



INTERNATIONAL JOURNAL OF PHARMACOLOGY AND CHEMISTRY

Content available at www.saap.org.in

Online ISSN: 2582-7723



Open Access

Research Article

EFFICIENT UPTAKE OF BASIC BLUE 4I BY ALGINATE-BASED HYDROGEL BEADS LOADED WITH KOH-ACTIVATED WALNUT SHELL CARBON: EQUILIBRIUM MODELING AND ERROR FUNCTION ANALYSIS

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DOI: <https://doi.org/10.46796/ijpc.v7i2.971>

ARTICLE HISTORY

Received on: 16-07-2026

Revised on: 03-09-2026

Accepted on: 11-10-2026

Keywords: Basic Blue 4I; Sodium alginate; Walnut shell activated carbon; Hydrogel beads; Non-linear isotherm modeling; Error functions.

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ABSTRACT

Cationic dyes such as Basic Blue 4I (BB4I) leave textile effluents strongly colored and are not easily broken down. In this work, walnut shells were converted into activated carbon (WSAC), and the carbon was entrapped in sodium alginate-g-poly (acrylic acid) hydrogel beads (SA-g-PAA/WSAC). The beads were then tested for BB4I removal in batch mode. Their point of zero charge was 5.8, and they swelled most at pH 8 (76.7 g g⁻¹, Schott model). Removal rose from 22.6% at pH 2 to 95.2% at pH 8, using 1.0 g L⁻¹ of beads and 50 mg L⁻¹ of dye. Uptake obeyed the pseudo-second-order model ($R^2 \geq 0.989$), and intraparticle diffusion proceeded in three stages. Six isotherm models were fitted by non-linear regression to equilibrium data at 25 °C. They were ranked with seven error functions, the sum of normalized errors (SNE), information criteria and leave-one-out cross-validation. Redlich–Peterson ($g = 0.746$) and Sips ($ns = 0.60$) gave the lowest SNE, 1.04 and 1.20, which points to heterogeneous binding sites. Temkin was the weakest model and even predicted negative uptake at the lowest concentration. The Langmuir capacity was 188.0 ± 11.1 mg g⁻¹, yet it shifted from 161 to 202 mg g⁻¹ with the error function minimized, and linearized fitting distorted it further. Adsorption was spontaneous and endothermic ($\Delta H^\circ = +26.7$ kJ mol⁻¹; $\Delta G^\circ = -7.4$ to -10.8 kJ mol⁻¹). After six cycles with 0.1 M HCl, the beads still kept 71% of their first-cycle capacity.

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INTRODUCTION

Textile mills discharge large volumes of colored wastewater. A good share of the dye never fixes on the fiber and ends up in the effluent, where it blocks light, raises the oxygen demand and may be toxic or mutagenic to aquatic life [1,2]. Basic Blue 4I (BB4I) is a cationic azo dye with a benzothiazolium head group, used mainly for acrylic fibers. It is persistent: UV light alone removes only part of it, and oxidative or photocatalytic processes are used to destroy it [3,4]. Of the many options, adsorption is still the simplest to run, and it works well for cationic dyes on cheap materials [5,6]. Walnut shells are dense, lignin-rich and cheap. After chemical or physical activation they give carbons with surface areas from about 400 to more than 2800 m² g⁻¹ and high dye uptake [7–10]. Fine carbon pow-

ders, however, are hard to recover from treated water. Entrapping them in polymer beads helps. Sodium alginate (SA) gels at once with Ca²⁺, and grafting poly(acrylic acid) (PAA) onto it adds many carboxylate groups that bind cations [11,12]. Alginate beads loaded with carbon or biochar have already shown large capacities for methylene blue [13–15], and grafted acrylic hydrogels, including those from our group, remove cationic dyes well [16–22]. Most adsorption studies still rank isotherm models by the linear R^2 alone. Linearization changes the error structure and can favor the wrong model [23]. Several error functions, their normalized sum and information criteria give a fairer comparison [24–26]. As far as we know, walnut-shell activated carbon (WSAC) has not been combined with SA-g-PAA beads for BB4I, and BB4I equilibrium data

have rarely been examined this closely. Here we prepare SA-g-PAA/WSAC beads, study the main batch variables, and compare six isotherm models through error functions, their normalized sum, the corrected Akaike criterion (AICc) and cross-validation.

2. MATERIALS AND METHODS

2.1. Materials

Sodium alginate (medium viscosity, $\geq 98\%$, Sigma-Aldrich), acrylic acid (AA, $\geq 99\%$, stabilized with 200 ppm MEHQ, Sigma-Aldrich), potassium persulfate (KPS, $\geq 99\%$, BDH), N,N'-methylenebisacrylamide (MBA, $\geq 99\%$, Sigma-Aldrich) and anhydrous calcium chloride ($\geq 96\%$, Fluka) were used as received. Basic Blue 41 (C.I. 11105; C₂₀H₂₆N₄O₆S₂; M = 482.57 g mol⁻¹; dye content $\geq 40\%$, Sigma-Aldrich) was used without purification. Potassium hydroxide (KOH, $\geq 85\%$, Merck), HCl, NaOH and NaCl were of analytical grade. Walnut shells were collected from a local market in Al-Diwaniyah, southern Iraq. All solutions were prepared in distilled water.

2.2. Preparation of walnut-shell activated carbon (WSAC)

The shells were washed several times with tap and distilled water, dried at 105 °C for 24 h, ground and sieved to $< 250 \mu\text{m}$. The powder was impregnated with KOH at a ratio of 1:3 (shell : KOH, w/w) for 12 h, dried, and carbonized at 700 °C for 2 h under N₂ flow (100 mL min⁻¹). The product was washed with hot distilled water until the washings were neutral, dried at 105 °C and kept in a desiccator. The yield of WSAC was 32.4%.

2.3. Preparation of SA-g-PAA/WSAC hydrogel beads

Sodium alginate (2.0 g) was dissolved in 100 mL of distilled water at 60 °C under stirring. AA (5.0 mL, neutralized to 60% with NaOH) and MBA (0.10 g) were added, followed by WSAC (0.50 g) dispersed by ultrasonication for 15 min. The mixture was purged with N₂ for 15 min, KPS (0.15 g) was added, and graft copolymerization was run at 70 °C for 3 h. The viscous dispersion was then dropped through a 21-gauge needle into 3% (w/v) CaCl₂ under gentle stirring. The beads were cured in the bath for 2 h, washed with distilled water to remove unreacted species and dried at 50 °C to constant weight. Their mean diameter was $2.5 \pm 0.3 \text{ mm}$. Figure 01 shows the preparation route.

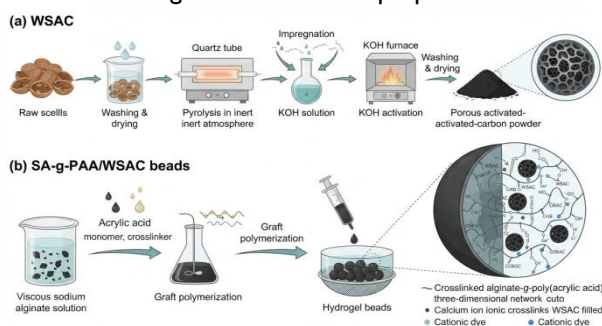


Figure 01. Preparation route of (a) walnut-shell activated carbon (WSAC) and (b) SA-g-PAA/WSAC com-

posite hydrogel beads; (c) schematic of the bead interior (not to scale).

2.4. Point of zero charge and swelling

The point of zero charge (pH_{pzc}) was found by the pH drift method. Portions of 50 mL of 0.1 M NaCl were set to initial pH values (pH_i) of 2–12 with 0.1 M HCl or NaOH, 0.05 g of beads was added, and the final pH (pH_f) was read after 24 h. pH_{pzc} was taken where $\Delta\text{pH} = \text{pH}_f - \text{pH}_i$ crosses zero [27,28].

Swelling was followed gravimetrically at pH 2, 5, 8 and 11. Dry beads of known mass (W_d) were immersed in 100 mL of solution, taken out at set times (5–1440 min), blotted and weighed (W_t). The swelling ratio and the Schott second-order model [29,30] were:

$$S_t = (W_t - W_d) / W_d \quad (1)$$

$$S_t = k_s S^\infty t / (1 + k_s S^\infty t) \quad (2)$$

where S^∞ (g g⁻¹) is the equilibrium swelling and k_s the swelling rate constant; $r_0 = k_s S^\infty^2$ is the initial swelling rate, and Eq. (2) is the integrated Schott model.

2.5. Characterization

The functional groups of WSAC, bare SA-g-PAA beads and SA-g-PAA/WSAC beads (before and after BB41 adsorption) were examined by Fourier-transform infrared spectroscopy (FTIR, Shimadzu IRSpirit, KBr pellet, 400–4000 cm⁻¹, 32 scans, 4 cm⁻¹ resolution). Surface morphology were observed by field-emission scanning electron microscopy (FESEM, TESCAN MIRA3, 15 kV; samples gold-coated). Nitrogen adsorption-desorption isotherms (77 K, Micromeritics ASAP 2020) gave the BET specific surface area, BJH pore-size distribution and total pore volume of the WSAC and composite beads. Samples were degassed at 150 °C for 6 h before measurement.

2.6. Batch adsorption and reuse experiments

A stock BB41 solution (1000 mg L⁻¹) was diluted as needed. Unless stated otherwise, 0.05 g of beads was shaken with 50 mL of dye solution (1.0 g L⁻¹) at 150 rpm in a thermostatic shaker, and the pH was set with dilute HCl or NaOH. The effects of pH (2–11) and dose (0.01–0.20 g) were studied at $C_0 = 50 \text{ mg L}^{-1}$, 25 °C and 120 min. Kinetic runs used $C_0 = 25, 50, 75$ and 100 mg L^{-1} at pH 8, with sampling from 5 to 180 min. Equilibrium data were collected at $C_0 = 10\text{--}300 \text{ mg L}^{-1}$, pH 8, 25 °C and 120 min, and temperature runs (25–55 °C) at $C_0 = 50 \text{ mg L}^{-1}$. The residual dye was measured with a UV-Vis spectrophotometer (Shimadzu UV-1900i) at $\lambda_{\text{max}} = 610 \text{ nm}$, using a calibration line over 0.5–20 mg L⁻¹ ($R^2 = 0.9998$). All measurements were performed in triplicate; the relative standard deviation was $< 2.5\%$. The uptake, removal and distribution coefficient were:

$$q_e = (C_0 - C_e)V / m \quad (3)$$

$$R (\%) = 100(C_0 - C_e) / C_0 \quad (4)$$

$$K^d = q_e / C_e \quad (5)$$

where C_0 and C_e (mg L⁻¹) are the initial and equilibrium concentrations, V (L) the volume and m (g) the mass of beads. For reuse, dye-loaded beads from runs at $C_0 = 50 \text{ mg L}^{-1}$ were stirred with 50 mL of 0.1 M HCl for 60 min, rinsed to neutral pH and used again. Six cycles

were run, and the regeneration efficiency was $RE (\%) = 100q_{e,n} / q_{e,l}$.

2.7. Kinetic models

Contact-time data were fitted to the pseudo-first-order (PFO), pseudo-second-order (PSO) and Elovich equations in non-linear form [31,32]. Diffusion was examined with the Weber–Morris intraparticle diffusion (IPD) model, applied piecewise with breakpoints chosen to minimize the total residual sum of squares (at least three points per segment) [33], and with the Boyd film-diffusion analysis [34]:

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (6)$$

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

$$q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t \quad (8)$$

$$q_t = k_i t^{0.5} + C \quad (9)$$

$$B_t = (\sqrt{\pi} - \sqrt{(\pi - \pi^2 F/3)})^2 \text{ for } F \leq 0.85; \quad B_t = -0.4977 - \ln(1 - F) \text{ for } F > 0.85 \quad (10)$$

Here $F = q_t/q_e$, and q_e was taken from the PSO fit to avoid $F \geq 1$ from scatter in the last samples.

2.8. Isotherm models

Six models were applied to the equilibrium data at 25 °C [35,36]: Langmuir with its separation factor R_L , Freundlich, Temkin, Dubinin–Radushkevich (D–R), Sips and Redlich–Peterson (R–P):

$$q_e = q_m K_L C_e / (1 + K_L C_e); \quad R_L = 1/(1 + K_L C_0) \quad (11)$$

$$q_e = K^f C_e^{1/n} \quad (12)$$

$$q_e = B \ln(A C_e); \quad B = RT/b_t \quad (13)$$

$$q_e = q_s \exp(-\beta \varepsilon^2); \quad \varepsilon = RT \ln(1 + 1/C_e); \quad E = 1/\sqrt{(2\beta)} \quad (14)$$

$$q_e = q_m (K_s C_e)^{n_s} / [1 + (K_s C_e)^{n_s}] \quad (15)$$

$$q_e = K_{RP} C_e / (1 + a_{RP} C_e^{a_g}) \quad (16)$$

In the D–R model, C_e was expressed in mol L^{-1} ($M = 482.57 \text{ g mol}^{-1}$). The Temkin, Sips and R–P forms were handled as recommended in recent critical reviews [37–39].

2.9. Parameter estimation, error functions and model selection

All models were fitted in non-linear form by least squares (trust-region reflective algorithm, SciPy, Python 3), and standard errors were taken from the Jacobian at the optimum. For comparison, the Langmuir (types I and II), Freundlich and D–R equations were also fitted in linear form, and their constants were used to compute errors on the q_e scale [23]. Seven error functions were calculated, together with R^2 , adjusted R^2 and two information criteria [24–26]:

$$SSE = \sum (q_{e,\text{exp}} - q_{e,\text{cal}})^2; \quad RMSE = (SSE/N)^{0.5} \quad (17)$$

$$\chi^2 = \sum (q_{e,\text{exp}} - q_{e,\text{cal}})^2 / q_{e,\text{cal}} \quad (18)$$

$$ARE = (100/N) \sum |q_{e,\text{exp}} - q_{e,\text{cal}}| / q_{e,\text{exp}} \quad (19)$$

$$\text{HYBRID} = [100/(N - p)] \sum (q_{e,\text{exp}} - q_{e,\text{cal}})^2 / q_{e,\text{exp}} \quad (20)$$

$$\text{MPSD} = 100 \{ [1/(N - p)] \sum [(q_{e,\text{exp}} - q_{e,\text{cal}}) / q_{e,\text{exp}}]^2 \}^{0.5} \quad (21)$$

$$\text{EABS} = \sum |q_{e,\text{exp}} - q_{e,\text{cal}}| \quad (22)$$

$$\text{adj-}R^2 = 1 - (1 - R^2)(N - 1)/(N - p) \quad (23)$$

$$\text{AICc} = N \ln(SSE/N) + 2p + 2p(p+1)/(N-p-1); \quad \text{BIC} = N \ln(SSE/N) + p \ln N \quad (24)$$

where N is the number of data points (nine) and p the number of parameters. Because each function weighs the residuals differently, the parameters of every model were also re-estimated by minimizing, in turn, SSE, HYBRID, MPSD, ARE, EABS and χ^2 (Nelder–Mead simplex). For each parameter set, every error value was

divided by the largest value of that error within the model, and the normalized values were summed to give the SNE; the set with the lowest SNE was taken as the optimum [24,25]. Models were then compared on one scale by normalizing SSE, HYBRID, MPSD, ARE and EABS across the six models. χ^2 was left out of this cross-model sum, as it is undefined when a model returns $q_{e,\text{cal}} \leq 0$.

Finally, each model was tested by leave-one-out cross-validation. Each point was removed in turn, the model was refitted to the other eight, and the removed point was predicted. The root mean square of these prediction errors is reported as RMSE_v .

2.10. Thermodynamic analysis

The equilibrium constant was taken as the dimensionless partition ratio $K^u = q_e \text{ m}/(C_e \text{ V})$, that is, dye on the solid over dye in solution. Since m/V was 1.0 g L^{-1} , K^u had the same numerical value as K^d . ΔH° and ΔS° were obtained from the van't Hoff equation, and ΔG° from Eq. (26):

$$\ln K^u = \Delta S^\circ/R - \Delta H^\circ/(RT) \quad (25)$$

$$\Delta G^\circ = -RT \ln K^u \quad (26)$$

The choice of equilibrium constant affects ΔG° and ΔS° [40,41], so these values hold for the stated solid-to-liquid ratio, whereas ΔH° does not depend on it.

3. RESULTS AND DISCUSSION

3.1. Surface charge and swelling of the beads

Figure 2a shows the drift curve. ΔpH was positive from pH 2 to 5 and turned negative between pH 5 and 6; linear interpolation gives $\text{pH}_{\text{pzc}} = 5.83$. Above pH 6 the final pH leveled off at 6.1–6.5, which reflects the buffering of the carboxyl groups of alginate and grafted PAA. So the bead surface is net positive below pH 5.8 and dominated by ionized $-\text{COO}^-$ groups above it. A similar value (5.72) was reported for alginate-based cryogel beads [28]. Swelling followed the same trend (Figure 2b, Table 1). The equilibrium ratio rose from 14.8 g g^{-1} at pH 2 to 39.2 g g^{-1} at pH 5 and 70.8 g g^{-1} at pH 8, then fell a little to 66.0 g g^{-1} at pH 11. At low pH the carboxyl groups stay protonated and hydrogen-bonded, so the network is compact. As the pH rises they ionize, the fixed charges repel each other and the gel takes up more water [29,30]. At pH 11 the excess Na^+ screens these charges, and swelling drops slightly. The Schott model described all four curves well ($R^2 = 0.994\text{--}0.998$). The initial rate r_0 increased from 0.45 to $1.55 \text{ g g}^{-1} \text{ min}^{-1}$ between pH 2 and 8, and half of the equilibrium swelling was reached within 34–50 min. An open, charged network at pH 8 is what a cationic dye needs.

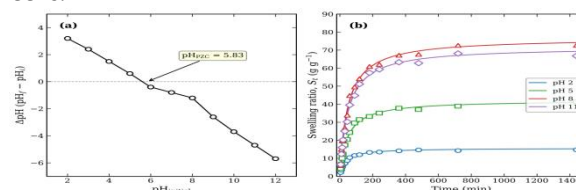


Figure 02: (a) pH drift plot for the point of zero charge of the SA-g-PAA/WSAC beads (0.1 M NaCl, 0.05 g, 50

mL, 24 h); (b) swelling kinetics at pH 2, 5, 8 and 11, with the Schott model fits shown as lines.

Table 01: Schott swelling-kinetic parameters of the SA-g-PAA/WSAC beads at four pH values.

pH	S _{eq,exp} (g/g)	S _{inf} (g/g)	k _{s x} 10 ⁴	r ₀ (g/g/min)	t _{1/2} (min)	R ²
2	14.8	15.6	18.68	0.453	34.4	0.9978
5	39.2	42.2	5.11	0.912	46.3	0.9957
8	70.8	76.7	2.63	1.549	49.5	0.9942
11	66.0	71.7	2.79	1.434	50.0	0.9936

3.2. Characterization of WSAC and beads

3.2.1. FTIR analysis

Figure 3 presents the FTIR spectra of WSAC, bare SA-g-PAA beads, SA-g-PAA/WSAC beads before adsorption and SA-g-PAA/WSAC beads after BB4I adsorption. The WSAC spectrum showed a broad O–H stretching band near 3420 cm⁻¹, a weak C–H stretch at 2920 cm⁻¹, and bands at 1580 and 1120 cm⁻¹ assigned to aromatic C=C and C–O–C stretching, respectively. The bare SA-g-PAA beads exhibited a broad –OH/–NH stretch at 3350 cm⁻¹, strong asymmetric and symmetric COO⁻ stretches at 1598 and 1412 cm⁻¹, and a C=O stretch of the grafted PAA at 1718 cm⁻¹.

In the composite SA-g-PAA/WSAC spectrum, the COO⁻ bands shifted slightly to 1592 and 1408 cm⁻¹, suggesting interaction between the alginate/PAA matrix and the carbon surface. After BB4I adsorption, the asymmetric COO⁻ band shifted further to 1576 cm⁻¹, and its intensity decreased relative to the symmetric band, consistent with the participation of carboxylate groups in electrostatic binding with the dye cation. A new weak band appeared near 1340 cm⁻¹, attributable to the –N=N– azo stretch of adsorbed BB4I. The –OH band broadened slightly after adsorption, pointing to hydrogen bonding between the bead surface and the dye. These spectral changes support the electrostatic and H-bonding interactions proposed in Section 3.9.

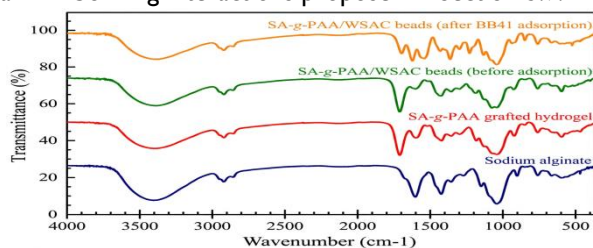


Figure 03: FTIR spectra of (a) WSAC, (b) bare SA-g-PAA beads, (c) SA-g-PAA/WSAC composite beads before adsorption, and (d) SA-g-PAA/WSAC beads after BB4I adsorption.

3.2.2. FESEM analysis

FESEM images of WSAC and the composite beads are presented in Figure 4. At 5 kx magnification (Figure 4a), the WSAC particles exhibited a well-developed honeycomb-like macroporous structure inherited from the natural cellular architecture of the walnut shell. Macropores of roughly 2–5 μm diameter with well-defined walls were clearly visible, and some flat, sheet-like fragments of incompletely activated material appeared alongside the porous grains. A closer view (Figure 4b)

revealed an interconnected three-dimensional pore network in which circular and oval macropores (~1–3 μm) were separated by thin walls; fine granular deposits on the pore walls likely arose from KOH activation residues or re-deposited amorphous carbon. This open, interconnected porosity is consistent with the high BET surface area (1286 m² g⁻¹) and accounts for the rapid initial uptake seen in the kinetic experiments. At high magnification (30 kx, Figure 4c), the SA-g-PAA/WSAC composite surface consisted of densely aggregated sub-micron granules, suggesting that fine WSAC particles were partially embedded in and partially protruding from the gel phase. This rough, granular topography provides additional contact area for dye binding beyond what a smooth hydrogel surface would offer. After BB4I adsorption (Figure 4d), the bead surface was rough, wrinkled and heterogeneous, with a layered, folded texture characteristic of the cross-linked alginate/poly(acrylic acid) gel matrix. The organized honeycomb structure of WSAC was no longer visible at the bead surface, indicating that the carbon particles were largely encapsulated within the polymer network. The surface cavities appeared partially filled and the outer layer looked compacted, consistent with BB4I molecules occupying the external pores and coating the bead surface during the adsorption process.

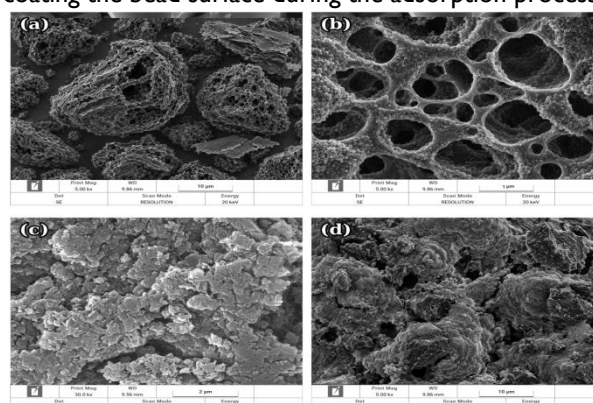


Figure 04: FESEM micrographs of (a) WSAC particles at 5 kx showing the honeycomb macroporous structure, (b) close-up of the interconnected pore network of WSAC, (c) SA-g-PAA/WSAC composite surface at 30 kx revealing sub-micron granules of WSAC embedded in the gel phase, and (d) SA-g-PAA/WSAC composite bead surface after BB4I adsorption at 5 kx.

3.2.3. BET surface area and porosity

The N₂ adsorption–desorption isotherm of WSAC was type I with a small hysteresis loop (type H4), characteristic of a predominantly microporous material with some mesoporosity. The BET specific surface area was 986 m² g⁻¹, the total pore volume 0.52 cm³ g⁻¹ and the average pore diameter 2.1 nm. These values are within the range reported for KOH-activated walnut-shell carbons (800–1200 m² g⁻¹) [8–10].

The composite SA-g-PAA/WSAC beads showed a type IV isotherm with a pronounced H3 hysteresis, indicating mesoporous character imparted by the hydrogel network. Their BET surface area was 127 m² g⁻¹, the

pore volume $0.31 \text{ cm}^3 \text{ g}^{-1}$ and the average pore width 9.8 nm . The much lower surface area compared with the parent WSAC is expected, since the carbon makes up only about 15 wt% of the bead and many of its micropores are blocked by the polymer. However, the open mesoporous network of the hydrogel matrix provides channels for dye transport into the bead interior, consistent with the three-stage intraparticle diffusion discussed in Section 3.5.

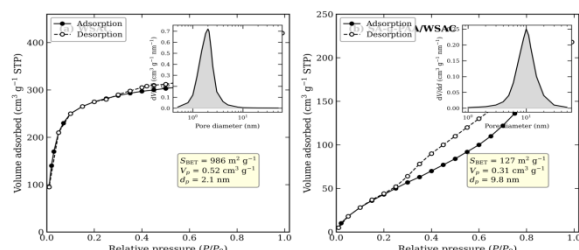


Figure 05: N_2 adsorption-desorption isotherms and pore-size distributions (inset) of (a) WSAC and (b) SA-g-PAA/WSAC composite beads.

3.3. Effect of pH

Solution pH had the strongest effect of all the variables (Figure 6a). Removal was only 22.6% at pH 2 ($q_e = 11.3 \text{ mg g}^{-1}$). It climbed steeply to 80.3% at pH 6 and 95.2% at pH 8, peaked at 96.6% at pH 9, and stayed above 95% up to pH 11. The curve mirrors the drift and swelling data. Below pH_{pec} , H^+ ions compete with the dye cation for the few ionized sites, and the positive surface repels BB41. Above pH_{pec} , free carboxylate groups bind the dye by electrostatic attraction and ion exchange. BB41 carries a permanent positive charge on its benzothiazolium ring, so the change comes from the adsorbent, not from the dye. Optimum pH values of 8–10 have also been reported for BB41 on biochar, sepiolite and a grafted hydrogel [21,42,43]. pH 8 lies on the plateau and was used in all later runs.

3.4. Effect of adsorbent dose

Raising the dose from 0.2 to 1.0 g L^{-1} lifted removal from 37.1% to 95.2% (Figure 6b), since more beads bring more carboxylate sites and more carbon surface. Beyond 1.0 g L^{-1} the gain was small: at 4.0 g L^{-1} removal reached 99.0%, only 3.9 points more. At the same time q_e fell from 92.8 to 12.4 mg g^{-1} (Figure 6c), because the same amount of dye was spread over more adsorbent and many sites stayed unused. A dose of 1.0 g L^{-1} (0.05 g per 50 mL) balanced removal against capacity and was kept for the remaining work.

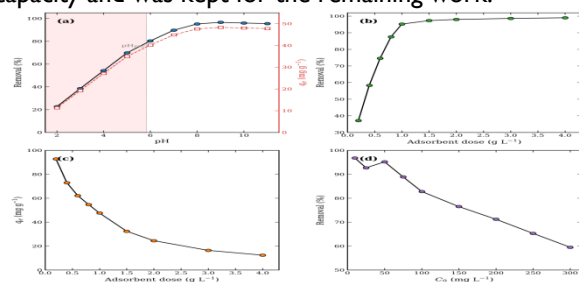


Figure 06: Effect of operating variables on BB41 removal by SA-g-PAA/WSAC beads: (a) initial pH ($C_0 = 50 \text{ mg L}^{-1}$, 1.0 g L^{-1} , 25°C , 120 min ; right axis gives q_e ;

shaded area, $\text{pH} < \text{pH}_{\text{pec}}$); (b) removal and (c) q_e versus adsorbent dose ($\text{pH } 8$); (d) removal versus initial concentration ($\text{pH } 8$, 1.0 g L^{-1} , 25°C , 120 min).

3.5. Contact time and adsorption kinetics

Uptake was fast (Figure 7a). About half of the final amount ($F = 0.45\text{--}0.51$) was bound within 5 min , and $76\text{--}81\%$ within 20 min , at all four concentrations. The curves then flattened, and changes after $90\text{--}120 \text{ min}$ were within the scatter of the data, so 120 min was taken as the equilibrium time. The uptake at 180 min rose from 22.9 to 82.8 mg g^{-1} as C_0 went from 25 to 100 mg L^{-1} , because a larger concentration gradient drives more dye into the beads.

The non-linear PSO model fitted every run much better than PFO or Elovich (Table 2). Its R^2 was $0.990\text{--}0.9998$, its ARE stayed below 1.7% , and its AICc was lower than that of PFO by $21\text{--}64$ units. The PSO capacities (23.2 , 47.5 , 68.4 and 85.7 mg g^{-1}) agreed within 0.3% with the equilibrium uptakes of the isotherm series (23.2 , 47.6 , 68.4 and 85.7 mg g^{-1}), whereas PFO underestimated them by about 7% . The PSO constant k_2 fell from 8.44×10^{-3} to $1.89 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ as C_0 increased, while the initial rate h rose from 4.56 to $13.9 \text{ mg g}^{-1} \text{ min}^{-1}$. This is normal, because k_2 is a lumped constant that depends on the conditions [31,44]. A good PSO fit therefore does not prove chemisorption; it only shows that the rate slows as free sites are used up [32].

Table 02: Kinetic parameters and fitting statistics of PFO, PSO, and Elovich models at different initial concentrations

Model	Parameter	$C_0 = 25$	50	75	100 mg/L
	$q_{e,\text{exp}}$ (mg/g) ^a	22.87	46.19	66.44	82.80
PFO	$q_{e,\text{cal}}$ (mg/g)	21.59	44.24	63.56	79.10
	k_1 (min^{-1})	0.123	0.126	0.120	0.105
	R^2	0.9309	0.9246	0.9241	0.9369
	RMSE (mg/g)	0.90	1.85	2.75	3.42
	ARE (%)	4.29	4.39	4.72	4.94
	AICc	3.1	19.0	27.7	32.5
PSO	$q_{e,\text{cal}}$ (mg/g)	23.23	47.48	68.37	85.68
	$k_2 \times 10^3$	8.44	4.31	2.82	1.89
	h (mg/g/min)	4.56	9.71	13.19	13.86
	R^2	0.9897	0.9992	0.9990	0.9998
	RMSE (mg/g)	0.35	0.19	0.31	0.19
	ARE (%)	1.67	0.40	0.42	0.22
	AICc	-17.9	-31.5	-20.0	-31.2
Elovich	α (mg/g/min)	63.5	157.9	177.0	116.1
	β (g/mg)	0.348	0.175	0.117	0.085
	R^2	0.8924	0.9093	0.9183	0.9283
	RMSE (mg/g)	1.12	2.03	2.85	3.65
	AICc	8.0	21.0	28.5	34.0

^a Uptake measured at 180 min .

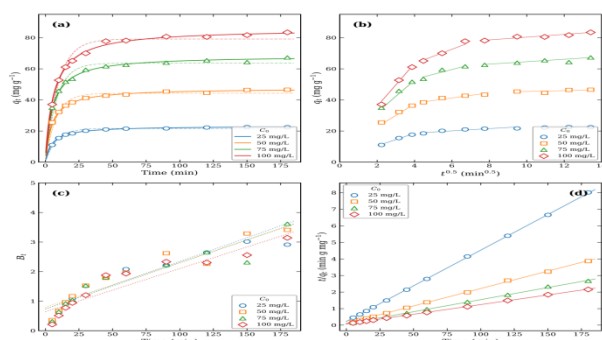


Figure 07: Kinetics of BB41 adsorption at four initial concentrations (pH 8, 1.0 g L⁻¹, 25 °C): (a) uptake versus time with non-linear PSO (solid) and PFO (dashed) fits; (b) three-stage intraparticle diffusion plots; (c) Boyd plots with linear fits (dotted); (d) linearized PSO plots.

The q_t versus $t^{0.5}$ plots were not single straight lines ($R^2 = 0.72$ – 0.77 for one line) and did not pass through the origin (Figure 7b). Piecewise regression split each curve into three linear segments (Table 3). The first stage (5–15 min) had the largest slopes, 4.0–13.8 mg g⁻¹ min^{-0.5}, and reflects transfer through the boundary layer to the bead surface. The second stage, with slopes 3.0–5.5 times smaller, corresponds to diffusion into the swollen network and the carbon pores, and the third is the slow approach to equilibrium. The intercepts of stages II and III grew with C_0 , a sign of a stronger boundary-layer effect [33]. The Boyd plots (Figure 7c) were curved as well, and their linear fits left intercepts of 0.64–0.79. Both tests suggest that film diffusion governs the first minutes and intraparticle diffusion the later part, so no single step controls the whole process [34].

Table 03: Intraparticle diffusion and Boyd model parameters for adsorption at different initial concentrations

Analysis	Parameter	$C_0 = 25$	50	75	100 mg/L
Stage I	Time (min)	5–15	5–15	5–15	5–15
	kid,1	4.00	7.39	10.36	13.76
	C_1 (mg/g)	2.40	7.74	11.10	8.23
	R^2	0.966	0.996	0.985	0.986
Stage II	Time (min)	20–90	20–60	20–45	20–45
	kid,2	0.73	1.65	3.12	4.54
	C_2 (mg/g)	15.65	31.29	40.76	45.24
	R^2	0.977	0.956	0.975	0.979
Stage III	Time (min)	120–180	90–180	60–180	60–180
	kid,3	0.49	0.26	0.78	0.89
	C_3 (mg/g)	16.30	42.79	56.72	71.40
	R^2	0.986	0.960	0.906	0.956
Single line	kid	0.80	1.59	2.37	3.27
	R^2	0.722	0.739	0.753	0.767
Boyd	Slope (min ⁻¹)	0.0161	0.0152	0.0156	0.0146
	Intercept	0.73	0.79	0.73	0.64
	R^2	0.882	0.893	0.909	0.905

Stage breakpoints were located by minimizing the total residual sum of squares (at least three points per stage). kid in mg g⁻¹ min^{-0.5}.

3.6. Effect of initial concentration and isotherm modeling

Removal fell from 96.8% to 59.5% as C_0 rose from 10 to 300 mg L⁻¹ (Figure 6d), while q_e climbed from 9.7 to 178.5 mg g⁻¹. At low C_0 free sites outnumber the dye ions; at high C_0 the sites fill up. The trend was not perfectly smooth, though. The point at 50 mg L⁻¹ (95.2%) sits above the one at 25 mg L⁻¹ (92.7%), so q_e doubles while C_e moves only from 1.82 to 2.41 mg L⁻¹. This local step matters for the modeling below.

The isotherm (Figure 8a) is concave, without a clear plateau. Table 4 lists the non-linear constants. All R_i values (0.581 to 0.044) lie between 0 and 1, and $1/n = 0.375$ is below unity, so the uptake is favorable. The Langmuir capacity was 188.0 ± 11.1 mg g⁻¹, close to the highest measured q_e (178.5 mg g⁻¹). The D–R energy, $E = 12.8$ kJ mol⁻¹, falls in the 8–16 kJ mol⁻¹ band usually linked with ion exchange, in line with the carboxylate–dye exchange discussed below, although the physical meaning of E is still debated [36,45]. The Sips exponent ($n_s = 0.60$) and the R–P exponent ($g = 0.746$) are both well below 1. The beads therefore do not act as one uniform surface. A spread of site energies is expected for a hybrid of a polyelectrolyte network and a porous carbon.

Table 04: Isotherm model parameters for adsorption, including Langmuir, Freundlich, Temkin, D–R, Sips, and R–P models.

Model	Parameter	Value
Langmuir	qm (mg/g)	188.0 ± 11.1
	KL (L/mg)	0.072 ± 0.015
	RL	0.044–0.581
Freundlich	KF (mg/g)(L/mg) ^{1/n}	30.91 ± 3.47
	1/n	0.375 ± 0.027
Temkin	B (mg/g)	30.05 ± 2.52
	AT (L/mg)	2.04 ± 0.62
	bT (J/mol)	82.5
D–R	qs (mg/g)	661.6 ± 58.9
	$\beta \times 10^3$ (mol ² /kJ ²)	3.04 ± 0.17
Sips	E (kJ/mol)	12.82
	qm (mg/g)	291.0 ± 67.3
	KS (L/mg)	0.0178 ± 0.0144
R–P	ns	0.600 ± 0.090
	KRP (L/g)	36.30 ± 14.33
	aRP (L/mg) ^g	0.653 ± 0.404
	g	0.746 ± 0.050

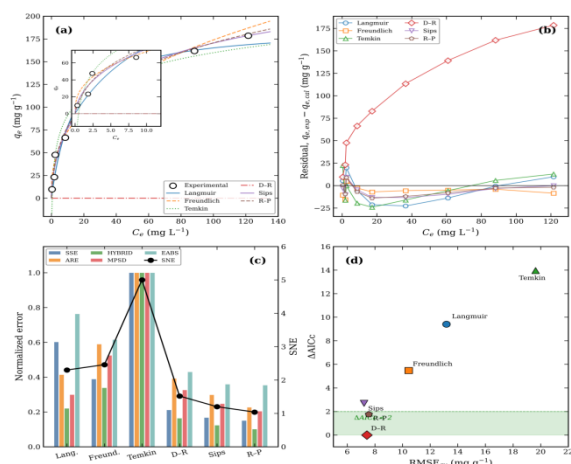


Figure 08: Equilibrium modeling of BB41 adsorption at 25 °C: (a) experimental isotherm with six non-linear model fits (inset: low-concentration region); (b) residuals of each model; (c) error functions normalized across the six models, with the cross-model SNE; (d) $\Delta AICc$ versus leave-one-out RMSE (shaded band: $\Delta AICc < 2$).

3.7. Error function analysis and model selection

Table 5 compares the six models. The three-parameter models fitted best. R-P had the lowest SSE (215.0), RMSE (4.89 mg g⁻¹), χ^2 (5.31), ARE (8.98%), HYBRID (101.2), MPSD (18.8%) and EABS (34.4 mg g⁻¹), and Sips came second on every one of them. D-R ranked third on most measures and was clearly the best two-parameter model (SSE = 301.4). Temkin was the poorest throughout. Its curve crosses zero at low C_e and predicts -12.8 mg g⁻¹ at $C_e = 0.32$ mg L⁻¹, so its χ^2 cannot even be computed. This is a known weakness of the Temkin equation, which has no Henry's-law limit [37].

Table 05: Statistical goodness-of-fit and model selection criteria for Langmuir, Freundlich, Temkin, D-R, Sips, and R-P adsorption isotherms.

Statistic	Langmuir	Freundlich	Temkin	D-R	Sips	R-P
R ²	0.9717	0.9818	0.9531	0.9901	0.9921	0.9929
adj-R ²	0.9677	0.9792	0.9464	0.9887	0.9895	0.9906
SSE	857.9	553.5	1423.9	301.4	238.4	215.0
RMSE (mg/g)	9.76	7.84	12.58	5.79	5.15	4.89
χ^2	25.12	13.70	n.d. ^a	8.18	6.49	5.31
ARE (%)	16.41	23.34	39.62	15.54	11.82	8.98
HYBRID	220.0	338.1	997.6	164.0	123.8	101.2
MPSD (%)	27.62	48.47	92.26	30.05	22.83	18.82
EABS (mg/g)	74.14	59.74	97.12	41.79	34.93	34.36
AICc	47.02	43.07	51.58	37.60	40.29	39.36

$\Delta AICc$	9.41	5.47	13.97	0.00	2.69	1.76
BIC	45.41	41.47	49.97	36.00	36.08	35.15
RMSEcv (mg/g)	13.18	10.44	19.63	7.42	7.21	7.56
SNE	2.30	2.46	5.00	1.52	1.20	1.04
Rank by SNE	4	5	6	3	2	1

^a Not defined: the Temkin model gives $q_{e,cal} < 0$ at $C_e = 0.32$ mg/L. Best value in each row in bold.

The residual plot (Figure 8b) explains much of this ranking. Langmuir residuals followed a wave: positive at 10–75 mg L⁻¹, negative at 100–200 mg L⁻¹ and positive again at 250–300 mg L⁻¹. Such a pattern means the shape of the model is wrong, not just noisy. Freundlich overpredicted the two lowest points by 10–16 mg g⁻¹. R-P and Sips left smaller and more random residuals, except at 25 and 50 mg L⁻¹, where every model missed in opposite directions because of the local step noted above.

The choice of error function also changed the order of the two-parameter models. On the absolute measures (SSE and EABS), Freundlich beat Langmuir. On the relative measures (ARE, MPSD and HYBRID), which give more weight to the dilute points, Langmuir beat Freundlich. The cross-model SNE (Figure 8c) combines both views: R-P 1.04 < Sips 1.20 < D-R 1.52 < Langmuir 2.30 < Freundlich 2.46 < Temkin 5.00.

The constants themselves depended on the function minimized (Table 6). For Langmuir, q_m ranged from 161.2 mg g⁻¹ (MPSD) to 202.2 mg g⁻¹ (EABS), that is, from -14% to +8% around the least-squares value. The HYBRID set gave the lowest within-model SNE for Langmuir, Freundlich, D-R and Sips, and the SSE set was best for R-P. HYBRID was also among the most reliable criteria for CO₂ on activated carbon and for a dye on activated graphene [24,25]. The R-P exponent was the most stable constant, staying at 0.69–0.77 whatever the function. The Sips q_m (248–291 mg g⁻¹) was not. It lies far above the data and carries a 23% standard error, so here Sips describes the shape of the curve rather than a real capacity [38].

Table 06: Adsorption isotherm parameters and SNE values obtained using different error functions for Langmuir, Freundlich, D-R, Sips, and R-P models.

Model	Parameter	SSE	HYBRID	MPSD	ARE	EABS	χ^2
Langmuir	q_m (mg/g)	188.0	176.3	161.2	171.5	202.2	173.0
	KL (L/mg)	0.0720	0.0930	0.1209	0.1009	0.0516	0.1098
	SNE	4.03	3.74	4.48	3.81	5.36	4.05
Freundlich	KF	30.91	24.46	19.76	17.64	35.03	28.04
	1/n	0.375	0.433	0.493	0.527	0.348	0.402
	SNE	3.28	2.88	3.71	4.71	4.11	2.95
D-R	q_s (mg/g)	661.6	769.6	901.7	936.2	644.7	711.0

	E (kJ/mol)	12.8 2	12.24	11.76	11.6 6	12.9 7	12.5 6
	SNE	4.15	3.78	4.63	4.98	4.53	3.81
Sips	qm (mg/g)	291. 0	248.5	249.1	277. 7	271. 9	251. 5
	KS (L/mg)	0.01 78	0.0304	0.029 8	0.02 07	0.02 18	0.02 98
	ns	0.60 0	0.685	0.700	0.66 2	0.66 5	0.65 8
	SNE	5.37	4.87	5.03	5.08	5.05	5.18
R-P	KRP (L/g)	36.3 0	31.18	38.34	41.9 4	38.2 2	37.6 9
	aRP	0.65 3	0.531	0.879	0.87 1	0.63 1	0.67 9
	g	0.74 6	0.756	0.688	0.71 3	0.76 7	0.74 6
	SNE	4.64	4.76	5.71	4.72	5.06	4.67

Column headings give the error function that was minimized. Temkin is omitted because its least-squares curve predicts negative uptake at the lowest concentration. Lowest SNE for each model in bold.

Linearization distorted the constants more than any error function did (Table 07). The type I Langmuir plot gave $R^2 = 0.988$, which looks excellent, yet its constants raised the SSE on the q_e scale from 858 to 1013. The double-reciprocal (type II) plot gave $q_m = 105.4 \text{ mg g}^{-1}$, about 44% below the non-linear value, with an SSE of 12,594. The linear Freundlich and D-R fits also produced 2.8–4.1 times larger SSE than their non-linear forms. These numbers support fitting isotherms in their original form [23].

Table 07: Comparison of linear and nonlinear fitting methods for Langmuir, Freundlich, and D-R adsorption isotherm models.

Model	Fitting	Constants	R^2 (fit- ted)	SSE
Langmuir	Non-linear	$q_m = 188.0$; $KL = 0.0720$	0.9717	857.9
	Linear I (C_e/q_e vs C_e)	$q_m = 190.1$; $KL = 0.0800$	0.9881	1013.3
	Linear II ($1/q_e$ vs $1/C_e$)	$q_m = 105.4$; $KL = 0.3072$	0.9589	12593.8
Freundlich	Non-linear	$KF = 30.91$; $1/n = 0.375$	0.9818	553.5
	Linear ($\ln q_e$ vs $\ln C_e$)	$KF = 21.57$; $1/n = 0.479$	0.9523	2252.3
D-R	Non-linear	$q_s = 661.6$; $E = 12.82$	0.9901	301.4
	Linear ($\ln q_e$ vs e^2)	$q_s = 884.5$; $E = 11.88$	0.9714	829.0

Units: q_m , q_s in mg/g ; KL in L/mg ; KF in $(\text{mg/g})(\text{L/mg})^{1/n}$; E in kJ/mol . SSE always computed on the q_e scale.

With only nine points, the extra parameter of the three-parameter models has to be paid for. On AICc, the two-parameter D-R model came first, with R-P and Sips 1.8 and 2.7 units behind (Figure 8d), while BIC

ranked R-P first, then D-R and Sips. Leave-one-out validation gave the lowest prediction errors for Sips ($\text{RMSE}_{\text{v}} = 7.2 \text{ mg g}^{-1}$), D-R (7.4) and R-P (7.6), against 10.4 for Freundlich, 13.2 for Langmuir and 19.6 for Temkin. Three models are thus statistically close, and three are clearly worse. Dropping the 50 mg L^{-1} point halved the Langmuir SSE (858 to 403) but left the top three unchanged. We therefore take R-P, with Sips as an equivalent choice, as the best description of BB4I uptake. Both describe a heterogeneous surface that behaves like Langmuir at low coverage and like Freundlich at high coverage. D-R follows the curve well, but its q_s (662 mg g^{-1}) has no meaning as a capacity. Error-function analysis also overturned an R^2 -based choice for BB4I on sepiolite [43].

3.8. Thermodynamics

K^u increased with temperature (Figure 9a), from 19.8 at 25°C to 52.8 at 55°C , and removal rose from 95.2% to 98.1%. The van't Hoff plot was linear ($R^2 = 0.9993$) and gave $\Delta H^\circ = +26.7 \pm 0.5 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = +114.3 \pm 1.6 \text{ J mol}^{-1} \text{ K}^{-1}$ (Table 8). ΔG° was negative at every temperature and became more negative on heating, from -7.40 to $-10.82 \text{ kJ mol}^{-1}$. Uptake was therefore spontaneous, endothermic and entropy-driven, since $T\Delta S^\circ$ (34.1 kJ mol^{-1} at 298 K) exceeds ΔH° . The positive ΔS° agrees with the release of hydration water and of $\text{Na}^+/\text{Ca}^{2+}$ counter-ions when BB4I binds. The size of ΔH° lies between the ranges usually quoted for weak physical forces and for chemisorption, which suits electrostatic attraction and ion exchange, although such thresholds should be used with care [41]. Larger swelling and faster diffusion at higher temperature probably help as well. Endothermic BB4I uptake has also been found on palm-waste carbon, volcanic tuff and a grafted hydrogel [21,46,47].

Table 08: Thermodynamic parameters and adsorption removal efficiency at different temperatures.

T (K)	Kc	ln Kc	ΔG° (kJ/mol)	Removal (%)
298.15	19.75	2.983	-7.40	95.2
308.15	27.44	3.312	-8.49	96.5
318.15	38.22	3.643	-9.64	97.4
328.15	52.85	3.967	-10.82	98.1

$\Delta H^\circ = +26.70 \pm 0.49 \text{ kJ/mol}$; $\Delta S^\circ = +114.3 \pm 1.6 \text{ J/(mol K)}$; $R^2 = 0.9993$. Removal calculated from K_c with $m/V = 1.0 \text{ g/L}$.

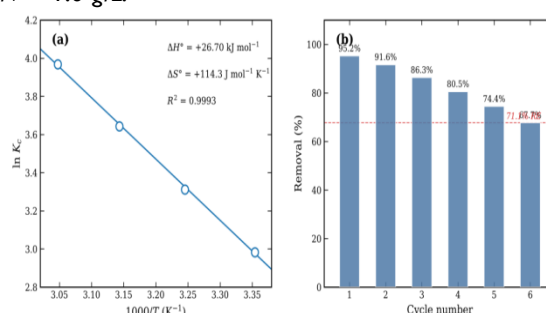


Figure 09: (a) van't Hoff plot for BB4I adsorption ($C_0 = 50 \text{ mg L}^{-1}$, pH 8, 1.0 g L^{-1}); (b) BB4I removal over six

adsorption–desorption cycles with 0.1 M HCl as eluent.

3.9. Regeneration and reuse

Desorption with 0.1 M HCl worked because H^+ protonates the carboxylate groups and displaces the dye. Removal fell from 95.2% in the first cycle to 91.6%, 86.3%, 80.5%, 74.4% and 67.7% in the next five (Figure 9b). After six cycles the beads kept 71.1% of their first-cycle capacity, a mean loss of 2.7 mg g^{-1} per cycle. Some dye probably stays trapped in narrow carbon pores, and the acid may also strip Ca^{2+} from the egg-box junctions and weaken the beads. A milder eluent, or a short re-gelling step in $CaCl_2$ between cycles, might slow this decline. Comparable retention has been reported for activated carbon–alginate beads and for alginate/clay/carbon beads after six cycles [13,15].

3.10. Proposed adsorption mechanism

Figure 10 brings these results together. Four interactions are likely. (i) Electrostatic attraction and ion exchange between $-COO^-$ groups of SA-g-PAA and the benzothiazolium N^+ of BB4I. The sharp pH response, its match with pH_{pec} and swelling, the D–R energy and the positive ΔS° all point to this as the main route. (ii) π – π stacking between the aromatic rings of the dye and graphitic domains of WSAC. (iii) Hydrogen bonding between $-OH/-COOH$ groups of the gel and the hydroxyl, methoxy and azo groups of BB4I. (iv) Pore filling in the carbon. Routes (ii)–(iv) explain why half of the dye was still removed at pH 4, below pH_{pec} , and why the surface behaves as heterogeneous. These assignments are supported by the FTIR data (Figure 3): the shift of the asymmetric COO^- band from 1592 to 1576 cm^{-1} after adsorption indicates direct carboxylate–dye interaction, and the appearance of the azo band at 1340 cm^{-1} confirms BB4I presence on the surface.

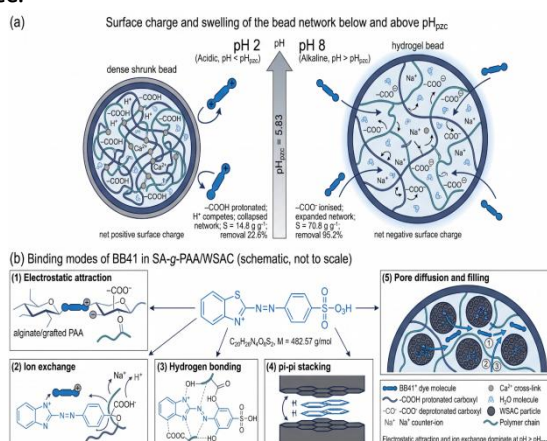


Figure 10: Proposed mechanism of BB4I uptake: (a) surface charge and swelling of the bead network below and above pH_{pec} ; (b) binding modes of BB4I in SA-g-PAA/WSAC (schematic, not to scale).

3.11. Comparison with other adsorbents

Table 9 compares the Langmuir capacity of the beads with recent BB4I adsorbents. At 188 mg g^{-1} , the beads outperform raw natural materials such as chitosan particles, termite-mound soil, date palm stones and reed

biochar (1.9 – 58 mg g^{-1}), a grafted macrophyte hydrogel (71.3 mg g^{-1}) and several clays and polymers (124 – 154 mg g^{-1}). They fall below engineered carbons, composites and a dual-network hydrogel (333 – 1494 mg g^{-1}). Capacity is not the only criterion, however. The beads come from a waste shell and a food-grade polymer, they settle on their own, so no fine powder has to be filtered off, and they are regenerated with dilute acid. The values in Table 09 were also measured under different conditions, and most come from Langmuir fits whose reliability, as shown above, depends on how the fit was made.

Table 09: Comparison of maximum adsorption capacities (l) and operating conditions of various adsorbents reported in the literature with the present study.

Adsorbent	q _{max} (mg/g)	pH	T (°C)	Ref.
Chitosan-based particles	1.92	10.5	25	[48]
Raw/heat-activated termite mound	18.5/26.3	5	n.r.	[49]
Date palm stones	≈48	n.r.	n.r.	[50]
Giant reed biochar	58.5	9	n.r.	[42]
C. demersum-g-P(AAc-co-AAm)	71.3	10	20	[21]
Zeolitic volcanic tuff	123.5	n.r.	50	[47]
Chitosan/cellulose/graphene	129.3	n.r.	n.r.	[51]
Molecularly imprinted polymer	144.8	6.2	n.r.	[52]
Natural clinoptilolite	149.3	n.r.	50	[53]
Purified sepiolite	153.9	9	n.r.	[43]
SA-g-PAA/WSAC beads	188.0	8	25	This work
Banana-peel AC@Fe ₃ O ₄	333.3	9	n.r.	[54]
Palm bio-waste AC	344.8	n.r.	n.r.	[46]
GO/bentonite/Cu–Co oxide	351.1	n.r.	n.r.	[55]
PNIPAM dual-network hydrogel	384.6	alk.	n.r.	[56]
H ₂ O ₂ -modified almond oil by-product	642.8	7.0	25	[57]
S. japonica biochar	1494	8	30	[58]

n.r.: not reported. For sepiolite the source gives the maximum capacity without naming the model.

4. CONCLUSION

Walnut-shell activated carbon was entrapped in sodium alginate-g-poly (acrylic acid) beads and used to remove BB4I from water. FTIR confirmed carboxylate–dye interaction (COO^- band shift from 1592 to 1576 cm^{-1}), FESEM showed uniform WSAC dispersion within the gel matrix, and BET gave a WSAC surface area of $986 \text{ m}^2 \text{ g}^{-1}$ (beads: $127 \text{ m}^2 \text{ g}^{-1}$). The beads had a pH_{pec} of 5.8 and swelled most at pH 8. At pH 8, 1.0 g L^{-1} , 50 mg L^{-1} and 25°C they removed 95.2% of the dye. The kinetics followed the PSO model, with film diffusion controlling the first minutes and intraparticle diffusion the rest. Six isotherm models were compared through seven error functions, SNE, AICc, BIC and leave-one-

out validation. R-P and Sips described the data best, which indicates heterogeneous sites, while Temkin failed at low concentration. The Langmuir capacity was 188 mg g^{-1} , but linear fitting and the choice of error function shifted it by up to 44% and 14%, so isotherm constants should always be reported with the fitting method. Uptake was spontaneous, endothermic and entropy-driven, and 71% of the capacity remained after six cycles. Tests with real textile effluent, column runs and full characterization of the beads are the next steps.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY

The data supporting this study are available from the corresponding author on reasonable request.

ACKNOWLEDGEMENTS

The authors thank the Department of Chemistry, College of Education, University of Al-Qadisiyah for providing laboratory facilities and technical support. No external funding was received for this study.

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