SUPPORTING INFORMATION Nanoscale

Nano-silica fabricated with silver nanoparticles: antifouling adsorbent for efficient dye removal, effective water disinfection and biofouling control

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Experimental Section

Preparation of cell free extract from *R. oryzae*

The *R. oryzae* (MTCC 262) used in this study was maintained in potato dextrose agar (2% potato extract, 2% dextrose and 2% agar) slants. Potato dextrose broth was used as growth medium for cultivation of the organism. The medium was inoculated with mycelium and incubated at 30 °C for 72 h under static condition. Mycelia were harvested from the culture medium after fermentation, thoroughly washed with phosphate buffer solution (50 mM, pH 7.2), and then crushed with sea sand with a mortar and pestle at 4 °C. The cell free protein extract was collected after centrifugation at 15,000 rpm for 30 min and dialyzed (10 kDa molecular weight cut off) overnight against the same buffer at 4 °C. The protein content in the dialyzed cell free extract was measured by the Bradford method and used for AgNP synthesis.

Biofilm assay by crystal violate

Both nano-silica and NSAgNPs were collected after incubation with bacteria and washed with sterile double distilled water to remove loosely attached cells from the surfaces. Following washing, both nano-silica and NSAgNP materials were stained with 500 µL of 0.5% crystal violet solution for 30 min. At the end of incubation, nano-silica and NSAgNP were collected and washed with sterile double distilled water thrice followed by destained with 3 mL of 95% ethanol solution for 30 min. The ethanol solution was collected and absorbance was recorded at 595 nm by a spectrophotometer.

Live/Dead viability assay

The LIVE/DEAD viability kit contains DNA-binding fluorescent dyes SYTO 9 (green) and propidium iodide (PI, red). The two stains differ in their permeability to the bacterial cells. SYTO 9 stains both live and dead bacteria; while, PI strains dead cells only. Thus the live bacteria stain with green fluorescent color, and dead bacteria exhibit strong red emission. The excitation/emission maxima for these dyes are approximately 480/500 nm for SYTO 9 stain and 490/635 nm for PI. The bacterial cells were stained with LIVE/DEAD kit following interaction with NSAgNP and nano-silica, and then micrographs were recorded on a fluorescence microscope (Olympus BX-61) using an excitation filter of BP 460–495 nm and a band absorbance filter covering wavelengths below 505 nm. Living and dead cells in the same microscopic fields were viewed separately with different fluorescence filter sets. The cell viability was then assayed by counting green (live) and red (dead) cells.

Results and Discussion

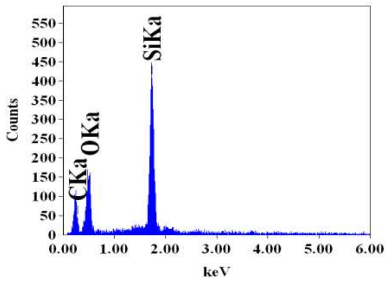

Fig. S1 EDXA spectrum of control nano-silica.

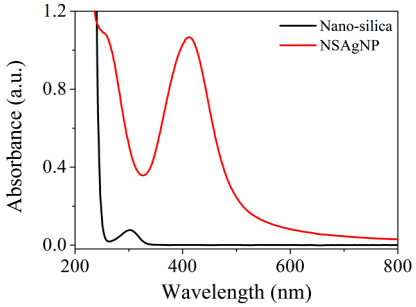

Fig. S2 UV-vis spectra of the dispersed solution of NSAgNP synthesized by 'post-deposition' route.

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Kinetic rate models

The linearized forms of pseudo first and second order rate kinetics models are expressed as

$$\log (q_e\text{-}q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (1)$$

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

where q_e is the amount of dye adsorbed (mg g^{-1}) at equilibrium, 't' is the time, k_1 (min^{-1}) and k_2 (g $mg^{-1}min^{-1}$) are the first and second order rate constants, respectively; q_t is the amount of dye adsorbed (mg g^{-1}) per gram of the biomass at time 't'.

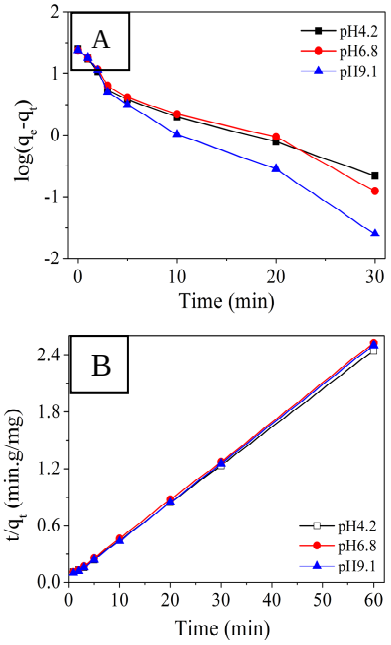

Fig. S3 Pseudo first (A) and second-order plot (B) of adsorption of cocktail dye NSAgNP at different pH values. Initial dye concentration = 50 mg L^{-1}, temperature 30 °C, and shaking speed 120 rpm.

The intra-particle diffusion model can be represented as

$$q_t = k_i t^{1/2} \qquad (3)$$

Therefore, the plot of uptake (q_t) versus square root of time ($t^{1/2}$) would be linear under a diffusion controlled transport mechanism and if the line passes through the origin then intra-particle diffusion would be the rate controlling step. The biphasic nature of the curve (**Fig. S4**) suggested that adsorption process occurred in two steps. Most of the dyes adsorbed on the surface adsorption process at the external binding sites followed by diffusion into the pore of the adsorbent. The surface adsorption process occurred during initial 10 min and then transported inside the pore of NSAgNP. Thus pore diffusion also took place in the present binding process, but is not the rate determining step in the present adsorption process because of low r^2 values.

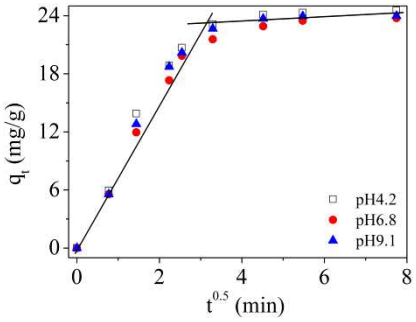

Fig. S4 Plots for the intraparticle diffusion for the adsorption of cocktail dye by NSAgNP. Initial dye concentration = 50 mg L^{-1}, temperature 30 °C, and shaking speed 120 rpm.

Table S1. Parameters of rate kinetic models for adsorption of cocktail dyes on NSAgNP

pH	Pseudo-first order kinetic model		Pseudo-second order kinetic model		Intraparticle diffusion model	
	k_1 (1 min^{-1})	r^2	k_2 (g mg^{-1}.min)	r^2	k_i (mg $g^{-1}min^{-1/2}$)	r^2
4.2	1.44×10^{-1}	0.91	3.25×10^{-2}	0.999	2.99	0.628
6.8	1.56×10^{-1}	0.89	4.57×10^{-2}	0.999	2.95	0.665
9.1	2.727×10^{-1}	0.82	3.11×10^{-2}	0.998	2.96	0.631

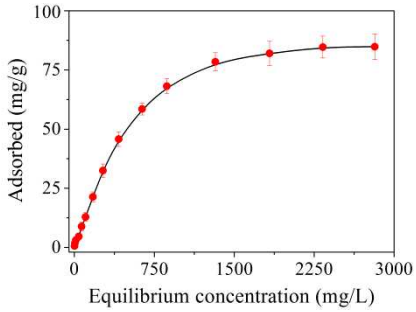

Fig. S5 Adsorption isotherm of cocktail dye on activated carbon

Table S2 Summary of dye adsorption capacities of various adsorbents

Dye	Adsorbents	Uptake (mg g^{-1})	References
Congo red	Fly ash adsorbed	4.12	1
Congo red	Bentonite	158.7	2
Congo red	SA/N/CaFe	189.0	3
Congo red	Coir pith carbon	6.7	4
Methylene blue	Ordered mesoporous silica	54.0	5
Methylene blue	Carboxylic functionalized superparamagnetic mesoporous silica microspheres	101.9	6
Methylene blue	Activated carbon	80.0	7
Methylene blue	Jute steak powder	35.7	8
Methylene blue	Magnetic multi-wall carbon nanotube	11.86	9
Rhodamine B	Sodium montmorillonite	178.57	10
Rhodamine B	*Rhizopous oryzae*	39.21	11
Rhodamine B	Reduced graphene oxide-Fe_3O_4 hybrid	44.4	12
Rhodamine B	Jute steak powder	87.7	8
Methyl blue	Crosslinked PEI/PVA nanofibrous mats	209.63	13
Acrydin orange	Carboxylic functionalized superparamagnetic mesoporous silica microspheres	109.6	6
Napthol blue black	Magnetically modified *Saccharomyces cerevisiae*	11.6	14
Direct red	$ZnAlNO_3$	36.37	15

Adsorption isotherm

The Langmuir isotherm, which assumes monolayer coverage with chemical interaction, is represented as

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \qquad (1)$$

where q_e and C_e are the concentration of dye molecules at equilibrium in the solid (mg g^{-1}) and aqueous phase (mg L^{-1}), respectively; a_L (L mg^{-1}) and K_L (L g^{-1}) are the Langmuir constants.

The Freundlich isotherm, which assume multilayer coverage with physisorption, is expressed as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (2)$$

In the above equation, K_F (L g^{-1}) is the Freundlich constant, $\frac{1}{n}$ is the heterogeneity factor.

The Dubinin–Radushkevitch isotherm model, which is based on the Polanyi theory, is as expressed in linear form Eq. (3) as

$$\ln\ q_e = \ln\ q_D - 2\,B_D\,\mathrm{RT}\ln\left(1 + \frac{1}{C_e}\right) \qquad (3)$$

where ε, Polanyi potential, is correlated to

$$\varepsilon = RT \ln\left(1+\frac{1}{C_e}\right) \quad (4)$$

The constant 'B_D' gives the mean free energy 'E' of sorption per molecule of the sorbate when it is transferred to the solid surface from the solution and can be computed by using the relationship:

$$E = \frac{1}{\sqrt{2B_D}} \quad (5)$$

where R is the gas constant (8.314 J $mol^{-1}K^{-1}$) and T is the absolute temperature.

The Tempkin isotherm used for fitting of isotherm data is expressed in the following form

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (6)$$

where

$$B_T = \frac{RT}{b_T} \quad (7)$$

B_T is Temkin isotherm constant, A_T is the Temkin isotherm constant (L g^{-1}), R the gas constant (8.314 J $mol^{-1}K^{-1}$), b_T is the Temkin constant related to heat of adsorption (J mol^{-1}), and T is the temperature (K).

Among the different models tested, the highest regression coefficient values (r^2= 0.997) for Langmuir model demonstrated that chemical interaction plays dominant role in the present adsorption process, however, physisorption also take place in certain amount. The heat of adsorption (b_T) calculated from Temkin isotherm was 49.46 j mg^{-1}.

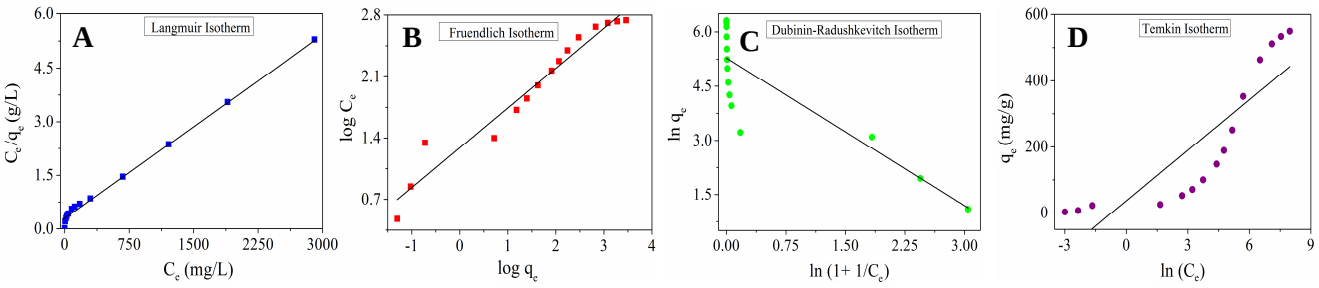

Fig. S6 Adsorption isotherm of cocktail dye on NSAgNP following Langmuir (A), Freundlich (B), Dubinin–Radushkevich (C) and Temkin (D) model.

Table S3 Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin isotherm constants for adsorption of cocktail dyes on NSAgNP

Langmuir isotherm model				Freundlich isotherm model		
a_L (L mg^{-1})	K_L (L g^{-1})	Q_L (mg g^{-1})	r^2	K_F (L g^{-1})	n	r^2
0.0073	4.01	549.31	0.997	19.41	2.21	0.915

Dubinin–Radushkevich isotherm model				Temkin isotherm model			
E (J mg^{-1})	B_D (mg^2 J^{-2})	Q_D (mg g^{-1})	r^2	A_T (L g^{-1})	B_T	b_T (J mg^{-1})	r^2
43.48	2.69×10^{-4}	196.17	0.701	2.6	50.93	49.46	0.727

Table S4 Recovery of cocktail dye from loaded NSAgNP[a] by different eluents at 30 °C

Desorption agents	Recovery (mg dye g^{-1} NSAgNP)	Amount recovered (%)
HCl (0.1 M)	2.4	9.8
H_2SO_4 (0.1 M)	2.57	10.5
$HN0_3$ (0.1 M)	2.36	9.6
NaOH (0.1 M)	2.25	9.18
Ethyl alcohol	19.66	80.2
Methyl alcohol	20.24	82.6
Acetone	21.27	86.8

[a]24.5 mg of cocktail dye was adsorbed per gram of NSAgNP

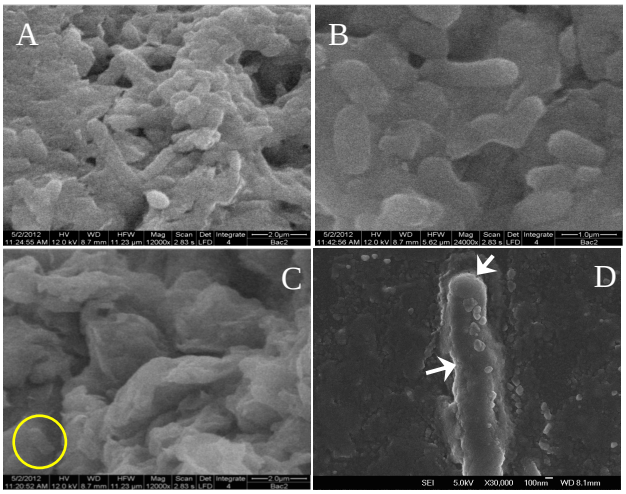

Fig. S7 SEM images of biofilm formation of *E. coli* on nano-silica (A-B) and NSAgNP (C-D) at low (A and C) and high (B and D) magnifications. Arrows in indicates formation of pore or leakage on the cell surface.

Table S5 Concentrations of dyes and bacteria in simulated contaminated feed water after treatment with Nano-silica and NSAgNP

Material	Time of incubation (min)	Dye (mg L^{-1})	*E. coli* (CFU mL^{-1})
Nano-silica	0	49.35	85×10^3
	5	10.52	102×10^3
	10	4.98	73×10^3
	30	0.62	45×10^3
	60	0.25	105×10^3
	120	0.02	215×10^3
	24 (h)	0.02	65×10^4
NSAgNP	0	49.35	85×10^3
	5	10.85	25×10^2
	10	5.2	65×10^1
	30	0.68	102
	60	0.35	65
	120	0.02	12
	180	0.02	-
	24 (h)	0.01	-
	80 (h)	0.01	-

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