Application of Super-Amphiphilic Silica-Nanogel Composites for Fast Removal of Water Pollutants

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Abstract: This work first reports the preparation of super-amphiphilic silica-nanogel composites to reduce the contact angle of water to increase the diffusion of pollutant into adsorbents. In this respect, the silica nanoparticles were encapsulated into nanogels based on ionic and nonionic polyacrylamides by dispersion polymerization technique. The morphologies and the dispersion stability of nanogel composites were investigated to clarify the ability of silica-nanogel composites to adsorb at different interfaces. The feasibility of silica polyacrylamide nanogel composites to act as a high-performance adsorbent for removal of methylene blue (MB) dye and heavy metals (Co^{2+} and Ni^{2+}) from aqueous solution was investigated. The surface tension, contact angle, average pore size, and zeta potential of the silica-nanogel composites have been evaluated. The MB dye and heavy metal adsorption capacity achieved $Q_{\text{max}} = 438--387$ mg/g which is considerably high. The adsorption capacity results are explained from the changes in the morphology of the silica surfaces as recorded from scanning electron microscopy (SEM).

Keywords: silica; nanogel; composites; water purification; adsorption

1. Introduction

It is found from numerous epidemiological studies that the cancer risks are increased from byproducts of chemicals used as common methods of water treatment, such as chlorination [1]. Recently, great efforts have been devoted to emphasize the application of nanomaterials as a safe technique for water purification [2–5]. Estimated worldwide annual production of silica nanosized materials exceeds 1.5 million metric tons [6], among other nanomaterials. Silica nanoparticles have shown adverse effects of both in vitro and in vivo toxicity, which has limited their application in water treatment [7–9]. It was reported that nanocomposites are safer and more effective nanomaterials to apply in the field of water purification [10]. Moreover, functionalization of inorganic nanoparticles, such as silica particles, with organic polymers enhanced their adsorption, mechanical, and exchange capacity [11–13]. However, the incorporation of new functionalized nanoporous materials is important for removing inorganic pollutants because the nanoparticles often exhibit superior properties [14].

The surface activities of the solid amphiphilic nanomaterials—such as adsorption, aggregation, and wetting properties—are of considerable interest due to their importance for selecting favorable potential applications of nanomaterials as wetting agents, dispersants, and so forth [15–20]. In our previous work [18–20] it was found that the surface activities of nanoparticles increased the ability of nanomaterials for use as anticorrosive coats, adsorbents for water pollutants, and effective amphiphilic emulsifiers. However, the design of super-amphiphilic solid nanomaterial surfaces that have a very low contact angle (close to zero) for both aqueous and nonaqueous liquids attracts great attention. In this respect, titanium dioxide nanoparticles possess surfaces combined with the photo-adsorbed
water layer, which is attributed to the “water wets water” mechanism, affected the application of TiO$_2$ film in a dark or non-UV environment \[21,22\]. Surface-engineered silica materials (SESMs) possessing surface activity successfully removed organic pollutants and bacteria from water \[23–26\]. They have greater tendency to deposit on metal and metal oxide surfaces for removal from water. Overall, SESMs have greater tendency to self-assemble on the pollutant surfaces, which facilitates their potential applications in water treatments without needing additional thermal or electrical energy requirements to operate. Their pollutant-removal capacities are affected by the type of coatings on the surface of silica. However, the use of hazardous organic solvents and organic materials during the coating of silica particles affects their applications for water treatment because these hazardous materials contaminate the treated water, and are therefore detrimental to the actual aim of producing clean water. For this reason, ionic liquids have been used as solvent and capping agent to activate the surface properties of silica to remove water pollutants \[27\]. In our previous work, the silica nanoparticles were activated with bio-based surfactants, based on rosin, to enhance their surface activity \[28\]. In this respect, nanogels based on ionic and nonionic monomers were selected to coat the silica surfaces to prepare novel water-based amphiphilic silica nanoparticles. The surface activities were determined by surface tension measurements to investigate their efficiency for the removal of water pollutants such as dye and inorganic heavy metals.

2. Results and Discussion

The present study aims to modify the surface of silica nanoparticles by surrounding the particles with nanogels using dispersion radical polymerization technique. In this respect, the present work selected acrylamide (AAm) and sodium 2-acrylamido-2-methylpropane sulfonate (AMPS-Na) monomers that contain amide and sulfonate groups that interact with hydroxyl groups of silica particles to form dispersed silica particles. Poly(vinyl pyrrolidone), PVP, was used as stabilizer and water/ethanol solvent was used as dispersed solvent \[29\]. Scheme 1 shows the diagram of the polymerization mechanism and the possible interactions between monomers and silica nanoparticles. It is expected that some of the silica nanoparticles cannot be converted to nanogel composites, as described by Ye et al. \[30\] and Wenbo et al. \[31\]. This expectation can be confirmed by different characterization techniques that are discussed in the forthcoming section.
2.1. Characterization of Silica-Nanogel Composites

The surface morphologies of the modified silica nanoparticles with poly(acrylamide) (PAAm), poly(sodium 2-acrylamido-2-methylpropane sulfonate (PAMPS-Na), and PAMPS-Na/AAm were confirmed by SEM analysis. Figure 1a shows the SEM image of silica nanoparticles that confirmed that the size of silica varied from 20 nm to 25 nm with homogeneous shapes and individual distribution. The size of particles was increased after modification with PAMPS-Na/AAm, PAAm, and PAMPS-Na nanogels as represented in Figure 1b–d. The surface of silica has led to pronounced aggregates, which are completely coated with nanogels, as represented for high resolution of the individual particles. There was more aggregation with the incorporation of PAAm than with PAMPS-Na/AAm and PAMPS-Na nanogels. Moreover, it was noticed that there were a few solid silica particles not coated with nanogels. These data are clearly denoting the ability of nanogels to cap the surface of silica particles to produce nanogel composites that cause aggregation of the silica nanoparticles, as illustrated in Scheme 1. It is clear from Scheme 1 that the silica particles interacted with AAm and AMPS-Na monomers through hydrogen bonding between hydroxyl groups of silica and amide groups of monomers. This interaction assists the polymerization of acrylic group monomers and facilitates the capping of silica with nanogels to form silica-nanogel composites.

![Figure 1. SEM micrographs of (a) silica; (b) silica poly(sodium 2-acrylamido-2-methylpropane sulfonate (PAMPS-Na) included high resolution SEM at 10 nm on left top; (c) silica PAMPS-Na/ acrylamide (AAm) included high resolution SEM at 10 nm on left top; and (d) poly(acrylamide) (PAAm) nanogels.](image)

The surface morphology and the shape of silica and modified silica-nanogel composites were also confirmed from transmittance electron microscope (TEM) analysis as represented in Figure 2. The silica nanoparticles, Figure 2a, mostly showed homogeneous spherical particle sizes which have a great tendency to form aggregates due to their high surface free-energy and area and the OH groups. The micrographs of modified silica-nanogel composites, Figure 2b–d, showed relatively better dispersion with the formation some agglomerations. The silica-nanogel composites modified with PAMPS-Na and PAMPS-Na/AAm, Figure 2b,c, had low tendency to aggregate, which was attributed to the steric repulsion of ionic sulfonate groups that enhanced their dispersibility in the aqueous medium [31]. Figure 2d shows more aggregates due to the interactions between acrylamide and hydroxyl groups of silica nanoparticles.
The particle size distribution, polydispersity index (PDI), and average hydrodynamic parameters for silica and its nanogel composites were measured by dynamic light scattering (DLS) analysis at 25 °C and 0.001 M of KCl, as listed in Table 1. The data of PDI revealed a uniform distribution of particle size diameter of silica and its nanogel composites with PAMPS-Na and PAMPS/AAm nanogel, which confirms the interaction between nanogel and hydroxyl group of silica. The data confirm that the particle size diameter of silica was increased with the formation of nanogels surrounding silica particles. The appearance of one indicates the good dispersibility of silica into nanogel composites. Moreover, the average diameter of silica was increased from 25 nm to 55.2 nm, 115.8 nm, and 158 nm with PAMPS-Na, PAMPS-Na/AAm, and PAAm, respectively. The average particle size and PDI values of PAMPS-Na/AAm and PAAm were increased and formed a broad peak to confirm the trapping or/and encapsulating of silica nanoparticles by the nanogel [30,32].

The interaction of nanoparticles with their surroundings and the stability of their dispersion in aqueous solvent were influenced by their surface charge [33,34]. It is reported that the stable, dispersed colloidal particle obtained a zeta potential of +35 or −35 mV. The zeta potential (mV) of silica nanoparticles and their nanogel composite was measured at different ranges of pH, as illustrated in Figure 3, to investigate the effect of acidity and basicity on the dispersion of silica nanoparticles.

Table 1. Dynamic light scattering (DLS) data of silica-nanogel composites.

| Sample            | DLS Data                  |
|-------------------|---------------------------|
|                   | PDI| Dispersion (nm) | Average Particle Size (nm) |
| Silica            | 0.046 ± 0.011 | 23.5 ± 2.4 | 30 ± 2.4 |
| PAMPS-Na          | 0.016 ± 0.001 | 45 ± 1.4  | 55 ± 3.3  |
| PAMPS-Na/AAm      | 0.153 ± 0.052 | 55 ± 3.1  | 115 ± 1.4 |
| PAAm              | 0.745 ± 0.124 | 85 ± 4.4  | 158 ± 5.4 |

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The data of the pure silica nanoparticle has a negative surface charge of \(-15\) to \(-50\) mV with increment pH of solution that was attributed to the deprotonation of hydroxyl groups on the surfaces of silica nanoparticles. The decrement of negative charges of zeta potential with pH from 2 to 12 was attributed to increasing the deprotonation rate of silica hydroxyl groups with increasing pH [35]. The highly negative z-potential values observed for silica coated with PAMPS-Na and PAMPS-Na/AAm nanogels over most of the studied pH range confirm the high dispersion stability of silica after coating with ionic nanogels. The dispersion stability of silica was decreased with coating by nonionic PAAm nanogel. The difference in zeta potential values elucidates the good interaction of the silica nanoparticles with the charged nanogels. Therefore, the variation in surface charge of the coated silica with the nanogel type is another clear indication of the capping of the silica nanoparticles.

![Zeta-potential data of silica-nanogel composites at different pH aqueous solutions.](image)

Figure 3. Zeta-potential data of silica-nanogel composites at different pH aqueous solutions.

It is important to determine the silica contents in their nanogel composites using thermogravimetric measurements, as determined and gathered in Table 2. The data confirmed that the silica and their nanogel composites with PAMPS-Na, PAMPS-Na/AAm, and PAAm show a strong weight loss of about 4\%-8\% with an onset temperature of about 60 °C. This was attributed to loss of adsorbed water on the silica particles [36]. The lower weight loss (4 wt %) of silica nanoparticles at a temperature lower than silica treated with nanogels indicates low water adsorption and increased hydrophilicity of treated silica nanoparticles. The nanogel composites start to decompose at temperature of 250 °C, as indicated in Table 2. The temperature range of 200–450 °C confirms the losses of water obtained from condensation of hydroxyl groups at the nanoparticles surface [36]. The data indicated that the silica-nanogel composite based on PAAm showed greater thermal stability (up to 550 °C) than other nanogels (Table 2), which lose 4 wt % from their initial weights. However, the PAAm nanogel composites possessed low silica contents as 34 wt % of silica-nanogel composite. The temperature zone (about 550–750 °C) confirms the weight loss of silica-nanogel composite due to the oxidation and dehydroxylation of the silane Si–C bonds at high temperatures. The increment of the rate of weight loss for silica coated with PAAm at this temperature (50 wt %) versus other nanogels confirms the strong chemical interaction between amide groups of PAAm and hydroxyl groups on the silica nanoparticles. It was also observed that the silica contents of nanogel composites are 51, 41, and 35 wt % for PAMPS-Na, PAMPS-Na/AAm, and PAAm, respectively. This means that the presence of sulfonate groups in nanogel composites increases the silica contents in the nanogel composites. However, a minimum surface coverage of nanogel component per gram of silica can be calculated as 2.18, 9.59, and 25.79 mmol/g silica for PAMPS-Na, PAMPS-Na/AAm and PAAm, respectively. These data elucidate that the excellent surface coverage value by nanogels on the high surface area of nano-silica particles is arranged in the order of PAMPS-Na > PAMPS-Na/AAm > PAAm.
Table 2. Thermogravimetric analysis (TGA) data of silica-nanogel composites.

| Silica Composite | Degradation Steps °C | Weight Loss (wt %) | Silica Contents (wt %) |
|------------------|-----------------------|--------------------|------------------------|
| Silica           | 25–250                | 8                  | 100                    |
|                  | 250–600               | 1                  |                        |
| PAMPS-Na         | 25–250                | 8                  |                        |
|                  | 250–350               | 10                 |                        |
|                  | 350–550               | 22                 |                        |
|                  | 550–750               | 9                  |                        |
| PAMPS-Na/PAAm    | 25–250                | 8                  |                        |
|                  | 250–350               | 6                  |                        |
|                  | 350–550               | 41                 |                        |
|                  | 550–750               | 4                  |                        |
| PAAm             | 25–250                | 8                  |                        |
|                  | 250–350               | 4                  |                        |
|                  | 350–550               | 50                 |                        |
|                  | 550–750               | 4                  |                        |

2.2. Surface Activity and Contact Angle of Silica-Nanogel Composites

In the previous work [28], the surface activity of silica was modified by using nonionic surfactants and the water surface tension was reduced from 72.1 mN/m to 32 mN/m due to adsorption of surfactants on the silica nanoparticles. In the present work, surface of silica nanoparticles was modified with ionic and nonionic nanogels to reduce the water surface tension to facilitate the diffusion of organic or inorganic pollutants from water to the silica-nanogel composites. The ability of amphiphilic silica nanogels to adsorb at interfaces or to aggregate in the water bulk solution can be investigated from the relation between surface tension of water (mN/m) and concentrations of nanogel composites (−\ln c; mol/L) as represented in Figure 4. The critical aggregation concentrations (cac; mol/L) and the water surface tension at cac (γcac) were calculated at increments of water surface tension with dilution of nanogel composite as represented in Figure 4. The data were calculated and are summarized in Table 3. The decrement of cac value of silica-nanogel composites confirms the hydrophobicity of silica surfaces that increased with using PAAm instead of PAMPS-Na. This means that the repulsion between ionic sulfonate groups increases their dispersion in water. Moreover, the intramolecular interactions between amide groups increased with the absence of sulfonate ionic groups which decrease the dispersibility of silica PAAm nanogel composites.

![Figure 4. Relation between surface tension and concentrations of nanogel composites at 25 °C.](image)
Table 3. Surface activity parameters of silica-nanogel composites in water at 25 °C.

| Designation       | Cm cmol/L × 10³ | γcac mN/m | Δγ mN/m | (−∂γ/∂ln c) | Γmax × 10¹⁰ mol/cm² | Amin nm²/molecule |
|-------------------|-----------------|-----------|---------|-------------|---------------------|------------------|
| silica            | -               | 72 ± 0.201| -       | -           | -                   | -                |
| PAMPS-Na          | 9.1             | 45.16     | 26.84   | 11.7        | 0.472               | 3.52             |
| PAMPS-Na/AAm      | 5.58            | 51.85     | 20.15   | 8.3         | 0.335               | 4.95             |
| PAAm              | 0.52            | 55.4      | 16.6    | 4.6         | 0.186               | 8.92             |

The effectiveness of the prepared surfactants can be directly calculated from Equation (1) [37],

$$\Delta \gamma = \gamma_{\text{water}} - \gamma_{\text{cmc}}$$  \hspace{1cm} (1)

The Δγ values indicated that PAMPS-Na has a strong ability to decrease the water surface tension, more so than PAMPS-Na/PAAm composites.

The surface excess of silica-nanogel composites at the liquid–air interface ($\Gamma_{\text{max}}$) and the minimum area of silica-nanogel composites ($A_{\text{min}}$) were calculated according to Equations (2) and (3) [37],

$$\Gamma_{\text{max}} = (-\partial \gamma / \partial \ln c)_T / RT$$  \hspace{1cm} (2)

$$A_{\text{min}} = 10^{16} / N\Gamma_{\text{max}}$$  \hspace{1cm} (3)

where ($-\partial \gamma / \partial \ln c)_T$, R, T, and N are the slope of the plots (Figure 4), temperature (K), the universal gas constant (in J·mol⁻¹·K⁻¹), and Avogadro’s number, respectively. The $\Gamma_{\text{max}}$, $A_{\text{min}}$, and ($-\partial \gamma / \partial \ln c$) of silica-nanogel composites were calculated and are summarized in Table 3. The data of $\Gamma_{\text{max}}$, $A_{\text{min}}$, and ($-\partial \gamma / \partial \ln c$) indicated that the silica-nanogel composites based on PAMPS-Na nanogels have greater tendency to reduce water surface tension and to adsorb at interface as confirmed by higher $\Gamma_{\text{max}}$ and lower $A_{\text{min}}$ values. It has also been suggested that the sulfonate groups of PAMPS-Na facilitate the adsorption of silica at the interface due to a strong interaction between silica nanoparticles and nanogels. Consequently, the silica-nanogel composites based on PAMPS-Na nanogels will pack perpendicular at interface. The PAAm nanogels will pack as flat at the air-water interface, which inhibits their adsorption at this interface. Finally, it can be concluded that the amide groups of PAAm strongly interacted with silica, and the polymer backbone will increase the hydrophobicity of the silica. The hydrophilicity of silica was enhanced by the presence of sulfonate groups of PAMPS-Na and PAMPS-Na/PAAm nanogels.

The hydrophilicity and hydrophobicity of silica nanoparticles coated with nanogel can be evaluated from its surface wettability by measuring the contact angles between aqueous dispersion of nanogel composites and fire-polished glass. The concentrations of silica nanogels at cac (Table 3) were used to measure the contact angles between water and glass. Surprisingly, both distilled water (DW) and deionized water (DI) contact angles of silica PAMPS-Na nanogel composite droplets on glass were reduced from 50° ± 1.5° and 40° ± 1.7° to zero at an exposure time of 15 s, which indicates that the silica surface becomes super-amphiphilic at interfaces. The contact angle values of silica PAMPS-Na/AAm eventually reached nearly 4° ± 3.5° at an exposure time of around 60 s, demonstrating a super-amphiphilic surface. The unmodified silica droplet shows contact angle 30° ± 1.1° on the glass surface. The silica PAAm nanogel composite reduced the water contact angle on the glass to 20° ± 3.5°, which confirmed the hydrophobicity of PAAm on the silica surfaces.

2.3. Sorption of MB and Isotherm Studies on Silica-Nanogel Composites

The high surface activity and wetting characteristics of the prepared silica-nanogel composites are being derived to apply these materials as adsorbents for water purification. It was previously reported [38] that the modification of clay mineral with nanogel produced amphiphilic clay with excellent wetting characteristics and achieved high adsorption rates for both organic and inorganic water pollutants. In this work, the negative charges were increased on the surface of silica nanoparticles by formation of ionic nanogel composites based on PAMPS-Na and PAMPS-Na/AAm, as determined
from zeta-potential data (Figure 3), which facilitate the adsorption of cationic pollutants such as heavy metals and MB dye. Moreover, the amide and sulfonate groups of nanogels assist chelation of pollutants on the surfaces of nanogel composites. For these reasons, the application of these super-amphiphilic silica-nanogel composites to the fast removal of water pollutants such as MB, Co$^{2+}$, and Cd$^{2+}$ cations will be investigated in this section.

The pH of pollutant in aqueous solution is considered as an effective parameter that facilitates or inhibits the adsorption of pollutants from aqueous solution. It is well established that the variation of hydrogen ion concentration affects both the solubility of pollutants and activity of adsorbent surfaces. The effect of pH of MB in aqueous solution (1000 ppm) on sorption capacities ($Q_{\text{max}}$; mg/g) of silica-nanogel composites is represented in Figure 5. The unmodified silica nanoparticles were not used because they showed low adsorption and were not easily separated from their aqueous solution. Careful inspection of Figure 5 confirms that the silica-nanogel composites based on PAMPS-Na and PAMPS-Na/PAAm show high adsorption capacity above pH 7, which reflects the complete ionization of sulfonate groups that increase the density of negative charges on the silica nanoparticles. Consequently, the adsorption of cationic MB dye increased in the basic condition. Moreover, increasing the pH of water to more than 9 influenced the sorption capacity of silica-nanogel composites due to salt screen of ionic sulfonate groups when pH increased more than 9 [39].

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![Figure 5. Relation between adsorption capacities of silica-nanogel composites for 1000 ppm of methylene blue (MB) and their pH of solutions at constant ionic strength, 1 M.](image-url)

The efficiency of silica-nanogel composites to adsorb and remove MB from aqueous solution is due to the reduction of silica particle size to nanosized particles. Accordingly, at a higher pH of aqueous solution, a complete ionization and higher degree of deprotonation of sulfonate functional groups occurs, which increases the number of binding sites on the silica surface thus improving the MB adsorption. It was also noticed that the silica PAMPS-Na shows higher adsorption capacity in comparison with PAMPS-Na/PAAm and PAAm nanogel composites. It is expected that the MB can interacts through the $\pi$-electron cloud of its benzene ring with lone pair of nitrogen, sulfur, and oxygen atoms of PAMPS-Na/PAAm, or hydrogen bonding with nitrogen and sulfur atoms of MB dye. It was expected that the incorporation of PAAm of $\text{-CONH}_2$ groups of the polyacrylamide chains will create additional binding sites (in comparison to PAMPS-Na) with the dye molecule. It was found that the acrylamide groups decreased the $Q_{\text{max}}$ of silica-PAMPS-Na/PAAm more that PAMPS-Na nanogel composites. This can be due to the good interaction between amide groups and extra silanol -OH groups decreasing the chelating binding sites with MB dye in comparison with silica-PAMPS-Na [40].
The effect of contact time between aqueous solution of MB (1000 ppm) at pH and its sorption capacity was represented in Figure 6. The data indicate that the silica-nanogel composite based on PAMPS-Na is the fastest adsorbent for removing MB from water during 25 min, which is one of their advantages beside their ability to reduce surface tension of water and enhanced the wettability of silica. Moreover, silica-nanogel composites based on AMPS-Na/AAm removed MB during 35 min. On the other hand, the silica nanogel based on PAAm is less efficient due to a complete saturation of the surface with MB at a later stage.

![Figure 6](image-url)  
*Figure 6. Relation between adsorption capacities of silica-nanogel composites for 1000 ppm of MB and equilibrium adsorption time at constant ionic strength 1 M.*

The effect of pH value and contact time of the prepared silica-nanogel composites on the metal uptake was also investigated and evaluated as reported in the experimental section. The results of Co(II) and Ni(II) uptake using silica-nanogel composites are summarized in Table 4. It is evident that neutral pH 7.0 of water was suitable for extraction of Co(II) and Ni(II). The Ni(II) was found to be extracted to a higher degree compared with Co(II) at almost all evaluated pH values. This means that Ni(II) has high tendency to adsorb on the surface of silica-nanogel composites under a higher pH value of pollutant solution. Additionally, there is a higher tendency of surface oxygen donor functional groups of the sorbent, such as OH silanol, amide, and sulfonate functional groups, to greatly interact with heavy metal. Therefore, the optimum pH for sorption of Co(II) and Ni(II) was identified as 7.0 and is in agreement with reported results [41–43]. The predominant complex formation mechanism is preferred for interaction of heavy metal ions and silica-nanogel composites of PAMPS-Na and PAAm.

![Table 4](image-url)  
*Table 4. Adsorption data of silica-nanogel composites for Co and Ni cations from their aqueous solutions at pH 9, ionic strength 1 M, and temperature of 25 °C.*
The nature of the adsorption process of adsorbate on the surface of adsorbent can be estimated from adsorption isotherms which correlate the relationship between the amounts of adsorbate per unit mass of adsorbent and its concentration at constant temperature. There are different models used to investigate the adsorption processes, and the most common isotherms are Langmuir and Freundlich isotherms as determined from Equations (4) and (5), respectively [44,45]

\[
\frac{C_e}{Q_e} = \left[ 1 + \frac{Q_0}{Q_{\text{max}}} K_l \right] + \left( \frac{C_e}{Q_{\text{max}}} \right)
\]

(4)

\[
\log \left( \frac{Q_e}{Q_0} \right) = \log \left( K_l \right) + \frac{1}{n} \log \left( \frac{C_e}{Q_{\text{max}}} \right)
\]

(5)

where \(Q_e\), \(Q_0\), \(C_e\), \(n\), \(K_l\), and \(K_f\) are the equilibrium uptake capacity of adsorbents (mg/g), the equilibrium dye concentration (mg/L), empirical constant, and Langmuir and Freundlich constants, respectively.

The Langmuir and Freundlich constants are determined and listed with the experimental \(Q_{\text{max}}\) and \%E in Table 5. The sorption data of MB onto silica-nanogel composites based on PAMPS-Na, PAMPS-Na/AAm, and PAAm were evaluated at optimum buffering condition (pH 8.0) at constant temperature 25°C. Figure 7a and \(R^2\) data (Table 5) indicated that the sorption of MB by the three sorbents better fits to Langmuir isotherm rather than Freundlich isotherm. Moreover, the maximum loading capacity \(Q_{\text{max}}\) values (Table 5) that were calculated from Langmuir isotherm are identical for those determined practically using three different silica-nanogel composites. This confirms that MB molecules as adsorbate form a homogeneous monolayer to cover the silica-nanogel composites [46]. Moreover, the disappearance of S curve indicates that the MB molecules have a higher degree of intermolecular attraction with silica-nanogel composites that prevents the interaction of water molecules with composites. Percent extraction (%E)—determined experimentally to show the effectiveness of silica-nanogel particles to adsorb the pollutants from aqueous medium at different concentrations of MB—ranged from 100 to 1000 ppm.

**Table 5.** Adsorption isotherm parameters for removal of 1000 ppm of MB dye using silica nanogels at 25°C.

| Adsorbents          | Langmuir Isotherm Parameters | Freundlich Isotherm Parameters | Exp. Adsorption Capacity |
|---------------------|------------------------------|--------------------------------|--------------------------|
|                     | \(Q_{\text{max}}\) mg/g | \(K_l\) L/mg | \(R^2\) | \(1/n\) | \(K_f\) | \(R^2\) | \(Q_{\text{max}}\) mg/L | 1000 ppm | 100 ppm | 1000 ppm | 100 ppm | %E |
| Silica/PAMPS-Na     | 462             | 0.0352       | 0.992   | 0.5699 | 0.0600 | 0.962 | 438         | 48.3 | 87.6 | 96.15 |
| Silica/PAMPS-Na/AAm | 450             | 0.0336       | 0.999   | 0.5804 | 0.1580 | 0.930 | 424         | 48   | 84.8 | 96   |
| Silica/PAAm         | 391             | 0.0220       | 0.993   | 0.6039 | 0.1640 | 0.869 | 379.5       | 45.7 | 74.9 | 91.4 |

**Figure 7.** Adsorption isotherms (a) Langmuir and (b) Freundlich models of silica-nanogel composites.
One of the substantial advantages found was that the silica-nanogel composites were reused five times after deswelling (as reported in the Experimental section) without reducing the maximum loading capacity of MB or Co$^{2+}$, and Ni$^{2+}$ cations. Also, the efficient regeneration capability of the silica-nanogel composite indicated that PAMPS-Na and PAMPS-Na/AAm act as ion exchangers for dye or Co$^{2+}$ and Ni$^{2+}$ cations [47]. This suggests that the combination between nano-silica and nanogels improves the adsorption capacity of the nanogel composite, and has great prospective in practical applications for removing MB dye pollutant from aqueous solution.

3. Experimental Section

3.1. Materials

A hydrophilic precipitated silica nanoparticle (degree of hydrolysis 100%) was a gift from Eka Chemicals (Bohus, Sweden). Other chemicals were purchased from Aldrich Chemical Co. (Darmstadt, Germany).

3.2. Synthesis Procedure

The silica-nanogel composites based on AMPS-Na and AAm were prepared using dispersion crosslinking as reported in our previous work [29]. In brief, water/ethanol (60/40 vol %) was used as mixed solvent to increase the dispersion of silica and to prepare nanogel. In this respect, silica nanoparticle (2 g) and PVP (0.3 g) were stirred in water/ethanol (100 mL) at room temperature for 24 h. AMPS-Na monomer (2 mL) or AAm (1 g) was dissolved in the dispersed silica solution. APS (0.03 g), N,N,N'-methylenebisacrylamide (MBA) (0.03 g), and 20 µL of $N,N,N',N'$-tetramethylethylenediamine TEMED were dissolved in water (2 mL) and injected in the silica monomer dispersion under nitrogen gas atmosphere. The mixture was heated up to 45 °C under stirring for 24 h. The dispersed silica PAMPS-Na or PAAm was separated using an ultracentrifuge at 15,000 rpm for 60 min. The silica-nanogel composites were washed five times with ethanol and dried under vacuum at 30 °C.

The same procedure was repeated to encapsulate silica nanoparticles into nanogel composite based on PAMPS-Na/AAm copolymer; the molar ratio between AMPS-Na and AAm monomers is 1.

3.3. Characterization

The morphology of silica and their nanogel composites was evaluated by transmittance and scanning electron microscope (TEM; JEOL JEM-2100 F (Tokyo, Japan)); SEM; JEOL 6510 LA SEM, (Tokyo, Japan)).

Thermogravimetric analyses (TGA-50 SHIMADZU, (Shimadzu, Tokyo, Japan) was used via nitrogen atmosphere with flow rate 30 mL/min at a heating rate of 10 °C/min.

Laser Zeta meter Malvern Instruments (Model Zetasizer 2000, Montreal, QC, Canada) was used to determine zeta potential and particle size distribution and diameters of silica nanogels.

The surface activity of silica nanogels was determined from surface tension measurement in aqueous solution at 25 °C using drop shape analyzer model DSA-100 (KRÜSS GmbH, Hamburg, Germany). The same instrument was used to measure the contact angles of silica-nanogel composites on dry glass. Temperature and moisture was constant during the experiment (23 °C and 68%, respectively).

3.4. Adsorption and Desorption Experiments

UV–visible spectrophotometric was used to estimate the calibration curve of MB at wavelength of 662 nm by correlating the absorbance with MB concentrations. Different concentrations of MB (100–1000 ppm) were dissolved in 50 mL of PBS and stirred with 0.02 g of the silica nanogels into a 100 L conical flask at 25 °C. The silica-nanogel composites can be collected using Millipore membrane filtration device (Merck, San Diego, CA, USA) and the filtrate samples were analyzed after centrifuging the filtrate at different time intervals. The equilibrium maximum adsorption capacity of dye Q (mg/g) and extraction percentage (%E) determined as:
\[ Q = [(C_0 - C_e) \times V/(m)] \] (6)

\[ \%E = [(C_0 - C_e) \times 100/(C_0)] \] (7)

where \( C_0 \) and \( C_e \) (mg/L) are the liquid phase concentrations of dye at initial and equilibrium, respectively, \( V \) (L) the volume of the solution and \( W \) (g) is the mass of adsorbent used. The equilibrium times determined after the nanogel adsorbents reach a constant weight of pollutant. The samples left in aqueous solution under agitation for 24 h after they reached the equilibrium times to ensure the stability of equilibrium measurements.

Atomic adsorption spectroscopy (AAS; Perkin-Elmer 2380, Minneapolis, MN, USA) was used to determine the concentration of metals in the direct aspiration into an air-acetylene flam.

The used adsorbents were deswelled by a 0.1 M HCl solution, then washed several times with distilled water and dried to reuse at 80 °C.

4. Conclusions

Encapsulation on nano-silica into nanogel composites based on PAMPS-Na, PAMPS-Na/AAm, and PAAm was successfully achieved and applied for developing a highly effective adsorbent. The combination between inorganic silica nanoparticles and a nanogel polymer produces super-amphiphilic particles that have special wettability. The silica nanoparticles of particle size 17–25 nm were coated with nanogels to be in the order of 20–40 nm, having a spherical nanostructure, and high thermal stability. Different varieties of modified surface functional groups have good selectivity for removing dye and heavy metal water pollutants. The presence of sulfonate groups in the chemical structure of nanogels increased the surface activity and wetting characteristics of silica nanoparticles at interfaces. The silica-nanogel composites have been used here to effectively remove heavy metal and dye from waste water at neutral and slightly basic pH at room temperature. The high adsorption capacities for the prepared silica-nanogel composites suggest that removal efficiency of the silica nanoparticles for heavy metal is much higher than other adsorbents at the neutral pH.

The sorption equilibria of the prepared silica nanogels were reached in 10–25 min and the adsorption of MB on silica nanogels obeys Langmuir model, confirming formation of homogeneous monolayers of MB on their surfaces.

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Sample Availability: Samples of the all compounds are available from the authors.