Supporting information

Supersorption capacity of anionic dye by newer chitosan hydrogel capsules via green surfactant exchange method

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Section S1. Description of adsorption kinetic models

In this study, several kinetic models were applied to mathematically describe the intrinsic adsorption constants. The non-linearized forms of the pseudo-first-order [1], pseudo-second-order [2], and Elovich [3] models, are expressed in Equations 1, 2, and 3, respectively. The linear form of the intra-particle models [4] are given in Equation 4.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

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

$$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t) \quad (3)$$

$$q_t = k_{ip}\sqrt{t} + C \quad (4)$$

where k_1 (1/min), k_2 (g/mg×min), α (mg/g × min), and k_{ip} (mg/g×min$^{1/2}$) are the rate constants of the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, respectively; q_e and q_t are the adsorbate uptake per mass of adsorbent at equilibrium and at any time t (min), respectively; β (mg/g) is the desorption constant during any one experiment; and C (mg/g) is a constant describing the thickness of the boundary layer. Higher values of C correspond to a greater effect on the limiting boundary layer.

Section S2. Description of adsorption isotherm models

In this study, the Langmuir (Eq. 5) [5], Freundlich (Eq. 6) [6], Redlich-Peterson (Eq. 7) [7], and Dubinin-Radushkevich (Eqs. 8–10) [8] models were employed to describe the adsorptive behavior of CR onto the capsules samples. To minimize the respective error functions, the non-linear optimization technique was applied for calculating the adsorption parameters from these models.

$$q_e = \frac{Q^0_{\max} K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_F C_e^n \quad (6)$$

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^g} \quad (7)$$

$$q_e = q_{DR} e^{-K_{DR}\varepsilon^2} \quad (8)$$

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad (9)$$

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (10)$$

where q_e (mg/g) is the amount of CR adsorbed onto capsule at equilibrium; C_e (mg/L) is the CR concentration at equilibrium; Q^o_{max} (mg/g) is the maximum saturated monolayer adsorption capacity of adsorbent; K_L (L/mg) is the Langmuir constant related to the affinity between an adsorbent and adsorbate; K_F [(mg/g)/(L/mg)^n] is the Freundlich constant, which characterizes the strength of adsorption; n (dimensionless) is a Freundlich intensity parameter; K_{RP} (L/g) and a_{RP} (mg/L)$^{-g}$ are the Redlich–Peterson constants; g (dimensionless) is an exponent whose value must lie between 0 and 1; q_{RD} (mg/g) is the adsorption capacity; K_{RD} (mol^2/kJ^2) is the constant related to the sorption energy; ε is the Polanyi potential; and E (kJ/mol) is the mean adsorption energy.

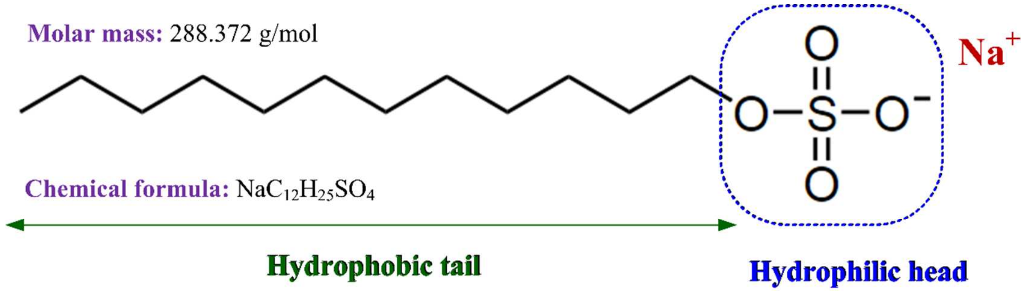

Figure S1. Chemical structure of sodium dodecyl sulfate

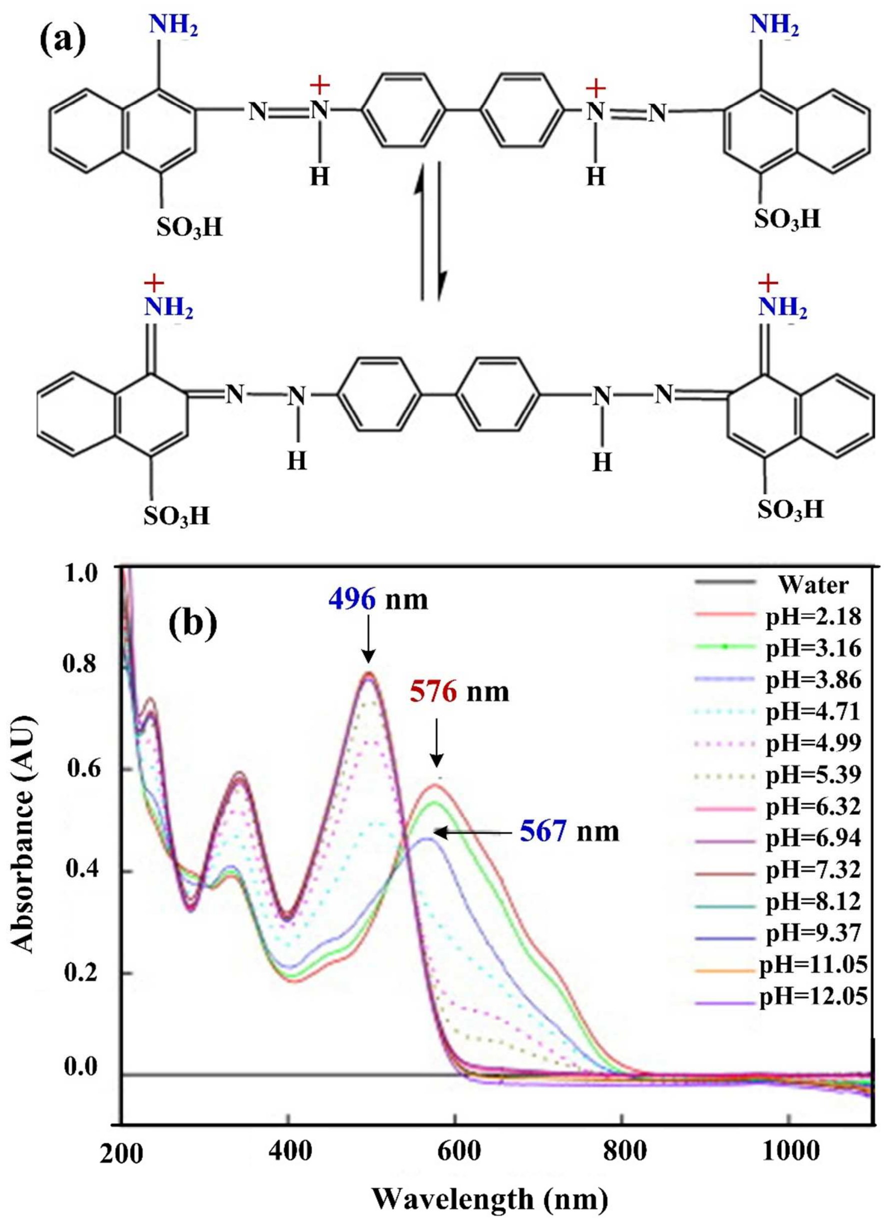

Figure S2. (a) Chemical structure of Congo Red and (b) UV-vis spectra of Congo Red solutions at different solution pH values [9])

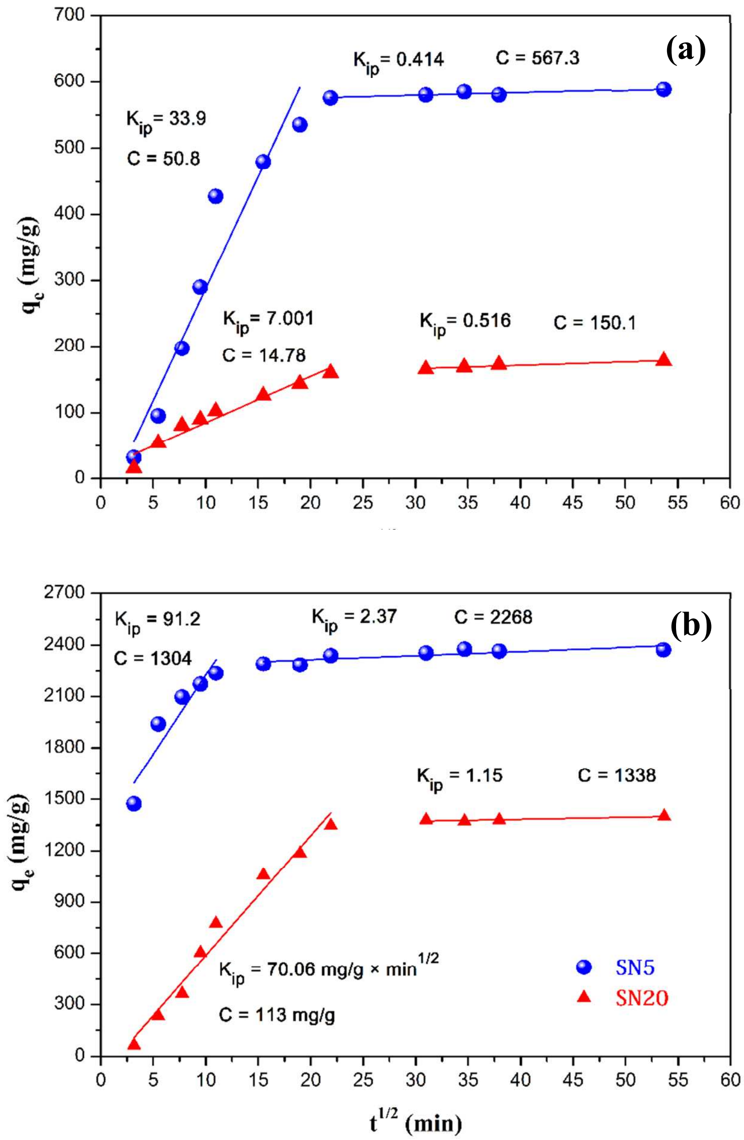

Figure S3. Intra-particle diffusion plot for CR adsorption of (a) pristine capsules (S5 and S20), and (b) NaOH-treated capsules (SN5 and SN20)

Table S1. Current treatment methods used to remove dye from effluents

Technology	References
Photodegradation or photocatalytic degradation	[10, 11]
Membrane	[12, 13]
Chemical coagulation and flocculation	[14-16]
Zonation	[16-18]
Biological treatment and biodegradation	[19, 20]
Adsorption	[21-23]
Advanced oxidation processes	[24, 25]
Electrochemical processes	[15, 26]
Ion exchange	[15, 27]

Table S2. Comparison of the maximum adsorption capacity (calculated from the Langmuir equation) of treated hydrogen capsules and other adsorbents reported in the literature

Adsorbent	Operation conditions				Q^o_{max} (mg/g)	Ref.
	C_o (mg/L)	t (h)	T (°C)	pH		
Chitosan-based hydrogel capsule treated with NaOH (SN5 sample)	100–3000	30	24	5.0	**2592**	**This study**
Biosorbents						
Palm Kernel Seed Coat	30–150	2	30	6.7	66	[28]
Neem leaf powder	20–60	4	27	6.7	41	[29]
Jute stick powder	5–200	24	30	6.0	36	[30]
Wheat bran	50–300	8.3	25	8.0	23	[31]
Orange peel	10–100	1.5	29	7.7	22	[32]
Banana peel	10–150	2	30	7.9	18	[33]
Rice bran	50–300	8.3	25	8.0	15	[31]
Orange peel	10–150	2	30	7.9	14	[33]
Biochar/Hydrochar						
Rice straw biochar	50–5000	24	30	7.0	191	[34]
Wood chip biochar	50–5000	24	30	7.0	110	[34]
Bamboo hydrochar	5–100	12	25	NA	97	[35]
Korean cabbage biochar	50–5000	24	30	7.0	96	[34]
Residual algae biochar	30–200	2	27	7.0	51	[36]
Vermicompost biochar	5–200	6	25	7.0	31	[37]
Activated carbon (AC)						
Mesoporous carbon fibers	50–1000	24	Room	NA	1067	[38]
Silkworm cocoon AC fiber	10–400	10	Room	3.0	1100	[39]
Commercial AC	200–450	2	30	7.4	491	[40]
Commercial Darco® AC	50–5000	24	30	7.0	449	[34]
Straw AC	75–175	2	30	7.4	401	[40]
Commercial AC	50–200	12	30	7.0	300	[41]
Rice husk AC	75–175	2	30	7.4	238	[40]
Coconut shell AC	75–175	2	30	7.4	188	[40]
Groundnut shell AC	50–150	2	30	7.4	111	[40]
Bamboo dust AC	50–150	2	30	7.4	102	[40]
Bael shell carbon	40–80	3	30	5.7	98	[42]
Layer double hydroxides (LDHs)						
NMA-LDHs calcined at 600 °C	40–300	24	30	7.0	1250	[43]

(Ni/Mg/Al layered double oxides)						
Flower-like porous microspheres derived from Ni/Al-LDHs	10–500	48	25	NA	1229	[44]
Magnetic polydopamine Mg/Al LDH nano-flakes	30–150	4	20	5.6	585	[45]
Ni/Mg/Al LHHs hierarchical flower-like hollow microspheres	40–300	24	30	7.0	286	[43]
Mg–Fe–CO_3–LDHs	5–50	1	25	4.0	105	[46]
Mg/Al-CO_3-LDHs	10–200	1	Room	NA	37	[47]
Zeolite and clay						
Clay mixture	50–600	24	30	NA	575	[48]
Bentonite	75–300	2	25	6.8	159	[49]
Na-Bentonite	50–1000	12	30	7.5	36	[50]
Montmorillonite	25–100	12	30	7.0	13	[51]
Commercial Ceram kaolin	25–500	24	30	7.5	7.3	[52]
Commercial K15GR kaolin	25–500	24	30	7.5	6.8	[52]
Commercial Q38 kaolin	25–500	24	30	7.5	5.4	[52]
Kaolin	50–1000	24	30	7.5	5.4	[50]
Zeolite	50–1000	24	30	7.5	3.6	[50]
Others						
Carbon nanotube/Mg(Al)O nanocomposites	200–800	24	25	7.0	1250	[53]
Functionalized carbon nanotube	200–800	24	25	7.0	882	[53]
$Fe(OH)_3$@Cellulose hybrid fibers	10–1000	24	25	NA	689	[54]
Chitosan hydrogel beads impregnated with carbon nanotubes	10–1000	24	30	5.0	450	[55]
Polyacrylamide-modified hydroxo aluminum/graphene composites (AGO)	100–500	12	35	3.0	424	[56]
Chitosan hydrogel beads impregnated with *cetyl trimethyl ammonium bromide*	10–1000	24	30	5.0	386	[57]
N,*O*-carboxymethyl-chitosan	200–1300	6	30	7.0	376	[58]
Sodium dodecylbenzene sulfonate modified-AGO	100–500	12	35	3.0	314	[56]
Cetyltrimethylammonium bromide modified -AGO	100–500	12	35	3.0	314	[56]
γ-Fe_2O_3 nanorod	50–300	3	Room	5.0	233	[59]

Guar gum-graft-poly (acrylamide)/silica hybrid nanocomposite	10–200	2	35	3.0	221	[60]
Chito-hyr-bead with BDS	10–1000	24	30	5.0	209	[61]
Chito-hyr-bead with SDBS	10–1000	24	30	5.0	207	[61]
Hollow microspheres NiO–Si	10–100	20	30	7.0	204	[62]
Chito-hyr-bead with SDS	10–1000	24	30	5.0	186	[61]
Chitosan-based hydrogel beads	10–1000	24	30	5.0	183	[57]
Hollow microspheres $Ni(OH)_2$–Si	10–100	20	30	7.0	114	[62]
Chito-hyr-bead with DSS	10–1000	24	30	5.0	114	[61]
$FeC_2O_4.2H_2O$ nanorod	50–300	3	Room	5.0	103	[59]
Chitosan	200–325	12	30	7.0	81	[51]
Chitosan	200–700	10	30	7.0	81	[58]
α-Fe_2O_3 nanorod	50–300	3	Room	5.0	78	[59]
N,O-carboxymethyl-chitosan/montm orillonite nanocomposites	100–500	8	30	7.0	74	[63]
*p*TSA-Pani@GO-CNT nanocomposite	25–200	10	30	5.0	67	[64]
Cellulose/Fe_3O_4/AC composite	5–70	12	25	5.0	66	[65]
ZrO_2 hollow spheres	15–55	24	30	7.0	59	[66]
Chitosan/montmorillonite nanocomposites	100–225	12	30	7.0	55	[51]
$CoFe_{1.93}Gd_{0.07}O_4$	25–120	3	20	NA	26	[67]
ZrO_2 solid spheres	15–55	24	30	7.0	21	[66]
ZrO_2 reagent	15–55	24	30	7.0	4.8	[66]

***NA:** not adjusted*

Chito-hyr-bead (Chitosan hydrogel bead); SDS (sodium dodecyl sulfate); SDBS (dodecyl benzenesulfonic acid sodium salt); DS (sodium decyl sulfate), DSS (dioctyl sulfosuccinate sodium salt)

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