

Fabrication of SA-SiO₂ capsules with 3D microscopic re-entrant structures via one-step titration-gel method for the removal of methylene blue from water

D. C. Lin¹, M. Shi², Y. Cao¹, J. F. Cao³, C. S. Peng^{1,3*}

¹The Key Lab of Marine Environmental Science and Ecology, Ministry of Education, College of Environmental Science and Engineering, Ocean University of China, 266100 Qingdao, China

²Institute of Coastal Environmental Pollution, and Ministry of Education Key Laboratory of Marine Environment and Ecology, College of Environmental Science and Engineering, Ocean University of China, 266100 Qingdao, China ³School of Environmental and Chemical Engineering, Zhaoqing University, 526061 Zhaoqing, China

Received 19 September 2018; accepted in revised form 14 November 2018

Abstract. In this paper, the eco-friendly sodium alginate-silicon oxide capsule (SASC) with a brilliantly wide pH tolerance property was obtained via the one-step titration-gel method and *in-situ* sol-gel progress. The spherical droplets with SA and tetraethyl orthosilicate (TEOS) casting mixture were directly injected into the calcium chloride (CaCl₂) solution. The effects of SiO₂ nanoparticles (SiO₂ NPs) on the morphology and adsorptive properties of the capsules were investigated. The interface of the SASC with micro-porous fracture aperture and microscopic re-entrant structures help to provide a stronger interaction between MB and surface channel thus increased its removed capacity during the courses of adsorption. The maximum absorption amount of the SASC against methylene blue (MB) was found to be 350.80 mg/g at 25 °C and the solution pH value of 8, which had a 12.82% enhancement compared with the neat capsule. The adsorption isothermal model. Moreover, the pH of the MB solution was evidently declined after adsorption, indicating that the adsorption mechanism of the capsules against MB might be dominated by ion-exchange and electrostatic attraction. This facile method which was used to generate free-standing spherical support structures with specialized morphology might be more suitable for removing cationic pollutants from alkaline wastewater.

Keywords: polymer gels, one-step titration-gel, SA-SiO₂ capsule, re-entrant structure, adsorptive performance

1. Introduction

Adsorption is a phenomenon to bind the solute, which happens in water on the surface of a liquid or solid [1]. Adsorption is advantageous over other water treatment techniques, such as the traditional membrane filtration, Fenton oxidation and coagulation, etc., because of its higher removal efficiency, faster adsorption rate and more cost-effective applicability, which has been widely used to remove heavy metals, crude-oil, dyes or other pollutants from water, wastewater, and soil [2, 3]. The ideal absorbents for adsorption should have the properties of high specific surface area, non-toxicity, and physicochemical stability [4, 5]. However, nowadays, the real performance of these absorbents is not always satisfactory in practical use. For example, activated carbon, carbon nanotubes and other nano-adsorbents have high surface area, which are more active to fully interact with the targeted compounds to remove Cu^{2+} , Pb^{2+} , dyes, etc., from water/wastewater, but it is very difficult to separate and re-cycle them from the environment after use because of their

^{*}Corresponding author, e-mail: <u>pcs005@ouc.edu.cn</u> © BME-PT

dispersibility and divisibility in aqueous solution [6– 8]. The biomass adsorbents are green but their adsorptive performance is not good enough [9, 10]. In addition, REDOX adsorbents, such as activated alumina and iron oxide, have higher removal rates but might easily precipitate again as the free-ions during adsorption process [11, 12]. These situations cause not only the waste of resources but also a secondary hazard to the environment [13, 14].

On the contrary, hydrogel is a kind of polymer material with three-dimensional network structure and super-hydrophilicity [15, 16]. It can rapidly capture the pollutants from wastewaters, hold much water, and can be permeated by oxygen and nutrients [17]. The hydrogel may have various functional groups such as carboxyl, amide, hydroxyl and sulfonic acid radical, etc., compared with other polymers, which is very easy to be directly hybridized and functionally modified with organic and inorganic materials [18, 19]. Moreover, the mechanical property of the hydrogel could be further improved after chemical and physical modification, inducing utilization under practical conditions. For instance, the hybrid PVA/ MA/TEOS membrane for desalination [20]; the biocompatible PVA-CS for drug release [21]; Bio-inspired anti-oil-fouling CS coated mesh for oil/water separation [22]. The inorganic materials, however, which have been directly added into the casting sol will interact with each other, then, agglomerate in the hydrogel matrix [23]. They cannot maximize the original adsorption ability. Besides, the adsorption capacity of the hydrogel evidently decreases as the cross-linked reaction excessively consumes the functional groups (adsorption sites) of the polymer in spite of the evolving high mechanical performance [24].GA is commonly utilized to cross-link hydrogels for different applications but has a strong biological toxicity [25]. The aldol condensation reaction occurring between GA and the hydrogel is often reversible. For this reason, they cannot remain stable in too acidic or alkaline solutions, thus increasing the risk of secondary pollution to the environment [26].

SA is a by-product after extracting iodine and mannitol from the kelp or sargassum [27]. It is a kind of natural polysaccharide/polymer with chemical stability, solubility, viscosity and biological safety for pharmaceutical preparations and porous membrane fabrication [28, 29]. For example, SA worked as a non-toxic and biocompatible thin shell, which was used to encapsulate PCM. The prepared PCM capsules are featured with spherical shapes, highly monodisperse sizes and perfect core-shell microstructures [30, 31]; The effective CCN-Alg hydrogel bead with an extreme adsorption capacity against Pb(II) $(q_m =$ 338.98 mg/g), especially, which could still maintain an adsorption capacity of 223.2 mg/g after five repeated cycles under acid treatment [32], and so on. The molecules of SA are connected by G units (α -(1-4)- L- Guluronic acid) and M units (β - (1-4)- D-Mannuronic acid), which is eco-friendly and biodegradable [33]. And the –COONa in G unit of the SA can cross-link with some multivalent cations, such as Ca^{2+} and Ba^{2+} at pH 4 to form the SINPs. It has been proved that the polymer hydrogels with SIPNs comparably have a higher removal capacity than those with IPNs in adsorption [34].

The adsorption efficiency is ascertained by the force of interaction and affinity between the solute with the interface of the adsorbents [35, 36]. Some results have suggested that increasing the hydrophilic surface roughness can simultaneously improve their hydrophilicity to promote the interaction between the interface and solute in aqueous solution [37, 38]. Hence, it is meaningful that the prepared hybrid hydrogel adsorbents with the high specific surface area, stable chemical properties, ideal removal capacity and eco-friendly, which can be applied and recycled to the overly acid or alkali situation or even more comprehensive situation. Morevover the inorganic nanoparticles can disperse well and bond tightly into the polymer matrix to minimize their potential damage to the environment for what might be triggered by the free-diffusion. Herein, it was the first time to report this kind of spherical hydrogel adsorbents with microscopic re-entrant structures just via the one-step titration-gel method and in-situ sol-gel progress by injecting SA-TEOS spheroidal gelled sol into CaCl₂ solution. The hybrid capsules could be regenerated for MB removal for at least 3 times but their removal capacity was not evidently reduced.

2. Materials and methods2.1. Materials

TEOS (Vapor density, 7.2 (vs air); 99.999% trace metals basis; liquid) was supplied by Sigma-Aldrich Co., Ltd. (The USA). SA powders and CaCl₂ were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). The ultra-pure water was produced by

a Milli-Q BIOCEL unit (With the resistivity of $18 \text{ M}\Omega$ cm) from MilliPore Co., Ltd. (The USA).

2.2. Preparation of the casting solution

The SA solution with a concentration of 3 wt % was produced via dispersing 3 g SA powders into 100 ml pure water at 30 °C under stirring until completely dissolved. The SA-SiO₂ casting sol was prepared by *in-situ* introducing 0.5 ml TEOS solution was added into the above-mentioned 30 g SA solution after 3 h of magnetic stirring. Under this synthesis condition, the SiO₂ NPs accounted for 14.92 wt% of the SA (the mass ratio between the SiO₂ NPs and the substrate of SA could be calculated from the literatures [39, 40]).

2.3. Fabrication of the capsules

The capsules were fabricated via the one-step titration-gel method which as illustrated in Figure 1. Briefly, the 25 ml of the SA or SA-SiO₂ casting solutions were poured into a 50 ml syringe after standing-deaeration, respectively. With the power of the electric syringe pump, the precursor sols were driven through the catheter with an inner diameter of 3 mm at a feed flowed rate of 13 ml/h. Subsequently, the globular droplets were consecutively collected in a bath with 5 wt% CaCl₂ solution (Figure 1a). The distance from the nozzles to the surface of the CaCl₂ solution was 8 cm. After 1.5 h of titration, the capsules were kept immersing into the 5 wt% CaCl₂ solution for 12 h to continue crosslinking the nascent spherical droplets. Finally, the prepared capsules were repeatedly purged with pure water for removing the excess of CaCl₂. And the two kinds of capsules were obtained and expressed as SAC and SASC, respectively (Figure 1b).

2.4. Characterization of the prepared capsules

The morphology of the prepared capsules was observed via the field emission-scanning electron

1 cm



Figure 1. (a) Schematic procedure of the prepared capsules; (b) The real photograph of the prepared capsules.

microscope (FE-SEM) (HITACHI S-3000N, Hitachi Ltd., Japan) at 5 kV after completely freee-drying for 24 h. The formation principle of the capsules was also studied by FT-IR technique (UATR Two, Perkin-Elmer Ltd., The USA) with a resolution of 4 cm⁻¹, scans = 64 and a wavelength in the range of 650~4000 cm⁻¹. The diameter of the SiO₂ NPs was calculated in SA-SiO₂ casting solution by the particle size analyzer (Zetasizer Nano ZS ZEN 3600, Malvern Instruments Ltd., England) and statistically counted from each FE-SEM photograph of the hybrid capsules at 50 000 magnifications. The pH changes of the MB solution after adsorption equilibrium were recorded via a pH meter (S470-K, Mettler TOLEDO Ltd., Switzerland).

2.5. Adsorption and regeneration experiments

The adsorption experiments were carried out for removing 40 ml MB solute with different concentrations (100~1000 mg/l) from aqueous solution. Also, the dose of the capsules was fixed at 0.04 g. The adsorptive performance of the prepared capsules was thoroughly investigated under various conditions, such as the solution pH (i.e. $2\sim12$), temperatures $(25 \sim 65 \circ C)$ and the contact time $(0 \sim 72 h)$, etc. The absorbance of the MB solution was determined via the multiple dilution method through a UV-vis spectrophotometer (UV-2600, UNICO Co., Ltd., The USA) at 664 nm after shaking (at a speed of 120 rpm) for a given time interval. The progress of full scans was conducted at the wavelength from 190 to 1100 nm. The removed amount $q_t [mg/g]$ and efficiency R [%] of MB were calculated by the Equations (1) and (2):

$$q_{\rm t} = \frac{\left(C_0 - C_{\rm t}\right) \cdot V}{m} \tag{1}$$

$$R = \frac{\left(C_0 - C_{\rm e}\right) \cdot \%}{C_0} \tag{2}$$

where C_0 , C_t and C_e [mg/l] are the concentration of the MB solution at the initial time, and after *t* time adsorption and up until adsorption equilibrium; *V*[l] is the volume of the solution, which equal to 0.04; and *m* [g] is the mass of the dried capsules.

For regeneration, the hydrogel capsules were immersed in HCl solution with pH values of 4 under stirring at 350 rpm for 2 h, and these capsules were rinsed by the pure water until neutral then. Afterward, the capsules were used for adsorbing MB solution at 25 °C and the pH value of 8. The concentration of the MB solution was 100, 400 and 1000 mg/l, respectively. And the adsorbed capacity of the capsules was re-tested again as above mentioned. The experiments were repeated 3 times.

3. Results and discussion

3.1. Morphology analysis of the prepared capsules

The effects of SiO₂ NPs on the morphology of the prepared capsules were illustrated at different magnifications. As shown in Figure 2, the FE-SEM analysis exhibited that the surface of the prepared capsules had a micro-porous structure. Besides, the pores of the capsules exhibited a 'fracture aperture' like appearance and extended toward the kernel (Figure 2, γ , δ). The interface of the SAC was undulated and uneven, which had a 'ridged' texture (Figure 2, SAC-A). Furthermore, the fibers of the SAC were very smooth (Figure 2, SAC-C).

However, though the mean pore sizes of the prepared capsule decreased after TEOS was introduced into the polymer matrix (Figure 2, δ), it was observed that the appearance of the interface showed a more obviously 'ridged' architecture. The surface roughness of the hybrid capsule increased (Figure 2, α , β), which displayed a submicron scale (SiO₂ aggregation node) to nano scale (SiO2 NPs, 80~100 nm) hierarchical stratum morphology and re-entrant pattern compared with the neat capsule (Figure 2, SASC-C). The trigger for this was due to TEOS reacting with water in the SA solution. The SiO₂ NPs self-assembled and dispersed well in the polymer matrix. Also, the hydrophobic SiO₂ NPs coatings on the surface of the SA were highly homogeneous and had a good combination with the matrix via H-bonding [41].

3.2. Formation mechanism of the prepared capsules

The FT-IR spectra and formation principle of the prepared capsules were shown in Figure 3. The visible hydrogen bonding stretching vibration peak located in $3150 \sim 3300 \text{ cm}^{-1}$ intervals were caused by -OH and $-\text{COO}^-$ in the chain of SA interacting with each other (Figure 3a) [42, 43]. The $-\text{CH}_3$ and $-\text{CH}_2$ vibration peaks were observed around 2920 \sim 3050 cm⁻¹. The spectrum of SA at 1640, 1715 and 942 cm⁻¹. wavenumbers were C=O and O–Na in -COONa group, respectively [43, 44].



Figure 2. The FE-SEM results of the prepared capsules at different magnifications (a: SAC, b: SAS-C). (α , β) the surface roughness of the prepared capsules; (γ , δ) the fractured aperture of the prepared capsules.



Figure 3. (a) The FT-IR results of the prepared capsules at different stages; (b) The diameter distribution of the SiO₂ NPs in SA matrix; (c) The formation mechanism of the prepared capsules.

Furthermore, the stretching vibration peaks emerged near 1382 and 950 cm⁻¹ were –OH radical in-plane and out-of-plane vibrations exhibit a characteristic spectrum. The stretching vibration band of C-O in -COO⁻of the SA was ranging from 1080 to 1205 cm⁻¹ [44]. The above diagram served to illustrate the formation principle of the prepared capsules. In the first phase, the hydrophilic SiO₂ NPs were generated and well dispersed in the polymer matrix to form a homogenous system after TEOS was introduced to the SA solution (Figure 3c). The diameter of the particles was concentrated around 80~ 100 nm (Figure 3b). It should be noticed that the new absorption bands which significantly appeared around 1450, 1082, 772 and 772 cm⁻¹ [45–47] respectively corresponded to the O-H stretching vibration peak (Si-OH), Si-O-Si anti-symmetric stretching vibration peak and Si-O symmetric stretching vibration peak, indicating that SiO₂ NPs were successfully incorporated into the SA and had good compatibilities with the substrate.

In the preparation courses of the hybrid capsule, the liquid droplet with SA-TEOS mixture instantly gelled and transformed into a porous flexible solid-sphere once it has been injected into the cross-linked CaCl₂ solution (Figure 3c). As the reaction continued, a robust capsule with Semi-IPNs structure was produced due to the Ca²⁺ uninterruptedly coupled with $-COO^-$ in *G* unit of SA via chelating and covalent bonding. And at this moment, the O–Na (937 cm⁻¹ [42–44]) disappeared (Figure 3a). The hydrophilic functional groups (hydroxyl groups and carboxyl groups, etc.) of SA acted as the 'active sites' role in adsorbents,

which endowed them with brilliant capacity for removing MB from water.

3.3. Influence of solution pH on the removal performance of the capsules

In order to qualitatively explore the effect of pH on the properties of MB, the full-scan analysis was performed at different pH conditions before conducting the adsorption experiments. Initially, the absorbance of MB at the wavelength of 664 nm was indistinguishably measurable, but then drastically declined with the values of the pH increasing from 9 to 12 as shown in Figure 4a. At the meanwhile, the removal efficiency of the capsules against MB slowly increased from pH 2 to pH 9 while sharply decreased after the values of pH exceeding 9 (Figure 4b). The MB removed efficiency relatively increased by 12.82% after SiO₂ NPs were incorporated into the capsule. The optimal removal efficiency of MB by the SASC was 98.18 % (Figure 4b) at solution pH 9 (under the weak alkaline conditions) and the concentration of the MB was 400 mg/l.

The reason behind this phenomenon was understandable because the concentration of the H⁺ and MB was high under acidic condition (pH < 8). The removed sites of the capsule would be concurrently occupied and consumed by MB and H⁺ thereby inhibiting the combination between the MB and the SA, diminishing the adsorbed capacity. On the contrary, MB would degrade and transform into a complex precipitate in an over-alkaline situation (pH > 10) even it was beneficial for the adsorbents to remove MB (Figure 4a). The results might imply that



Figure 4. (a) The changes of the absorbance of MB at different pH; (b) The effect of solution pH on the capsules' removal efficiency.

the capsules had a brilliant pH resistance and were good at treating the alkaline and cationic contaminants. Thus, in order to avoid the influence of the precipitation on the results of the adsorption, the value of the solution pH was kept at 8 during the following experiments.

3.4. Adsorption isotherms studies of the prepared capsules

The plots of the adsorbed isotherms at different temperature could be defined as type-I (simple L-shaped) according to the IUPAC, as described in Figure 5, which usually happened upon the interface of the micro-pores. Therefore, the Freundlich and Langmuir isothermal models were accounted to use for fitting the adsorption of the capsules against MB at different concentration and temperature. The equation of the Freundlich and Langmuir isotherm models were formulated as Equations (3) and (4):

$$q_{\rm e} = K_{\rm F} C_{\rm e}^{1/n} \tag{3}$$

$$q_{\rm e} = \frac{q_{\rm m} K_{\rm L} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}} \tag{4}$$

where $C_e \text{[mg/l]}$ and $q_e \text{[mg/g]}$ are the concentration and removal amount of MB in adsorption equilibrium; $K_F \text{[(mg/g)/(mg/l)^{1/n}]}$ and $K_L \text{[l/mg]}$ are the parameters of the Freundlich and Langmuir and isotherm models; $1/_n$ is a constant related to the sorption strength.

The Langmuir model assumed that the adsorption, was mono-layer coverage only, occurred upon a homogenous surface. The possibility and affinity for adsorbate combination with the active sites of the interface of the adsorbents were equal. Moreover, the adsorbate molecules could not interact with each other once it had been adsorbed. But the Freundlich isothermal model was different.

As shown in Figure 5, the removal capacity of MB by the prepared capsules was improved with the increasing of the concentration of MB. Nevertheless, the adsorbed amount of MB would keep steady if the concentration was greater than or equal to 1000 mg/l. This result revealed that the active sites of the adsorbents for working were basically occupied and the adsorption had become dynamic balance. Thereto, as the temperature increased from 25 to 65 °C, the



Figure 5. The fitting results of the Langmuir model at various temperatures (a) SAC, (b) SASC; the fitting results of the Freundlich model at various temperatures (c) SAC, (d) SASC.

Tumos	Models	Coefficients	Temperatures			
Types			25°C	45°C	65°C	
	Langmuir	KL	0.033	0.066	0.342	
		$q_{\rm max}$	326.290	204.518	110.646	
SAC		R^2	0.999	0.999	0.999	
	Freundlich	K _F	71.851	76.000	82.133	
		1/ <i>n</i>	0.236	0.154	0.047	
		R^2	0.874	0.841	0.803	
SASC	Langmuir	$K'_{\rm L}$	0.490	0.093	0.347	
		$q'_{\rm max}$	363.885	231.664	130.057	
		R^2	0.999	0.999	0.999	
	Freundlich	$K'_{ m F}$	92.816	90.837	88.069	
		1/n'	0.219	0.149	0.062	
		R^2	0.854	0.830	0.786	

 Table 1. The parameters and coefficients of the Langmuir and Freundlich isotherm.

saturated removal amount of the MB visibly shrunk. It meant that the adsorbed processes of MB by the hydrogel contained an exothermic course. Increasing the adsorption temperature would inhibit the interaction between MB with the capsules.

The relevant coefficients R^2 of the Langmuir models were above 0.999, which were higher than that of the Freundlich (Table 1). It proved that the Langmuir isotherm equation was more appropriate for describing the adsorbed progress of MB by the capsules. The theoretical maximum adsorbed amount of the prepared capsules after calculated were very highly consistent with the adsorbed amount of the experiments (SAC: 310.934 mg/g at 25 °C, 200.456 mg/g at 45 °C and 110.478 mg/g at 65 °C, respectively; SASC: 350.797 mg/g at 25 °C, 228.929 mg/g at 45 °C and 129.840 mg/g at 65 °C, respectively). More importantly, the removed capacity of the capsules was increased by 12.82% after SiO₂ NPs incorporating into the polymer.

3.5. The changes of the pH after adsorption equilibrium at different temperature

The pH of the MB solution evidently descended after reaching adsorption equilibrium at different temperature, and this trend became more severe at high concentration (Figure 6). Whereas, at various concentrations, the solution pH gradually increased as the temperature raised from 25 to 65 °C (Figure 6a and 6b, 100, 400, 1000 ppm). This occurred as a result of the concentration of the H⁺ in the MB solution after adsorption equilibrium was higher than that of the initial, and implied an ion-exchange (H⁺) behavior in the adsorbed process. The reason why the increased



Figure 6. The variance of solution pH after adsorption at different temperature (a) SAC, (b) SASC; (c) ketch of the adsorption process of MB by the prepared capsules.

temperature prevented the adsorbed progress of the capsules against MB would be attributed to the following two processes.

Firstly, the adsorbents could aggressively release H⁺ and Na⁺ ions [33, 48] to the environment and became electronegative before binding MB from the water (Figure 6c, Step I). At this stage, it could be regarded as the dissociation of the SA, and the capsules simultaneously took the heat from the environment. Immediately, the negative hydrogel adsorbents conjugated and chelated with the positive MB in the solution, which was an exothermic combination (Figure 6c, Step II). The emitted calorific energies that the macromolecule (MB) was adsorbed by the capsules were much higher than the energies consumed during the small molecule (Na⁺, H⁺) releasing from the SA. Therefore, the adsorbed process of MB by the capsule was dominated by the thermopositive progress. Raising the temperature of the solution not only affected the interaction between the MB and the adsorbents to reduce the removed rate of MB, but also suppressed the production of the capsules with negative charge thus increased the solution pH after working. The changes of the pH performed comparatively much palliative after SASC were added into the MB solution, indicated that SiO2 NPs could maintain the stable electronegativity of the capsules.

3.6. Adsorption kinetics studies

The ambient temperature for working was fixed at $25 \,^{\circ}$ C to investigate the adsorbed kinetics of the capsules against MB. The first, second, and Weber-Morris (intra-particle diffusion) kinetic models, as the Equations (5), (6) and (7), were used to describe the adsorption behaviors of MB by the capsules:

$$\ln(q_{\rm e} - q_{\rm t}) = -k_1 t + \ln q_{\rm e} \tag{5}$$

$$\frac{t}{q_{\rm t}} = \frac{1}{k_2 q_{\rm e}^2} + \frac{t}{q_{\rm e}} \tag{6}$$

$$q_{\rm t} = k_{\rm WM} t^{1/2} + C \tag{7}$$

where q_t and q_e [mg/g] are the adsorbed amount of MB at the setting interval time and the equilibrium; k_1 [h⁻¹], k_2 [g/(mg·h)] and k_{WM} [g/(mg·h^{1/2})] are the coefficients of the first, second reaction kinetics and Weber-Morris models, respectively; *C* is a constant related to the adsorbed thickness and boundary layer.

As shown in Figure 7a and 7b, the adsorbed amount of MB steeply ascended within 4 h, and gently reached the adsorption equilibrium up until 16 h, after which time the adsorbed amount of MB kept stable. Furthermore, the rising of the solution concentration not only promoted the adsorbed amount of MB by the capsules but also boosted the speed rate for removing MB from the aqueous solution. These data support the conclusion that the prepared capsules were adept and fast for MB removal. The high concentration provided a strong osmotic pressure against the kernel of the capsule, thereby improving its adsorption capacity.

It should be noticed that the kinetic parameters, k_1 and k_2 (Table 2) of the SASC were larger than SAC at various concentrations, demonstrating the removed capacity and the speed rate of the capsules were simultaneously improved after SiO₂ NPs were added into the polymer. This phenomenon could be explained by the hydrophilic SiO₂ NPs aggregates homogeneously scattered in the polymer matrix to create a multi-scale re-entrant structure on its surface channel thus enriched the adsorbed sites of the SA. Fundamentally, the specialized morphology of the interface helped to promote the interaction opportunity and the affinity between the pollutants and adsorbents, thus, improved the capsules' adsorption ability.

The fitting results of the Weber-Morris model were not merely a line passing through the origin (Figure 7g and 7h), revealing the intra-particle diffusion was one of the adsorbed progresses during the adsorption but was not the sole dominant. The adsorbed process of MB by the capsules might include surface migration and adsorption, intra-particle diffusion and electrostatic attraction.

Initially, the concentration of the MB was high and there were plenty of adsorbed sites on the capsules for working. The positively charged contaminant fleetly diffused, migrated, and then consociated on the surface of the capsules. Immediately, the adsorbed sites in the skin of the capsules were substantially consumed. The cationic MB started spreading toward the capsule interior and being coupled upon their internal channel surface with the force of electrostatic attraction by the negative radicals $(-O^-, -COO^-)$ of the SA within 4 h. Thereby, the intra-particle diffusion was the primary controlling factor during this progress. Eventually, the adsorbed sites of the capsules were



Figure 7. The MB removed amount varies with time (a) SAC, (b) SASC; the fitting results of the pseudo-first-order kinetic (c) SAC, (d) SASC; pseudo-second-order kinetic (e) SAC, (f) SASC; intra-particle diffusion kinetic (g) SAC, (h) SASC.

completely depleted and reached the adsorption balance up until 16 h (Figure 7a and 7b).

The experimental values of the adsorbtion kinetics after calculating exhibited that the pseudo-second-

order was more suitable for expounding the adsorbtion progress (Figure 7e and 7f). The maximum MB removed amount after formulating were very close to the experimental values (SAC: 91.002 mg/g at

Iddle A Inc inthis results of the dasorption kinctics
--

Types	Models	Parameters				
Types			100	200	400	1000
	Pseudo-first-order kinetics	k_1	0.083	0.084	0.095	0.096
		$q_{\rm e}$	42.533	66.776	58.958	31.138
		R^2	0.968	0.918	0.883	0.913
	Pseudo-second-order kinetics	k_2	9.440.10-3	$6.178 \cdot 10^{-3}$	8.785·10 ⁻³	$2.905 \cdot 10^{-2}$
SAC		q_{e}	92.421	173.611	271.002	313.480
		R^2	0.999	0.999	0.999	0.999
	Intra-particle-diffusion	$k_{\rm WM}$	41.203	90.200	177.922	293.920
		С	-2.631	-5.341	-6.525	17.370
		R^2	0.954	0.960	0.982	0.927
SASC	Pseudo-first-order kinetics	k'_1	0.099	0.116	0.100	0.104
		$q_{ m e}$	39.886	75.174	69.270	25.827
		R^2	0.935	0.934	0.824	0.872
	Pseudo-second-order kinetics	k'_2	9.981·10 ⁻³	7.356.10-3	9.050.10-3	4.618.10-2
		$q'_{ m e}$	96.993	186.220	308.642	352.113
		R^2	0.999	0.999	0.999	0.999
	Intra-particle-diffusion	$k'_{\rm WM}$	42.438	100.237	229.855	336.414
		<i>c'</i>	-2.373	-3.817	-11.785	10.269
		R^2	0.965	0.976	0.970	0.976

100 mg/l, 171.526 mg/g at 200 mg/l, 269.248 mg/g at 400 mg/l and 313.212 mg/g at 1000 mg/l; SASC: 95.558 mg/g at 100 mg/l, 184.055 mg/g at 200 mg/l, 307.973 mg/g at 400 mg/l and 351.936 mg/g at 1000 mg/l, respectively). Moreover, the correlation coefficients R^2 of the pseudo-second-order were greater than 0.999.

3.7. Regeneration and adsorption mechanism of the capsules

The maximum adsorption rate of the capsules was equal to the ratio of the previous removal amount after regeneration. The recovery procedure of the capsules after adsorption has been shown in Figure 8a. The removed capacity of the capsules was no evidently different with that of the initial in 100 ppm after eluting, while diminishing as concentration increases. That was because the maximum adsorption rate of the capsules was determined by how many active sites could be recovered in the course of regeneration. MB just consumed parts of adsorbed sites of the capsules at low concentration. As for the remaining, they were still active for adsorption. However, the adsorbed sites of the hydrogels have been essentially/completely occupied at 400 or 1000 ppm. Therefore, at this moment, the secondary removed capacity of the capsules was determined by the level of elution and desorption. It should be noticed that the adsorbed capacity of the SAC marginally glided after regenerating for 3 times but still maintained above 70% of the original capacity (Figure 8b, the maximum adsorption amount of the SAC was 228.403 mg/g after 3 times regeneration). The results suggested that the prepared capsules could be continuously used and applied for MB adsorption at low concentration after regeneration even they had been worked at high concentration conditions. Furthermore, the lowest adsorption rate of the SASC was still above 75% of the original capacity after eluting (Figure 8c), demonstrating the removed capacity of the capsules has been improved after SiO₂ NPs were added into the polymer.

In summary, the adsorbed mechanism of the capsules against MB could be considered as the following stages. To begin with, the polymer of the capsules spontaneously dissociated H^+ and Na^+ to become electronegative (the polymer with $-O^-$ and $-COO^$ radical) and active for adsorption in MB solution. Quickly, the molecules of MB migrated, diffused and inoculated the active sites of the capsule from its skin to interior within 4 h. The surface of the capsules with unique re-entrant morphology helped to promote the degree of affinity between the interfaces with the pollutants thereby improving the speed rate



Figure 8. (a) The regenerated progress of the prepared capsules; the maximum adsorption rate with regenerated cycles of the (b) SAC, (c) SASC; (d) adsorption mechanism of MB by the capsules.

in adsorption (Figure 8d). Finally, the MB was trapped and coupled into the interface of the inner channel by electrostatic attraction, which reached a dynamic adsorption balance in 16 h.

As for regeneration, the situation was similar to the progress in above-mentioned. Briefly, after adsorption, the capsules initially released the molecules of MB to the ambient for recycling the cations (H^+) from the HCl solution. Eventually, the removal capacity of the capsules was slowly recovered up until MB was absolutely displaced by the H^+ .

3.8. Comparison of different hydrogels for the removal of MB

As shown in Table 3. The removed capacity and the speed rate of the prepared capsules against MB in this article were comparatively higher than that reported hydrogels.

Moreover, the method, which used to generate the capsules with free-standing spherical support structures and specialized morphology was very simple to be operated and manipulated. Therefore, the prepared capsule, especially, SASC, was a low-cost,

Types of the hydrogel adsorbents	Preparation method	q _m at 25 ℃ [g/mg]	Time for equilibrium [h]	Literatures
SAC	One-step titration-gel	310.934	4~10	This work
SASC	One-step titration-gel	350.797	4~8	This work
PSC-MMTNS	Hydrogen-bond and electrostatic interactions	<137.150	6~10	[49]
MMTNS-CS	Centrifugation and heated cross-linking (90 °C)	351.800	>10	[50]
HKUST-1@PVA-co-PE/PVA	High temperature (120 °C) poly-condensation for 12 h	481.500	10	[51]
AC-SA	A method contained mixing and dropping	230.00	6~8	[52]
ZNFSA	Mixing and co-precipitation technique	54.054	<1/12	[53]
RGO–SA	Freezing, solvent exchange and drying	<192.300	>10	[54]

Table 3. Comparison of the obtained results with earlier reported studies.

recyclable, eco-friendly and promising material for the removal of cationic pollutants from wastewater.

4. Conclusions

Altogether, the formation mechanism of the hybrid SASC with Semi-IPNs and wide pH tolerance nature was covalently bonded the sol of SA-TEOS with Ca²⁺ via one-step titration-gel. The interface of the hybrid capsule showed a micro-porous fracture aperture and microscopic re-entrant morphology based on the SiO₂ NPs self-assembling and well dispersing in the polymer of SA. The adsorption mechanism of the capsules against MB was dominated by ion-exchange and electrostatic attraction. Furthermore, the removal capacity and the speed rate of the MB by the capsules were synchronously boosted after SiO₂ NPs embedding in the polymer matrix. This hybrid capsule with specialized morphology could not only be used as an adsorbent for quickly removing the cationic contaminant (MB) from the aqueous solution, but also could be applied to biomedical and green science because of their eco-friendly property. The prepared capsules could be repeatedly regenerated for MB adsorption at least 3 times. Especially, they might have a good application prospect in alkaline and cationic removal.

Acknowledgements

The authors acknowledge the support of the State Key Laboratory of Environmental Criteria and Risk Assessment (SKLECRA2013FP12) and the Shandong Province Key Research and Development Program (2016GSF115040).

Nomenclature				
1.	SA	Sodium alginate		
2.	SiO ₂	Silicon oxide		
3.	TEOS	Tetraethyl orthosilicate		
4.	CaCl ₂	Calcium chloride		
5.	SiO ₂ NPs	SiO ₂ nanoparticles		
6.	MB	Methylene blue and applied chemistry		
7.	REDOX	Reduction-oxidation		
8.	PVA	Polyvinyl alcohol		
9.	MA	Maleic acid		
10.	CS	Chitosan		
11.	GA	Glutaraldehyde		
12.	PCM	Phase change material		
13.	CCN-Alg	Carboxylated cellulose nanocrystal-sodium alginate		
14.	SINPs	Semi-interpenetrating polymer networks		
15.	IPNs	Interpenetrating polymer networks		
16.	SAC	SA capsule		
17.	SASC	SA-SiO ₂ capsule		
18.	IUPAC	International Union of Pure		
19.	PSC-MMTNS	PVA-SA-CS-montmorillonite nano-sheets		
20.	PE	Polyethylene		
21.	AC-SA	Activated carbon-SA		
22.	ZNFSA	Zeolite/nickel ferrite/SA		
23.	RGO-SA	Reduced graphene oxide-SA		

References

 Hokkanen S., Bhatnagar A., Sillanpää M.: A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. Water Research, 91, 156– 173 (2016).

https://doi.org/10.1016/j.watres.2016.01.008

 [2] Ersan G., Apul O. G., Perreault F., Karanfil T.: Adsorption of organic contaminants by graphene nanosheets: A review. Water Research, 126, 385–398 (2017). https://doi.org/10.1016/j.watres.2017.08.010

- [3] Kim Y., Bae J., Park H., Suh J-K., You Y-W., Choi H.: Adsorption dynamics of methyl violet onto granulated mesoporous carbon: Facile synthesis and adsorption kinetics. Water Research, 101, 187–194 (2016). https://doi.org/10.1016/j.watres.2016.04.077
- [4] Yang K., Wang X., Zhu L., Xing B.: Competitive sorption of pyrene, phenanthrene, and naphthalene on multiwalled carbon nanotubes. Environmental Science and Technology, 40, 5804–5810 (2006). https://doi.org/10.1021/es061081n
- [5] Guo Y., Zhang H., Liu Y.: Desorption characteristics and kinetic parameters determination of molecular sieve by thermogravimetric analysis/differential thermogravimetric analysis technique. Adsorption Science and Technology, 36, 1389–1404 (2018). https://doi.org/10.1177/0263617418772665
- [6] Suhas, Gupta V. K., Carrott P. J. M., Singh R., Chaudhary M., Kushwaha S.: Cellulose: A review as natural, modified and activated carbon adsorbent. Bioresource Technology, **216**, 1066–1076 (2016). https://doi.org/10.1016/j.biortech.2016.05.106
- [7] Cazetta A. L., Pezoti O., Bedin K. C., Silva T. L., Paesano Junior A., Asefa T., Almeida V. C.: Magnetic activated carbon derived from biomass waste by concurrent synthesis: Efficient adsorbent for toxic dyes. ACS Sustainable Chemistry and Engineering, 4, 1058–1068 (2016).

https://doi.org/10.1021/acssuschemeng.5b01141

- [8] Bénard P., Chahine R.: Modeling of high-pressure adsorption isotherms above the critical temperature on microporous adsorbents: Application to methane. Langmuir, 13, 808–813 (1997). https://doi.org/10.1021/la960843x
- [9] Kian L. K., Jawaid M., Ariffin H., Alothman O. Y.: Isolation and characterization of microcrystalline cellulose from roselle fibers. International Journal of Biological Macromolecules, **103**, 931–940 (2017). https://doi.org/10.1016/j.ijbiomac.2017.05.135
- [10] Xu J., Lian F., Zhao L., Zhao Y., Chen X., Zhang X., Guo Y., Zhang C., Zhou Q., Xue Z., Pang X., Zhao L., Tong X.: Structural modulation of gut microbiota during alleviation of type 2 diabetes with a Chinese herbal formula. The ISME journal, 9, 552–562 (2015). https://doi.org/10.1038/ismej.2014.177
- [11] Ren T., Yang S., Jiang Y., Sun X., Zhang Y.: Enhancing surface corrosion of zero-valent aluminum (ZVAl) and electron transfer process for the degradation of trichloroethylene with the presence of persulfate. Chemical Engineering Journal, 348, 350–360 (2018). https://doi.org/10.1016/j.cej.2018.04.216
- [12] Tang J., Mu B., Zong L., Zheng M., Wang A.: Facile and green fabrication of magnetically recyclable carboxylfunctionalized attapulgite/carbon nanocomposites derived from spent bleaching earth for wastewater treatment. Chemical Engineering Journal, **322**, 102–114 (2017).

https://doi.org/10.1016/j.cej.2017.03.116

- [13] Yao W., Wang J., Wang P., Wang X., Yu S., Zou Y., Hou J., Hayat T., Alsaedi A., Wang X.: Synergistic coagulation of GO and secondary adsorption of heavy metal ions on Ca/Al layered double hydroxides. Environmental Pollution, 229, 827–836 (2017). https://doi.org/10.1016/j.envpol.2017.06.084
- [14] Contreras-Torres F. F., Rodríguez-Galván A., Guerrero-Beltrán C. E., Martínez-Lorán E., Vázquez-Garza E., Ornelas-Soto N., García-Rivas G.: Differential cytotoxicity and internalization of graphene family nanomaterials in myocardial cells. Materials Science and Engineering: C, 73, 633–642 (2017). https://doi.org/10.1016/j.msec.2016.12.080
- [15] Zhang Y., Zhang M., Jiang H., Shi J., Li F., Xia Y., Zhang G., Li H.: Bio-inspired layered chitosan/graphene oxide nanocomposite hydrogels with high strength and pHdriven shape memory effect. Carbohydrate Polymers, 177, 116–125 (2017). https://doi.org/10.1016/j.carbpol.2017.08.106
- [16] Yang K., Han Q., Chen B., Zheng Y., Zhang K., Li Q., Wang J.: Antimicrobial hydrogels: Promising materials for medical application. International Journal of Nanomedicine, 13, 2217–2263 (2018).

https://doi.org/10.2147/IJN.S154748

- [17] Kamoun E. A., Kenawy E. S., Chen X.: A review on polymeric hydrogel membranes for wound dressing applications: PVA-based hydrogel dressings. Journal of Advanced Research, 8, 217–233 (2017). https://doi.org/10.1016/j.jare.2017.01.005
- [18] Haq M. A., Su Y., Wang D.: Mechanical properties of PNIPAM based hydrogels: A review. Materials Science and Engineering: C, 70, 842–855 (2017). https://doi.org/10.1016/j.msec.2016.09.081
- [19] Ali M., Oshiki M., Rathnayake L., Ishii S., Satoh H., Okabe S.: Rapid and successful start-up of anammox process by immobilizing the minimal quantity of biomass in PVA-SA gel beads. Water Research, 79, 147– 157 (2015).

https://doi.org/10.1016/j.watres.2015.04.024

[20] Xie Z., Hoang M., Ng D., Doherty C., Hill A., Gray S.: Effect of heat treatment on pervaporation separation of aqueous salt solution using hybrid PVA/MA/TEOS membrane. Separation and Purification Technology, 127, 10–17 (2014).

```
https://doi.org/10.1016/j.seppur.2014.02.025
[21] Abureesh M. A., Oladipo A. A., Gazi M.: Facile syn-
thesis of glucose-sepsitive chitosan-poly(vinyl alcohol)
```

thesis of glucose-sensitive chitosan–poly(vinyl alcohol) hydrogel: Drug release optimization and swelling properties. International Journal of Biological Macromolecules, **90**, 75–80 (2016).

https://doi.org/10.1016/j.ijbiomac.2015.10.001

[22] Zhang S., Lu F., Tao L., Liu N., Gao C., Feng L., Wei Y.: Bio-inspired anti-oil-fouling chitosan-coated mesh for oil/water separation suitable for broad pH range and hyper-saline environments. ACS Applied Materials and Interfaces, 5, 11971–11976 (2013). https://doi.org/10.1021/am403203q

- [23] Hou D., Dai G., Fan H., Wang J., Zhao C., Huang H.: Effects of calcium carbonate nano-particles on the properties of PVDF/nonwoven fabric flat-sheet composite membranes for direct contact membrane distillation. Desalination, 347, 25–33 (2014). https://doi.org/10.1016/j.desal.2014.05.028
- [24] Yue Y., Han J., Han G., French A. D., Qi Y., Wu Q.: Cellulose nanofibers reinforced sodium alginate-polyvinyl alcohol hydrogels: Core-shell structure formation and property characterization. Carbohydrate Polymers, 147, 155–164 (2016).

https://doi.org/10.1016/j.carbpol.2016.04.005

[25] Lu T., Xiang T., Huang X-L., Li C., Zhao W-F., Zhang Q., Zhao C-S.: Post-crosslinking towards stimuli-responsive sodium alginate beads for the removal of dye and heavy metals. Carbohydrate Polymers, 133, 587– 595 (2015).

https://doi.org/10.1016/j.carbpol.2015.07.048

- [26] Beauchamp R. O., St. Clair M. B. G., Fennell T. R., Clarke D. O., Morgan K. T., Karl F. W.: A critical review of the toxicology of glutaraldehyde. Critical Reviews in Toxicology, 22, 143–174 (1992). https://doi.org/10.3109/10408449209145322
- [27] Webber R. E., Shull K. R.: Strain dependence of the viscoelastic properties of alginate hydrogels. Macromolecules, 37, 6153–6160 (2004). https://doi.org/10.1021/ma049274n
- [28] Kim J., Wang N., Chen Y., Lee S-K., Yun G-Y.: Electroactive-paper actuator made with cellulose/NaOH/ urea and sodium alginate. Cellulose, 14, 217–223 (2007). https://doi.org/10.1007/s10570-007-9111-6
- [29] Thakur S., Pandey S., Arotiba O. A.: Development of a sodium alginate-based organic/inorganic superabsorbent composite hydrogel for adsorption of methylene blue. Carbohydrate Polymers, 153, 34–46 (2016). https://doi.org/10.1016/j.carbpol.2016.06.104
- [30] Liang W-G., Yang C., Wen G-Q., Wang W., Ju X-J., Xie R., Chu L-Y.: A facile and controllable method to encapsulate phase change materials with non-toxic and biocompatible chemicals. Applied Thermal Engineering, **70**, 817–826 (2014).

https://doi.org/10.1016/j.applthermaleng.2014.06.006

[31] Bremond N., Santanach-Carreras E., Chu L. Y., Bibette J.: Formation of liquid-core capsules having a thin hydrogel membrane: Liquid pearls. Soft Matter, 6, 2484– 2488 (2010).

https://doi.org/10.1039/b923783f

- [32] Hu Z-H., Omer A. M., Ouyang X-K., Yu D.: Fabrication of carboxylated cellulose nanocrystal/sodium alginate hydrogel beads for adsorption of Pb(II) from aqueous solution. International Journal of Biological Macromolecules, **108**, 149–157 (2018). https://doi.org/10.1016/j.ijbiomac.2017.11.171
- [33] Etchepare M. D. A., Barin J. S., Cichoski A. J., Jacob-Lopes E., Wagner R., Fries L. L. M., Menezes C. R. D.: Microencapsulation of probiotics using sodium alginate. Ciência Rural, 45, 1319–1326 (2015). <u>https://doi.org/10.1590/0103-8478cr20140938</u>

- [34] Li Q., Li Y., Ma X., Du Q., Sui K., Wang D., Wang C., Li H., Xia Y.: Filtration and adsorption properties of porous calcium alginate membrane for methylene blue removal from water. Chemical Engineering Journal, 316, 623–630 (2017). https://doi.org/10.1016/j.cej.2017.01.098
- [35] Young T.: III. An essay on the cohesion of fluids. Philosophical Transactions, 95, 65–87 (1805). https://doi.org/10.1098/rstl.1805.0005
- [36] Liang J-Z.: Characteristics of melt shear viscosity during extrusion of polymers. Polymer Testing, 21, 307– 311 (2002).

https://doi.org/10.1016/S0142-9418(01)00088-5

- [37] Quéré D., Lafuma A., Bico J.: Slippy and sticky microtextured solids. Nanotechnology, 14, 1109–1112 (2003). https://doi.org/10.1088/0957-4484/14/10/307
- [38] Wenzel R. N.: Resistance of solid surfaces to wetting by water. Industrial and Engineering Chemistry, 28, 988–994 (1936).

https://doi.org/10.1021/ie50320a024

[39] Stöber W., Fink A., Bohn E.: Controlled growth of monodisperse silica spheres in the micron size range. Journal of Colloid and Interface Science, 26, 62–69 (1968).

https://doi.org/10.1016/0021-9797(68)90272-5

- [40] Zhou H., Wang H., Niu H., Gestos A., Lin T.: Robust, self-healing superamphiphobic fabrics prepared by twostep coating of fluoro-containing polymer, fluoroalkyl silane, and modified silica nanoparticles. Advanced Functional Materials, 23, 1664–1670 (2013). https://doi.org/10.1002/adfm.201202030
- [41] Goetz L. A., Jalvo B., Rosal R., Mathew A. P.: Superhydrophilic anti-fouling electrospun cellulose acetate membranes coated with chitin nanocrystals for water filtration. Journal of Membrane Science, 510, 238–248 (2016).

https://doi.org/10.1016/j.memsci.2016.02.069

[42] Mansur H. S., Oréfice R. L., Mansur A. A. P.: Characterization of poly(vinyl alcohol)/poly(ethylene glycol) hydrogels and PVA-derived hybrids by small-angle Xray scattering and FTIR spectroscopy. Polymer, 45, 7193–7202 (2004).

https://doi.org/10.1016/j.polymer.2004.08.036

[43] Shao Z-J., Huang X-L., Yang F., Zhao W-F., Zhou X-Z., Zhao C-S.: Engineering sodium alginate-based crosslinked beads with high removal ability of toxic metal ions and cationic dyes. Carbohydrate Polymers, 187, 85–93 (2018).

https://doi.org/10.1016/j.carbpol.2018.01.092

[44] Bekin S., Sarmad S., Gürkan K., Keçeli G., Gürdağ G.: Synthesis, characterization and bending behavior of electroresponsive sodium alginate/poly(acrylic acid) interpenetrating network films under an electric field stimulus. Sensors and Actuators B: Chemical, 202, 878–892 (2014).

https://doi.org/10.1016/j.snb.2014.06.051

[45] Li X., Yu X., Cheng C., Deng L., Wang M., Wang X.: Electrospun superhydrophobic organic/inorganic composite nanofibrous membranes for membrane distillation. ACS Applied Materials and Interfaces, 7, 21919– 21930 (2015).

https://doi.org/10.1021/acsami.5b06509

- [46] Rao A. V., Kalesh R. R., Pajonk G. M.: Hydrophobicity and physical properties of TEOS based silica aerogels using phenyltriethoxysilane as a synthesis component. Journal of Materials Science, 38, 4407–4413 (2003). https://doi.org/10.1023/A:1026311905523
- [47] Leng B., Shao Z., de With G., Ming W.: Superoleophobic cotton textiles. Langmuir, 25, 2456–2460 (2009). <u>https://doi.org/10.1021/la8031144</u>
- [48] Samanta H. S., Ray S. K.: Synthesis, characterization, swelling and drug release behavior of semi-interpenetrating network hydrogels of sodium alginate and polyacrylamide. Carbohydrate Polymers, 99, 666–678 (2014). https://doi.org/10.1016/j.carbpol.2013.09.004
- [49] Wang W., Zhao Y., Bai H., Zhang T., Ibarra-Galvan V., Song S.: Methylene blue removal from water using the hydrogel beads of poly(vinyl alcohol)-sodium alginatechitosan-montmorillonite. Carbohydrate Polymers, 198, 518–528 (2018).

https://doi.org/10.1016/j.carbpol.2018.06.124

[50] Kang S., Zhao Y., Wang W., Zhang T., Chen T., Yi H., Rao F., Song S.: Removal of methylene blue from water with montmorillonite nanosheets/chitosan hydrogels as adsorbent. Applied Surface Science, 448, 203–211 (2018).

https://doi.org/10.1016/j.apsusc.2018.04.037

- [51] Zhu Q., Li Y., Wang W., Sun G., Yan K., Wang D.: High performance HKUST-1@PVA-co-PE/PVA hybrid hydrogel with enhanced selective adsorption. Composites Communications, **10**, 36–40 (2018). https://doi.org/10.1016/j.coco.2018.05.005
- [52] Nasrullah A., Bhat A. H., Naeem A., Isa M. H., Danish M.: High surface area mesoporous activated carbon-alginate beads for efficient removal of methylene blue. International Journal of Biological Macromolecules, 107, 1792–1799 (2018).

https://doi.org/10.1016/j.ijbiomac.2017.10.045

- [53] Bayat M., Javanbakht V., Esmaili J.: Synthesis of zeolite/nickel ferrite/sodium alginate bionanocomposite via a co-precipitation technique for efficient removal of water-soluble methylene blue dye. International Journal of Biological Macromolecules, **116**, 607–619 (2018). https://doi.org/10.1016/j.ijbiomac.2018.05.012
- [54] Ma T., Chang P. R., Zheng P., Zhao F., Ma X.: Fabrication of ultra-light graphene-based gels and their adsorption of methylene blue. Chemical Engineering Journal, 240, 595–600 (2014).

https://doi.org/10.1016/j.cej.2013.10.077