Supporting Information

A Biocompatible, pH Sensitive and Magnetically Separable Superparamagnetic Hydrogel Nanocomposite as an Efficient Platform for Removal of Cationic Dyes in Wastewater Treatment

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Figure S1. Photograph showing the effect of higher wt. percent of SPIONs (above 6 wt. %) which results in impairment in hydrogel formation process.

To explore the possible upper limit of SPIONs’ content in such superparamagnetic composite hydrogel systems, AA-VSA-P/SPIONs, through the process mentioned in the main manuscript, the synthesis of AA-VSA-P/SPIONs system with higher concentration (wt. percent) of SPIONs (i.e., above ~ 6 wt. %) was also attempted, which ended up with an impairment in hydrogel formation process, as shown in Figure S1.
**Figure S2.** TEM image of SPIONs (i.e., Fe₃O₄ nanoparticles).

**Figure S2** represents the TEM image of SPIONs (i.e., Fe₃O₄ nanoparticles). The morphology and size of SPIONs (i.e., Fe₃O₄ nanoparticles) were analyzed by transmission electron microscope (FEI TEM, FEI Tecnai S-twin, the Electron Microscope Facility at Saha Institute of Nuclear Physics, Kolkata) operating at an acceleration voltage of 200 kV. The TEM specimens were prepared by dispersing the SPIONs with ethanol, then dropping the dispersion on a copper grid. As shown in Figure S2, the observed average size of nanoparticles was about 8-12 nm, which was consistent with the X-ray diffraction (XRD) result, where the particle size was estimated using Debye-Scherrer expression (as described in the main Manuscript, Section 3.1).
Table S1. Comparison of the adsorption capacities of AA-VSA-P/SPIONs-I hydrogel and other reported polymeric hydrogels for the removal of MB dye.

| Hydrogel                                      | Initial MB concentration (mg/l) | pH values | Equilibrium Time (Minutes) | Hydrogel dose per litre of MB dye solution (g/litre) | Adsorption capacity (mg/g) |
|-----------------------------------------------|---------------------------------|-----------|----------------------------|-----------------------------------------------------|--------------------------|
| [This study] AA-VSA-P/SPIONs-I                | 12                              | 7         | 470                        | 6                                                   | 1.61                     |
|                                               | 12                              | 9         | 470                        | 6                                                   | 1.76                     |
|                                               | 50                              | 9         | 470                        | 6                                                   | 7.92                     |
| ¹PAA coated magnetic nanocomposite            | 10                              | 7         | 360                        | 10                                                  | 0.819                    |
| ²Poly (acrylic acid-co-vinylsulfonic acid) hydrogel | 13                              | 7         | 470                        | 6                                                   | 1.6                      |
|                                               | 9                               |           | 470                        | 6                                                   | 1.9                      |
|                                               | 40                              | 9         | 470                        | 6                                                   | 6.7                      |
| ³Magnetite/phenylenediamine/cellulose acetate nanocomposite | 10                              | 7         | 360                        | 10                                                  | 1.55                     |
|                                               | 50                              | 7         | 360                        | 10                                                  | 7.24                     |
|                                               | 100                             | 7         | 360                        | 10                                                  | 23.35                    |
| ⁴Amine/Fe₃O₄-resin biopolymer                 | 200                             | 7         | 720                        | 1                                                   | 1.6                      |
|                                               | 9                               |           | 720                        | 1                                                   | 3.8                      |
| ⁵Xylan/poly(acrylic acid) magnetic nanocomposite | 100                             | 7         | 4320                       | 25                                                  | 28.1                     |
| ⁶Magnetic carboxymethyl starch/poly(vinyl alcohol) composite gel | 320                             | 7         | 700                        | 10                                                  | 22.5                     |
|                                               | 9                               |           | 700                        | 10                                                  | 22.5                     |
Figure S3. Plot of magnetization (M) as a function of applied magnetic field (H) for AA-VSA-P with 1.2 wt. % SPIONs and 3.2% SPIONs (i.e., AA-VSA-P/SPIONs-I, and the AA-VSA-P/SPIONs-II respectively).

Figure S3 represents the magnetic behaviors of AA-VSA-P with 1.2 wt. % SPIONs and 3.2% SPIONs (i.e., two low level loading of SPIONs, AA-VSA-P/SPIONs-I, and the AA-VSA-P/SPIONs-II) were studied by Quantum Design MPMS XL superconducting quantum interference device magnetometer at room temperature. Figure S3, presents the magnetization versus applied magnetic field strength plots for the two magnetic hydrogel nanocomposites (AA-VSA-P) having different weight percentage of SPIONs (AA-VSA-P/SPIONs-I and AA-VSA-P/SPIONs-II). The results demonstrate that both the AA-VSA-P/SPIONs systems exhibit superparamagnetic behavior with negligible coercivity and remanence.\textsuperscript{5}
It should be noted that, in this case, the AA-VSA-P/SPIONs magnetic hydrogel systems, have weak magnetic moment, and so the diamagnetic background dominates over the weak signal of the sample, leading to reduced saturation magnetization, and made it difficult for any quantification (from observed saturation magnetization values).

**Supporting Information S4, S5 and S6:**

**S4. Dye adsorption properties by AA-VSA-P/SPIONs-I for Rhodamine B dye (RhB)**

Dye adsorption properties of synthesized superparamagnetic hydrogel nanocomposites, AA-VSA-P/SPIONs, for another cationic dye, Rhodamine B having different chemical structure from MB dye, have been explored in this section.

Rhodamine B (RhB) is widely used in coloring paper, textile dyeing, and leather industries, but it has adverse effects on the human health even with trace amounts. It can cause redness and pain in eyes and skin, irritation to the gastrointestinal tract, and even cause cancer. However, RhB is nonbiodegradable because of its optical, thermal, and physical-chemical stability. And about 10-15% of unused dyes enter the wastewater directly in the dyeing process. Therefore, RhB must be removed from wastewater before it is discharged into natural environment in industrial production.

**S4.1. Impact of pH medium**

The dye adsorption (from aqueous solution) properties of the AA-VSA-P/SPIONs-I, i.e., 1.2 wt.% of SPIONs was demonstrated by using RhB dye solution, at different characteristic pH
values, such as pH 9, 7 and 1.4, as displayed in Figure S4. All these measurements were conducted at room temperature.

Approximately 0.3g of AA-VSA-P/SPIONs-I magnetic hydrogel was immersed in 0.05 l aqueous solution of Rhodamine B dye (12 mg/l). Figure S4(c) shows the UV-Vis absorption spectra of the RhB dye solution that were collected at different time intervals to evaluate the variation in the content of Rhodamine B dye (RhB) in the solution due to the adsorption by the superparamagnetic hydrogel. Here, the changes of normalized concentration (C/C₀) of RhB with time due to adsorption AA-VSA-P/SPIONs-I system, is considered to be proportional to the respective normalized RhB dye absorbance (A/A₀) at the main peak (at the wavelength of 554 nm) of the absorption spectrum of the RhB dye solution (Figure S4). The instantaneous dye adsorption capacity qₜ (mg/g) was estimated by eq (2) as mentioned in the main manuscript.

The impact of pH values of the medium on RhB dye removal by the superparamagnetic nanocomposite hydrogel, AA-VSA-P/SPIONs-I was examined under pre-optimized time for a given set of fixed parameters (C₀, V and W). The results demonstrate the vital role of pH of the medium in this context, which are displayed in Figure S4. Dye adsorption behavior (adsorption capacity as function time) of a characteristic AA-VSA-P/SPIONs system (AA-VSA-P/SPIONs-I) at different pH values is displayed in Figure S4. The results reveal that the maximum adsorption (or equilibrium adsorption) of RhB dye increases significantly with increasing pH value from 1.4 to 9, while such trend is consistent with the observation for MB dye, as discussed in main manuscript.
Figure S4. (a) Equilibrium adsorption capacity ($q_e$) of superparamagnetic hydrogel nanocomposites with 1.2 wt. % of SPIONs: AA-VSA-P/SPIONs-I for MB and RhB dye; (b) Adsorption behaviour: effect of contact time on the RhB dye uptake by AA-VSA-P/SPIONs-I [initial MB concentration is 12 mg/l, at pH 9, pH 7 and pH 1.4]; (c) UV–Vis absorbance spectra of RhB dye solution, at initial stage ($t_i$), i.e., before the adsorption, and at equilibrium stage after adsorption ($t_e$) by AA-VSA-P/SPIONs-I hydrogel, at pH 9 and pH 1.4.

The results show that the dye adsorption capacity of AA-VSA-P/SPIONs-I is less for RhB dye in comparison to MB dye. The effect is more prominent at higher pH values (pH 7, 9). This results can be attributed to the fact that at higher pH values there is an improvement in ionization of -COOH groups on RhB, causing the enhancement in electrostatic repulsion between the COO$^-$ groups of RhB and the COO$^-$ and SO$_3^-$ groups on AA-VSA-P/SPIONs-I hydrogel, which makes it difficult for RhB molecules to be adsorbed by of the magnetic hydrogel. Furthermore,
relatively lower adsorption capacity of RhB onto the AA-VSA-P/SPIONs-I compared with MB can also be explained by the larger molecular size of RhB in comparison to MB dye.\textsuperscript{11}

**S5. Dye Adsorption Kinetics**

The dye adsorption kinetics of AA-VSA-P/SPIONs-I (1.2 wt.% of SPIONs) for RhB dye at pH 7 and pH 1.4 (Figure S5) were explored by fitting the experimental data for $q_t$ vs. time (t), using various kinetic models including pseudo-first-order (PFO), pseudo-second-order (PSO), and Elovich models as discussed in main manuscript. The best fit parameters for the three kinetic models are shown in Table S2. The correlation coefficient ($R^2$), as summarized in Table S2 (along with the best fit parameters), offers a quantitative estimation of the pertinency of the best adsorption kinetics model to explain the experimental data.\textsuperscript{2, 12} The results reveal that the adsorption of RhB dye by AA-VSA-P/SPIONs-I composite hydrogel system at pH value 1.4 and 7 are better fitted by pseudo-first-order equation and pseudo-second-order equation over the Elovich model as shown in Figure S5. The results indicate that the physical adsorption process plays a significant role along with the chemisorption process in dye-adsorption kinetics, exhibiting an equally good agreement of the experimental data with pseudo-first-order\textsuperscript{13, 14} and pseudo-second-order model\textsuperscript{15}. The result implies that the larger specific surface area provided the adsorption sites, which facilitates the adsorption of RhB dye molecules,\textsuperscript{13} where the physical adsorption process shows reasonable contribution in determining the adsorption process and further the chemical adsorption process is taking place by the adsorption of RhB molecules on the active sites of adsorbent.\textsuperscript{16}
Figure S5. RhB dye adsorption by AA-VSA-P/SPIONs-I at (a) pH 7 and (b) pH 1.4: Experimental data fit with various kinetic models, Pseudo-first-order (top panel), Pseudo-second-order (middle panel), Elovich equation (bottom panel).

Table S2. Summary of results for experimental data fitting by different kinetic models for the RhB dye adsorption by the AA-VSA-P/SPIONs-I at pH 7 and pH 1.4.

| pH   | Kinetic Model      | Parameters               | RHB (12mg/l) |
|------|--------------------|--------------------------|--------------|
|      | AA-VSA-P/SPIONs-I |                          |              |
| 7    | Pseudo-first-order | $k_1$ (min$^{-1}$) 0.003 |              |
|      |                    | $q_e$ (cal.) (mg/g) 1.294 |              |
|      |                    | $q_e$ (exp.) (mg/g) 1.206 |              |
|      |                    | $R^2$ 0.99              |              |
|      | Pseudo-second-order| $k_2$ (g mg$^{-1}$ min$^{-1}$) 0.002 |
| Model          | $q_e$ (cal.) | $q_e$ (exp.) | $R^2$ |
|---------------|--------------|--------------|-------|
| Elovich       | 1.721        | 1.206        | 0.99  |
| Pseudo-first-order | 0.003       | 0.003        | 0.98  |
| Pseudo-second-order | 0.002      | 0.002        | 0.98  |
| Elovich       | 0.009        | 0.009        | 0.97  |

### Parameters

- **Elovich**
  - $\alpha$ (mg·g$^{-1}$·min$^{-1}$): 0.009
  - $\beta$ (g mg$^{-1}$): 2.45
- **Pseudo-first-order**
  - $k_1$ (min$^{-1}$): 0.003
- **Pseudo-second-order**
  - $k_2$ (g mg$^{-1}$·min$^{-1}$): 0.002
- **Elovich**
  - $\alpha$ (mg·g$^{-1}$·min$^{-1}$): 0.009
  - $\beta$ (g mg$^{-1}$): 3.22
S6. Dye Adsorption Isotherm

To further investigate the phenomena that occurred at the surface of superparamagnetic hydrogel nanocomposite, AA-VSA-P/SPIONs-I, during the adsorption process, the conventional adsorption isotherm models (Langmuir, Freundlich and Temkin models) were examined for RhB dye adsorption on AA-VSA-P/SPIONs-I, magnetic hydrogel, by conducting multiple separate measurements using different increasing initial concentrations of RhB dye solutions as described in main manuscript.

In order to examine the type of adsorption involved in case of RhB dye adsorption process by AA-VSA-P/SPIONs-I composite hydrogel system, the study was conducted through multiple separate measurements by varying the initial dye concentration ($C_0$), namely, 12 mg/l, 22 mg/l, 33 mg/l, 44 mg/l, and 50 mg/l, of RhB dye solutions at pH 9. Experimental data and corresponding fits with above mentioned three best fit isotherm models, using equations (11, 12 and 13) as described in the main manuscript, are displayed in Figure S6. The values of the extracted parameters are presented in Table S3. The Langmuir model was better fitted in the adsorption process of the uptakes of RhB by AA-VSA-P/SPIONs-I, suggesting that the adsorption process was monolayer adsorption. However, Freundlich was also fitted well with the experimental adsorption data (with n>1), which suggested that the adsorption of RhB onto AA-VSA-P/SPIONs-I was physical in nature, through heterogenous surface. The high $R^2$ value of the Temkin isotherm shows that this isotherm also fits the experimental data well. This result suggests that significant interaction is also observed among the RhB molecules.

The study suggests that RhB uptake by AA-VSA-P/SPIONs is favorably governed by the physisorption process and through monolayer coverage. Significant interaction is also evident...
among the RhB molecules. The process can be explained by the initial adsorption of RhB onto the reactive sites on the surface of the composite hydrogel system and subsequently percolation into the pores, where adsorbate-adsorbate interaction may also account for heterogeneity of the adsorption.\textsuperscript{18-20}

**Figure S6.** (a) Langmuir (b) Freundlich (c) Temkin, isotherm models for RhB dye adsorption onto the superparamagnetic hydrogel nanocomposites, AA-VSA-P/SPIONs-I at pH 9.

**Table S3.** Summary of results for experimental data fitting by various isotherm models for the RhB dye adsorption process by superparamagnetic nanocomposites hydrogel (AA-VSA-P/SPIONs-I) at pH 9.

| Isotherm Model | Parameters | AA-VSA-P/SPIONs-I |
|----------------|------------|-------------------|
| Langmuir       | $k_L$ (l/mg) | 0.018             |
|                | $q_m$ (mg/g) | 9.372             |
|                | $R^2$       | 0.98              |
| Freundlich     | $k_F$ (l/g)  | 0.306             |
|                | $n$         | 1.438             |
|                | $R^2$       | 0.96              |
| Temkin | $k_T$ | 0.238 |
|--------|--------|--------|
|        | $b_T$  | 1457.39 |
|        | $R^2$  | 0.97   |

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