrium mode. Typically, 3 mL of Acid Blue 25 (AB25) with a concentration of $4 \times 10^{-4} \text{ mol L}^{-1}$, at pH 7, was added to 3 mL of adsorbent (ICP-1, ICP-2 or ICP-3) suspension (4 g/L) in a 100 mL capped Erlenmeyer flask. The flasks were shaken in a thermostatic water shaker bath (Unitronic -Selecta) at 60 rpm and $25 \pm 0.2 \text{ }^\circ\text{C}$ to reach equilibrium. After equilibrium was attained and verified, samples were separated by centrifugation at 8000 rpm for 10 min. (Centrifuge-BL II Selecta). The concentration of the non-adsorbed dye in solution was determined from the measured absorbance at its $\lambda_{\text{max}} = 604 \text{ nm}$ using a UV-vis spectrometer. The equilibrium adsorption, q_e , was calculated using Equation 1:

$$q_e = (C_o - C_e)V / m \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations (mol L^{-1}) of AB25, respectively, V is the volume (mL) of solution, and m is the mass of the used adsorbent used in (g). The effect of pH on the adsorption of dye was studied in the range of pH 3–11. Dye solutions were prepared with distilled water and the pH was controlled with phosphate buffer. The experiments were conducted

at three different temperatures; 25, 35, and 45 ± 0.2 °C. The procedures for the kinetic experiments were identical to those of the equilibrium tests. At predetermined moments, dye solution was centrifuged and the concentration of the non-adsorbed AB25 was determined spectrophotometrically. The adsorbed quantity of AB25 at time t , q_t , and the removal percentage of AB25, % R) were calculated according to Equations 2 and 3, respectively:

$$q_t = (C_0 - C_t) V / m \quad (2)$$

$$\% R = ((C_0 - C_t) / C_0) \times 100 \quad (3)$$

where C_t (molL^{-1}) is the non-adsorbed dye concentration at time t . All experiments were done in duplicate and the average values were reported.

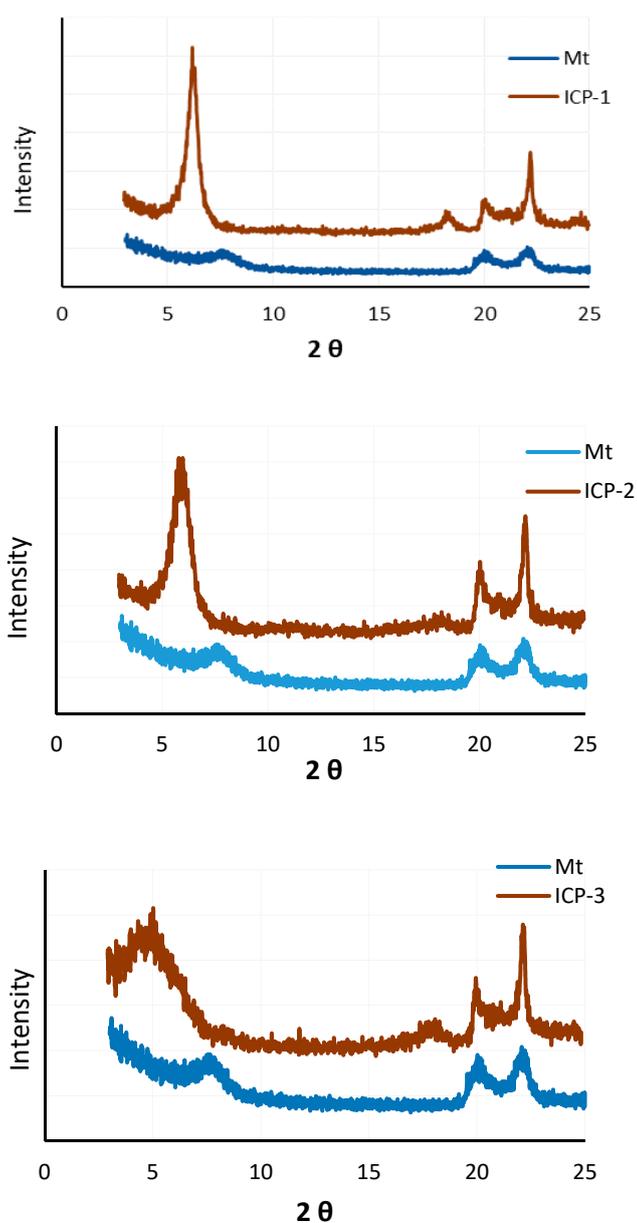


Figure S1. PXRD of Na^+ -Mt and nanocomposite samples ICP 1-3.

Table S4. Interlayer d-spacing and spacing shift.

| Material | 2θ | d spacing / Å | Layer expansion / Å |
|---------------------|-----------|---------------|---------------------|
| Na ⁺ -Mt | 7.600 | 11.64 | |
| ICP-1 | 6.240 | 14.17 | 2.53 |
| ICP-2 | 6.040 | 14.63 | 2.99 |
| ICP-3 | 5.160 | 17.13 | 5.49 |

Kinetic models

To inspect the mechanism of adsorption, two kinetic models were used to analyze the adsorption data; namely, non-linear and linear forms of pseudo-first-order (Eqs. 4, 5, respectively) and non-linear and linear forms pseudo-second order (Eqs. 6, 7, respectively) (1).

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (4)$$

$$\text{Log}(q_e - q_t) = \text{log } q_e - (k_1/2.303) t \quad (5)$$

where k_1 is the adsorption rate constant. The values of k_1 and q_e were evaluated from the slope and intercept of the relation between $\text{log}(q_e - q_t)$ and t , respectively.

$$q_t = k_2 q_e^2 t / (1 + q_e k_2 t) \quad (6)$$

$$t / q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

where k_2 is the second-order rate constant of adsorption.

Moreover, the kinetic data were introduced into intraparticle diffusion model which is expressed by equation (8) (2):

$$q_t = k_p t^{1/2} + C \quad (8)$$

k_p is the rate constant of the intraparticle diffusion (mol /g min^{0.5}) and C is a constant (mol /g) presenting data about the boundary thickness of the layer. The bigger C -value, the more influence of the boundary layer.

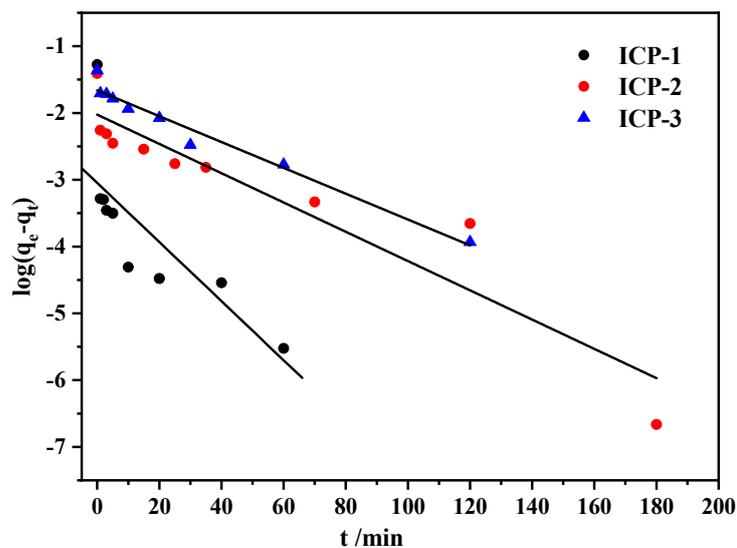


Figure S2. Linear plot of Pseudo-first-order model of AB25 adsorbed over nanocomposites ICP 1-3 at 25 °C, (ICP 1-3: 2.0 g/L), pH = 7, and [AB25] = 2×10^{-4} mol/L.

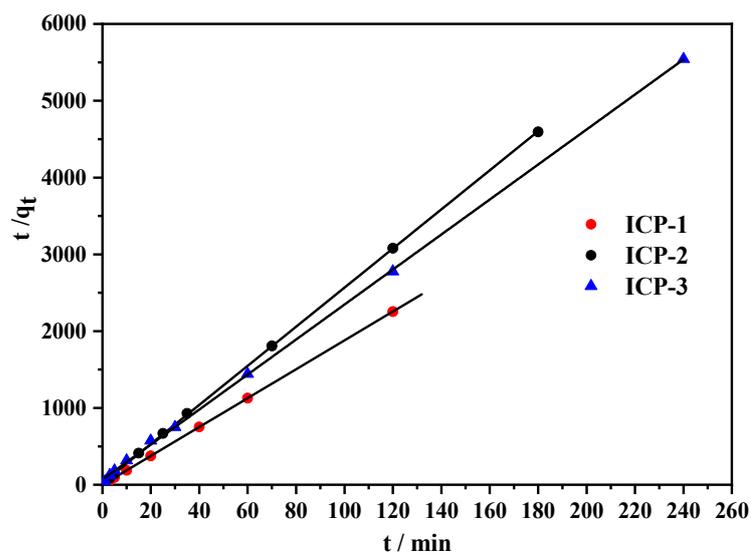


Figure S3. Linear plot of Pseudo-second-order model of AB25 adsorbed over nanocomposites ICP 1-3 at 25 °C, (ICP 1-3: 2.0 g/L), pH = 7, and [AB25] = 2×10^{-4} mol/L.

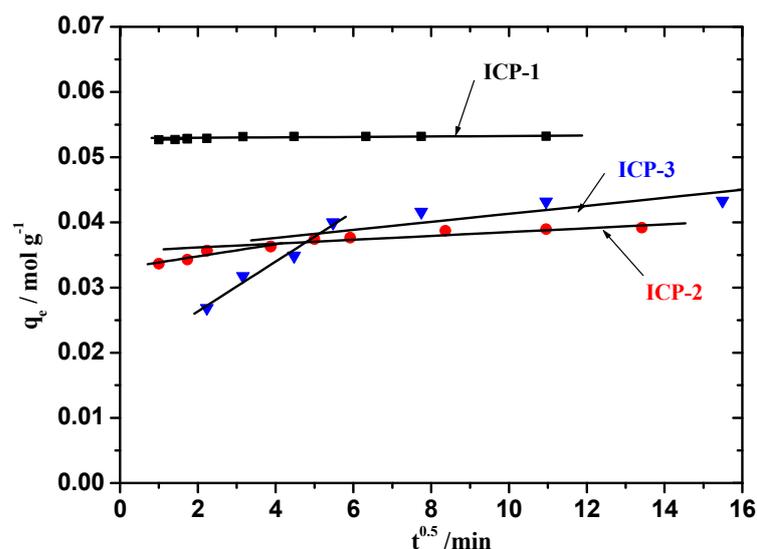


Figure S4. Intraparticle diffusion plot for adsorption of AB25 over nanocomposites ICP 1-3 at 25 °C, (ICP 1-3: 2.0 g/L), pH = 7, and [AB25] = 2 × 10⁻⁴ mol/L.

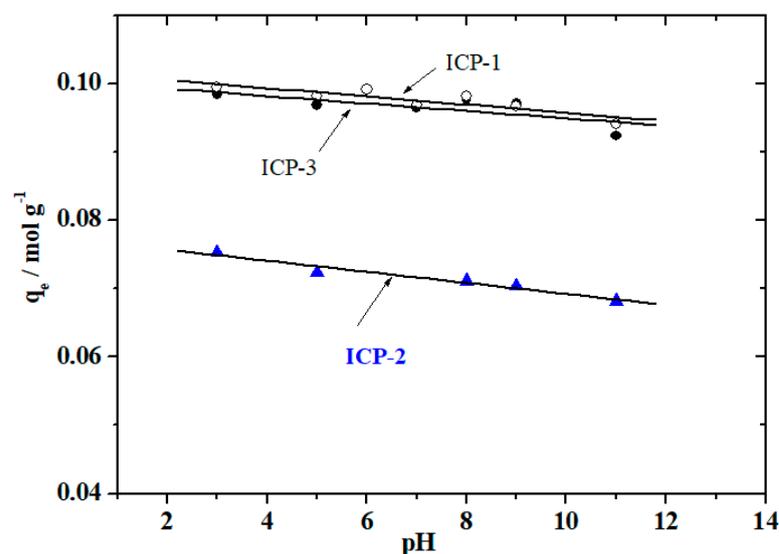


Figure S5. Effect of pH on the equilibrium adsorption of AB25 over nanocomposites ICP 1-3 at 25 °C, (ICP 1-3: 2.0 g/L), and [AB25] = 2 × 10⁻⁴ mol/L.

Isotherm models

Freundlich isotherm: Freundlich isotherm model is written as [3]:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{9}$$

K_F is the adsorption capacity and $1/n$ is Freundlich constant related to adsorption intensity. The linearity of $\ln q_e$ against $\ln C_e$ approves the rationality of Freundlich model.

Langmuir isotherm: The Langmuir isotherm [3] describes the monolayer sorption process and can be expressed as:

$$C_e/q_e = (1/q_{max} K_L) + C_e/q_{max} \tag{10}$$

q_{max} represents the maximum loading adsorption capacity and K_L is Langmuir adsorption constant linked with the adsorption energy. The values of q_{max} and k_L were obtained from its linearized form.

Dubinin-Radushkevich isotherm: Dubinin-Radushkevich equation postulates a constant sorption potential (3). Its linear form is given by

$$\ln q_e = \ln Q_m - B \varepsilon^2 \quad (11)$$

$$\varepsilon = RT \ln (1+1/C_e) \quad (12)$$

where ε is the Polanyi potential, Q_m is the monolayer capacity (mol g^{-1}), B is the constant correlated to the energy of adsorption ($\text{mol}^2 \text{J}^{-2}$). The values of Q_m and B were calculated from the intercept and slope of the plot $\ln q_e$ vs. ε^2 , respectively. The mean sorption energy, E is elaborated from the Eq. [3]

$$E = 1/(-2B)^{0.5} \quad (13)$$

References

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