Materials and instruments

Materials

Diclofenac sodium (DCF) was obtained from Aladdin Chemistry Co., Ltd (Shanghai, China). Sodium alginate (MW 120–190 g/mol, G/M = 1.56), and other materials of analytical grade were supplied by Merck including calcium chloride, sodium hydroxide, acetic acid, hydrochloric acid, sodium chloride, ethanol absolute.

Instruments

FT-IR spectra (KBr discs, 4000–400 cm^{-1}) by Jasco-4100 spectrophotometer. The structural differences of the as-prepared Zr-MOF were investigated using the X-ray diffraction (XRD) method. The powder XRD patterns were captured using a Siemens D-500 X-ray diffractometer equipped with a Cu Ka source of radiation. UV-visible spectra from a Perkin-Elmer AA800 spectrophotometer Model AAS with a 1.0 cm model system. The pH meter utilized was a WTW 720 model digital pH meter. On ASAP 2020, the surface area was calculated to use the Brunauer–Emmett–Teller (BET) method, and the pore volume of the BET surfaces and the Barrett–Joyner–Halenda (BJH) surface were calculated (Micrometrics, USA). FESEM QUANTA FEG 250. Made in Netherland EDX EDAX Element made in USA. The specimen was then deposited onto a copper substrate after being sputter-coated with a homogenous gold layer. XPS was measured using K-ALPHA (Themo Fisher Scientific, USA).

Adsorption isotherm

Isotherm studies give significant visions by clarifying the adsorbate distribution between solid and solution phase during the adsorption equilibrium, and adsorption isotherms expose the behavior of adsorbate how to interact with adsorbent. Equilibrium revisions that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and that remained in solution at equilibrium at fixed temperature. Numerous isotherm models have been used for considering the equilibrium adsorption of compounds from solutions such as Langmuir, Freundlich, Dubinin–Radushkevich and Temkin.

The Langmuir isotherm model accepts the uniform energies of adsorption onto the adsorbent surface. It is based on statement of the existence of monolayer adsorption onto a completely homogeneous surface with a fixed number of identical sites and with negligible interaction between adsorbed molecules. The Freundlich model is an empirical equation based on adsorption of heterogeneous surface or surface supporting sites of varied affinities. It is assumed that the stronger

binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. Dubinin–Radushkevich isotherm is an empirical model initially for the adsorption of subcritical vapors onto micropore solids following a pore filling mechanism. It is applied to distinguish the physical and chemical adsorption for removing a molecule from its location in the sorption space to the infinity. The Temkin isotherm assumes that the heat of adsorption of all molecules in the phase decreases linearly when the layer is covered and that the adsorption has a maximum energy distribution of uniform bond. The linear and nonlinear forms of Langmuir, Freundlich, Dubinin–Radushkevich and Temkin isotherm models and their parameters are shown in Table S1 where q_e the adsorbed amount of dye at equilibrium concentration (mmol/g), q_{mL} is the maximum sorption capacity (corresponding to the saturation of the monolayer, mmol/g) and K_L is the Langmuir binding constant which is related to the energy of sorption (L/mmol), C_e is the equilibrium concentration of dyes in solution (M). K_F (mmol/g) (L/mmol)$^{1/n}$ and n are the Freundlich constants related to the sorption capacity and intensity, respectively. K_{DR} (J^{2}mol^{-2}) is a constant related to the sorption energy, q_{DR} (mmol/g) is the theoretical saturation capacity, ε (J^{2}mol^{-2}) is the Polanyi potential. R (8.314 J.mol^{-1}K^{-1}) is the gas constant, T is the temperature where the adsorption occurs, A_T (L/mg) is the Temkin isotherm constant, b_T (J/mol) is Temkin constant in relation to heat of adsorption.

Table S1. Isotherms and their linear forms for the adsorption.

Eq. no.	Isotherm		Equation
(1)	Langmuir		The constants q_m and K_l are calculated by the plot of C_e/q_e *vs.* C_e with slope $1/q_m$ and intercept $1/(q_mK_L)$
(2)	Freundlich		K_F and n can be calculated from a linear plot of $\ln q_e$ *vs.* $\ln C_e$
(3)	Dubinin–Radushkevich		The slope of the plot of $\ln q_e$ *vs.* ε^2 gives K_{DR} (mol^2/kJ^2) and the intercept yields the adsorption capacity, Q_{DR} (mmol/g)
	Temkin		The parameters β and K_T are the Temkin constants that can be determined by the plot of q_e *vs.* $\ln C_e$

(4)			

Adsorption kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The rate of removal of tested dye by adsorption was rapid initially and then slowed gradually until it attained an equilibrium beyond which there was significant increase in the rate of removal Table S2.

where q_t is the amount of dye adsorbed (mg/g) at various times t, q_e is the maximum adsorption capacity (mg/g) for pseudo-first-order adsorption, k_1 is the pseudo-first-order rate constant for the adsorption process (min^{-1}), q_2 is the maximum adsorption capacity (mg/g) for the pseudo-second-order adsorption, k_2 is the rate constant of pseudo-second-order adsorption (g.mg^{-1}min^{-1}). The straight-line plots of log $(q_e - q_t)$ *vs. t* for the pseudo-first-order reaction and t/q_t *vs. t* for the pseudo-second-order reaction.

Table S2. Kinetic parameters and their correlation coefficients for the adsorption.

Eq. no.	Model	Equation	
(5)	Pseudo-First-order kinetic		The plot of ln (q$_e$ - q$_t$) against t gives a straight line with the slope -K_1 and intercept ln q$_e$
(6)	Pseudo-second-order kinetic		Values of K_2 and q$_e$ for different initial concentrations of dye were calculated from the slope and intercept of the linear plot of t/q$_t$ *vs.* t
(7)	Intraparticle diffusion		The parameters K$_{dif}$ and C were determined from the linear plot of q$_t$ *vs.* t$^{1/2}$
(8)	Elovich		The constants α and β were obtained from the slope and intercept of a line plot of q$_t$ *vs.* ln t

Since neither the pseudo-first-order nor the pseudo-second-order model can identify the diffusion mechanism, the kinetic results were further analyzed for diffusion mechanism by using the intra-particle diffusion model. The effect of intra-particle diffusion constant (internal surface and pore diffusion) on adsorption can be determined by the following Eq. (7). where I is the intercept and k_{id} is the rate constant of intra-particle diffusion ($mg.g^{-1}min^{1/2}$) which is determined from the linear plot of q_t *vs.* $t^{1/2}$, and it is usually used to compare mass transfer rates. According to this model, the plot of uptake, q_t, *vs.* the square root of time, $t^{1/2}$ should be linear if intra-particle diffusion is involved in the adsorption process and if these lines pass through the origin, then intra-particle diffusion is the rate controlling step. The intra-particle diffusion rate constant and intercept values are displayed in (Table S2).

The Elovich equation is used for general application to chemical adsorption. The equation has been applied satisfactorily to some chemical adsorption processes and has been found to cover a wide range of slow adsorption rates. The same equation is often valid for systems in which the adsorbing surface is heterogeneous, and is formulated as Eq. (8):

Where α is the chemical adsorption rate (mg/mg min) and β is a coefficient in relation with the extension of covered surface and activation energy of chemical adsorption (g/mg). Plot of q_t *vs.* ln t gave a linear relationship with slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln (\alpha\beta)$. The $1/\beta$ value reflects the number of sites available for adsorption whereas the value of $(1/\beta) \ln (\alpha\beta)$ indicates the adsorption quantity when ln t equal to zero.

Thermodynamics

It is important to investigate the effect of temperature on adsorption in a view of practical application. The adsorption experiments were carried out at different temperatures (Table S3, Supplementary material). The behavior confirms that the adsorption process if it endothermic or exothermic. This observation can be attributed to increasing of the mobility of the adsorbate molecules and rate of diffusion of adsorbate molecules across the surface of adsorbent with increasing temperature, which leads to an increase in the adsorption capacity. The adsorption equilibrium constant, K_c was determined (Eq. 9) and used with the van't Hoff equation (Eq. 10) and conventional thermodynamic equation (Eq. 11) for evaluating the thermodynamic constants of the sorbents (i.e., the standard enthalpy change, ΔH^o, the standard free Gibbs energy, ΔG^o, and the standard entropy change, ΔS^o).

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$$K_c = \frac{q_e}{C_e} \qquad\qquad (9)$$

Where q_e and C_e are equilibrium concentrations of pollutant on the adsorbent and in the solution, respectively.

$$\Delta G^o = - RT \ln K_c \qquad\qquad (10)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad\qquad (11)$$

Therefore the van't Hoff equation becomes:
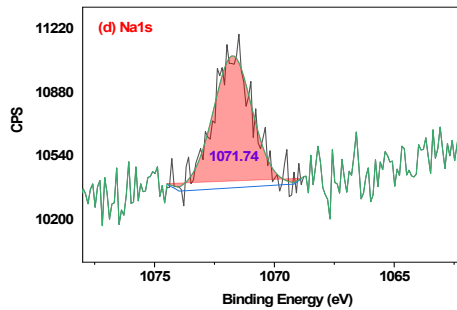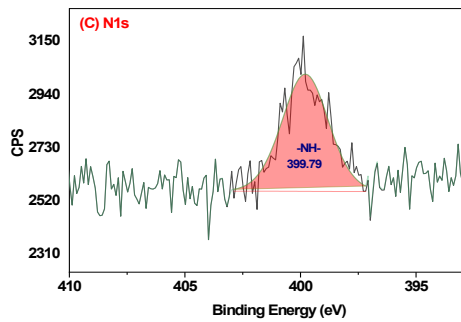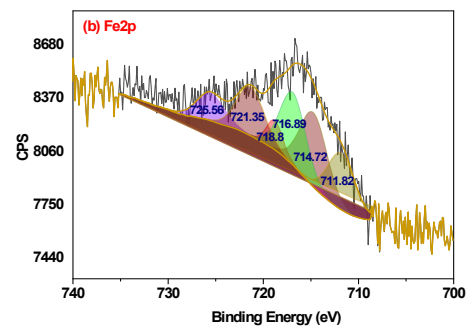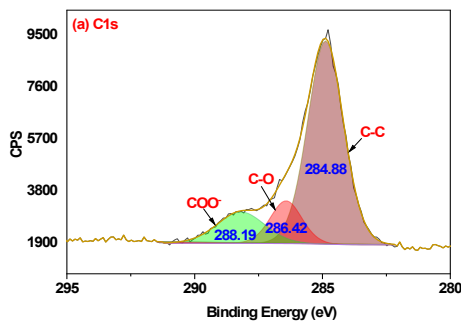
$$\ln K_C = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad\qquad (12)$$

The value of standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o) for the adsorption process are thus determined from the slope and intercept of the plot of $\ln K_c$ *vs.* $1/T$.

Table S3: List of abbreviation:

Symbol	Definition
q_e	the adsorbed amount of dye at equilibrium concentration (mmol/g)
q_{mL}	the maximum sorption capacity (corresponding to the saturation of the monolayer, (mmol/g))
K_L	Langmuir binding constant which is related to the energy of sorption (L/mmol)
C_e	is the equilibrium concentration of dyes in solution
K_F	Freundlich constants related to the sorption capacity (mmol/g) (L/mmol)$^{1/n}$
n	intensity
K_{DR}	constant related to the sorption energy ($J^2.mol^{-2}$)
q_{DR}	theoretical saturation capacity (mmol/g)
ε	Polanyi potential ($J^2.mol^{-2}$)
R	Gas constant ($8.314\ J.mol^{-1}K^{-1}$)
T	temperature where the adsorption occurs
A_T	Temkin isotherm constant
b_T	Temkin constant in relation to heat of adsorption (J/mol)
q_t	is the amount of dye adsorbed (mmol/g)

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K_1	Rate constant for Pseudo first order constant for the adsorption processes (min^{-1})
q_2	Maximum adsorption capacity for pseudo second order
K_2	Rate constant for Pseudo first order constant for the adsorption processes ($g.mg^{-1}min^{-1}$)
α	Chemical adsorption rate ($mgg^{-1}.min^{-1}$)
β	Coefficient in relation with extension of covered surface
ΔG^o	Free Gibb's energy
ΔH^o	Enthalpy
ΔS^o	Entropy
K_c	distribution coefficient
C_{eq}	Concentration at equilibrium (mg/L)
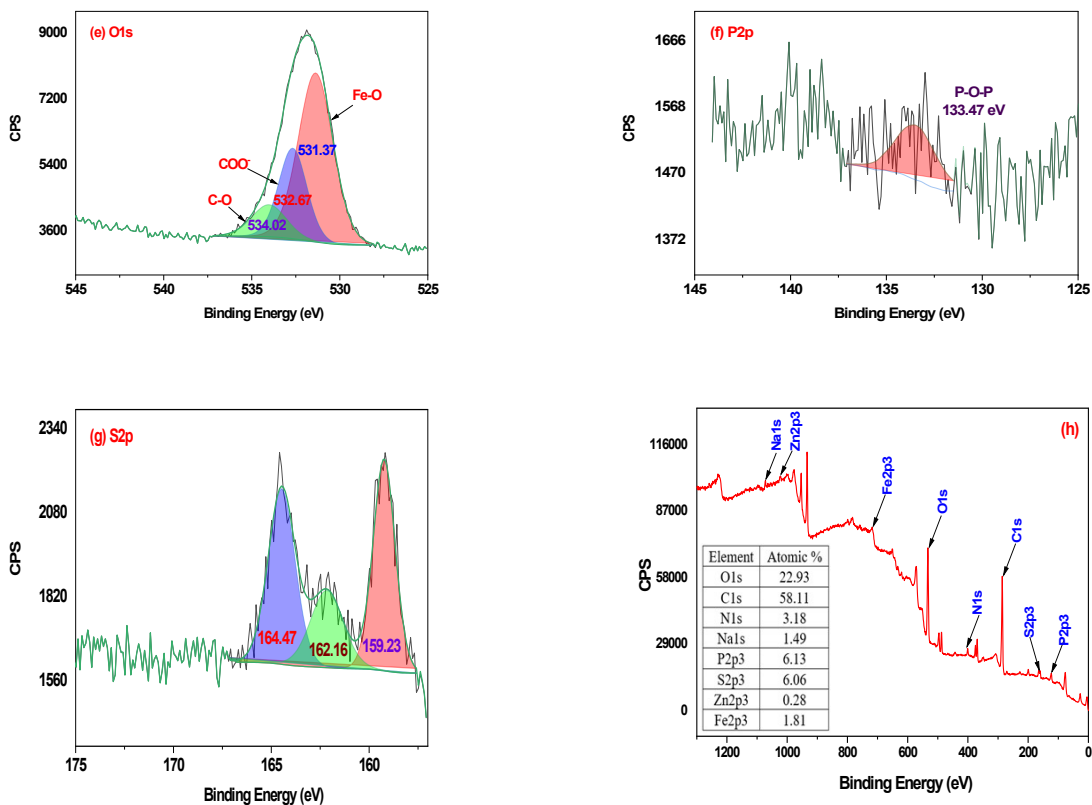
Fig. S1. XPS spectra of Fe$_3$O$_4$@TAC@SA polymer.
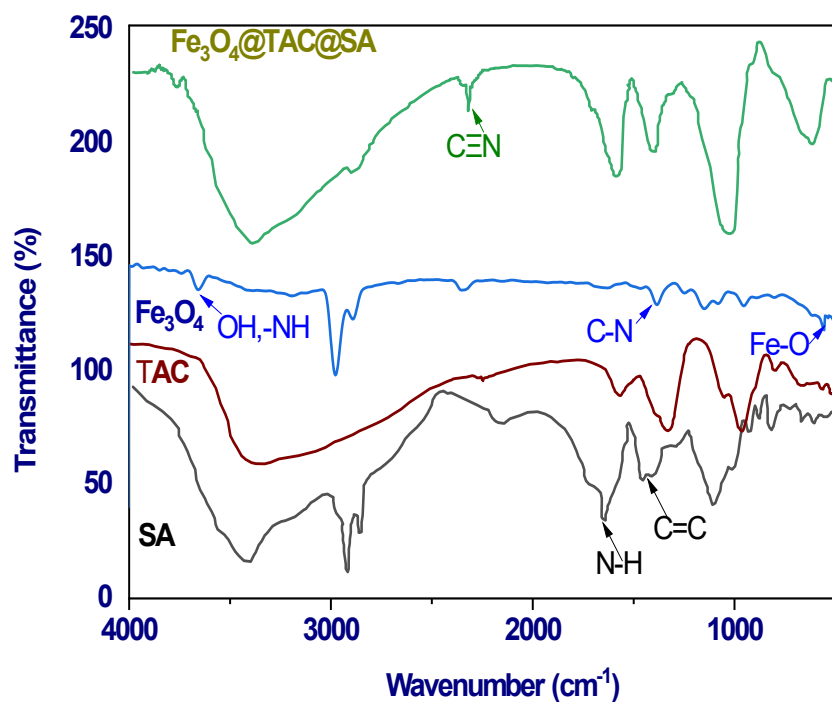
Fig. S2. FT-IR spectrum of SA, Fe$_3$O$_4$, TAC, and Fe$_3$O$_4$@TAC@SA polymer.
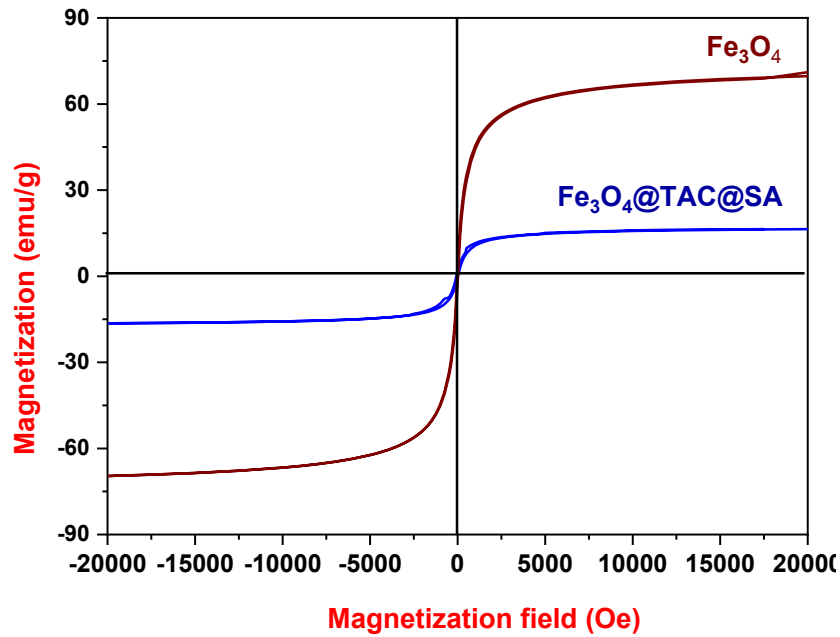
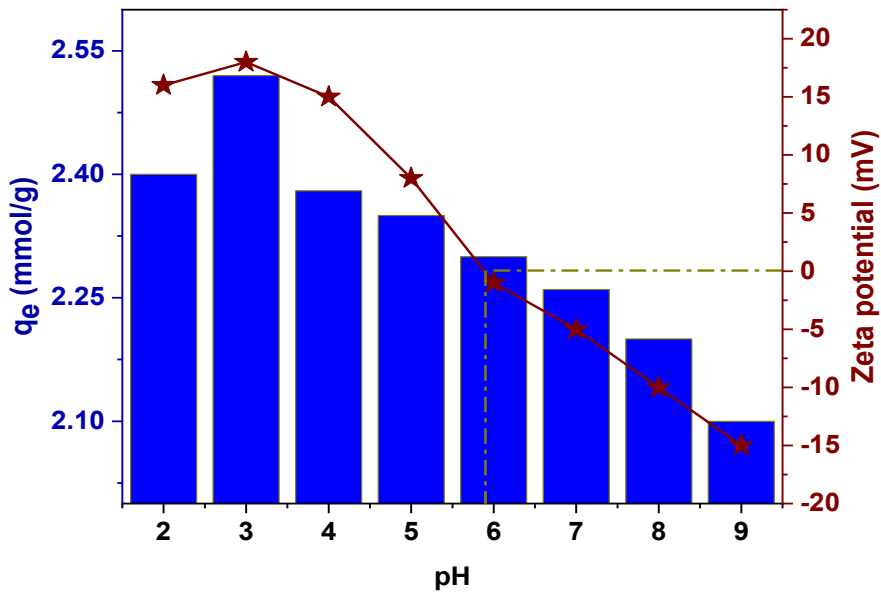Fig. S3. Magnetic spectrum of Fe$_3$O$_4$ and Fe$_3$O$_4$@TAC@SA polymer.

Fig. S4. Effect of pH on adsorption of DS at Fe$_3$O$_4$@TAC@SA polymer. (Dose: 0.02g/25mL, Conc. 2.22x10^{-3} mol, and time 30 min)
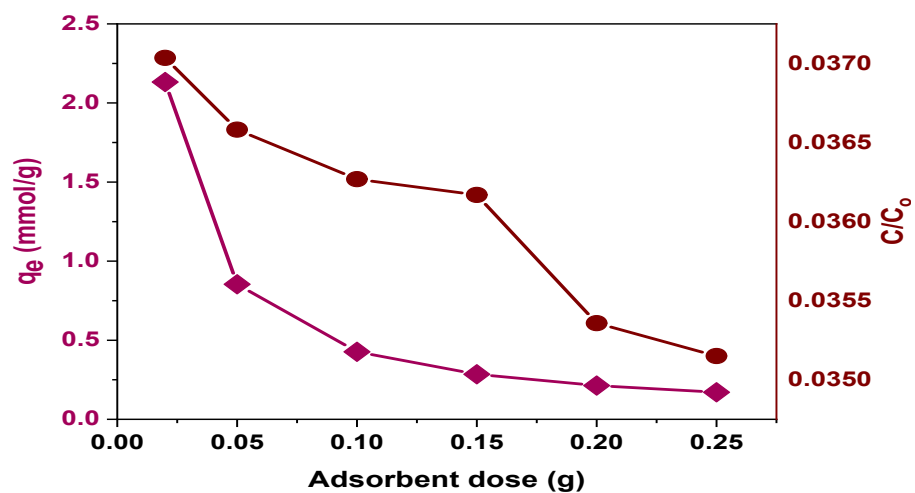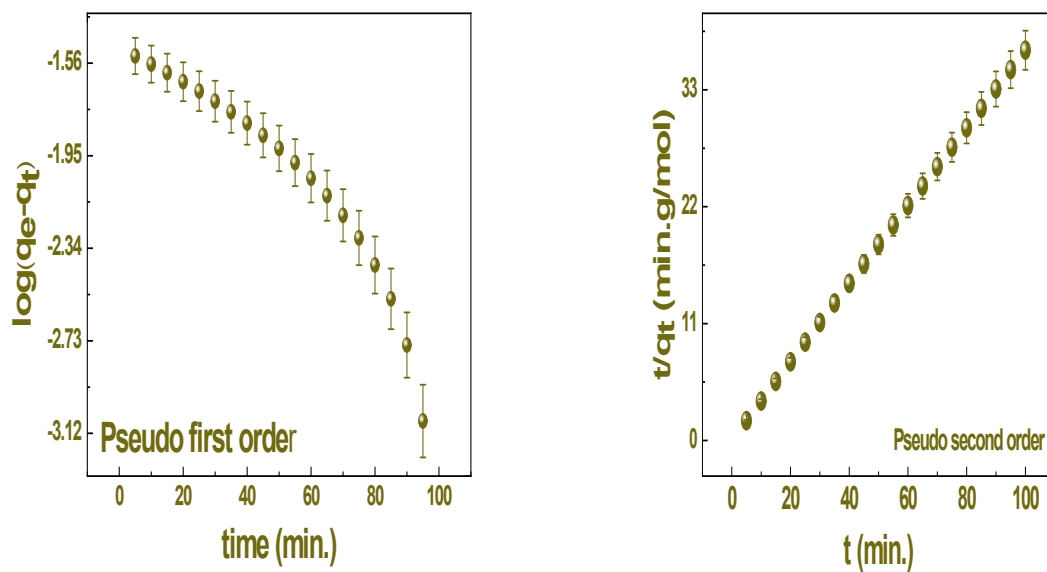
Fig. S5. Effect of dose of Fe_3O_4@TAC@SA polymer on adsorption of DS. (pH: 3, Dose: 0.02g/25mL, Conc. 2.22×10^{-3} mol, and time 30 min)

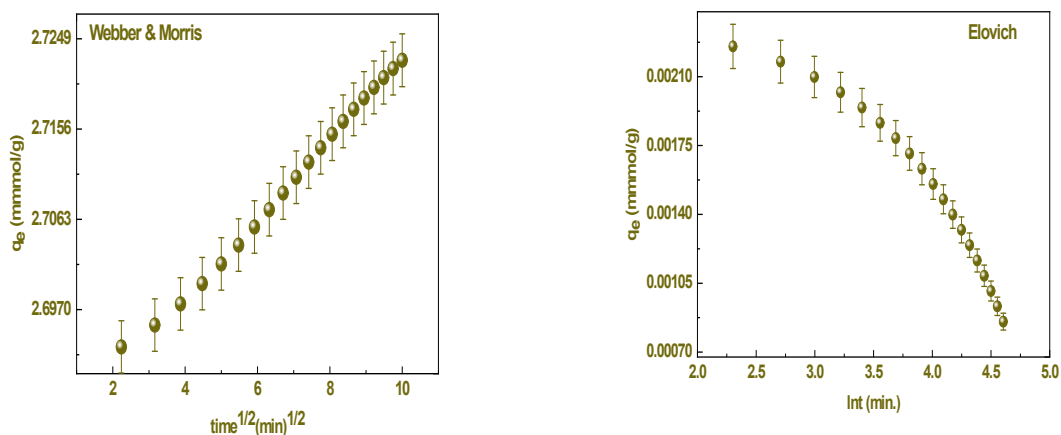**Fig. S6**. Kinetic models for adsorption of DS on Fe_3O_4@TAC@SA polymer. (pH: 3, Dose: 0.02g/25mL, Conc. 2.22×10^{-3} mol, and time 100 min)

Table S4. Kinetic parameter for DS on Fe_3O_4@TAC@SA polymer.

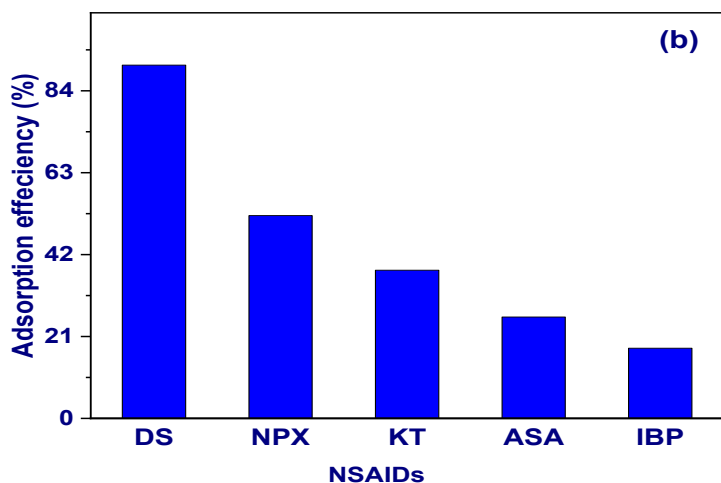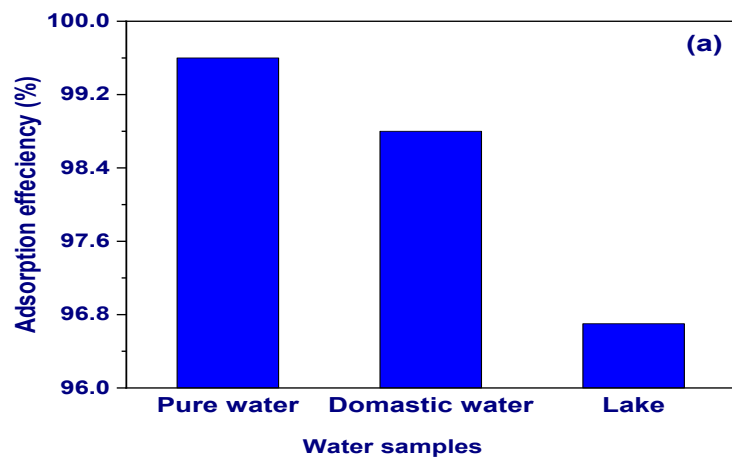| Models	Parameter	DS
Pseudo-First-order kinetic	K_1 (min^{-1})	0.00405
	R^2	0.898
Pseudo-second-order kinetic	K_2 (g.mg^{-1}min^{-1})	1.818
	q_e (mmol/g)	2.73
	R^2	0.999
Intraparticle diffusion	K_i (mg.g^{-1}min$^{1/2}$)	0.005
	X (mgg^{-1})	2.682
	R^2	0.995
Elovich	β (g/mg)	-1577.29
	α (mgg^{-1}.min^{-1})	1.003
	R^2	0.9098
Experimental data	q_e (mmol/g)	2.72

Fig. S7. (a) Adsorption of DS on Fe_3O_4@TAC@SA polymer from pure water, domestic water and lake samples with spiked DCF concentration of 10 mg/L; (b) Adsorption efficiency of NSAIDs on Fe_3O_4@TAC@SA polymer with the initial mixed NSAIDs concentration of 10 mg/L.