DFT and comparative adsorption study of NiO, MnO, and Mn_2NiO_4 nanomaterials for the removal of amaranth dye from synthetic water

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Supplementary data

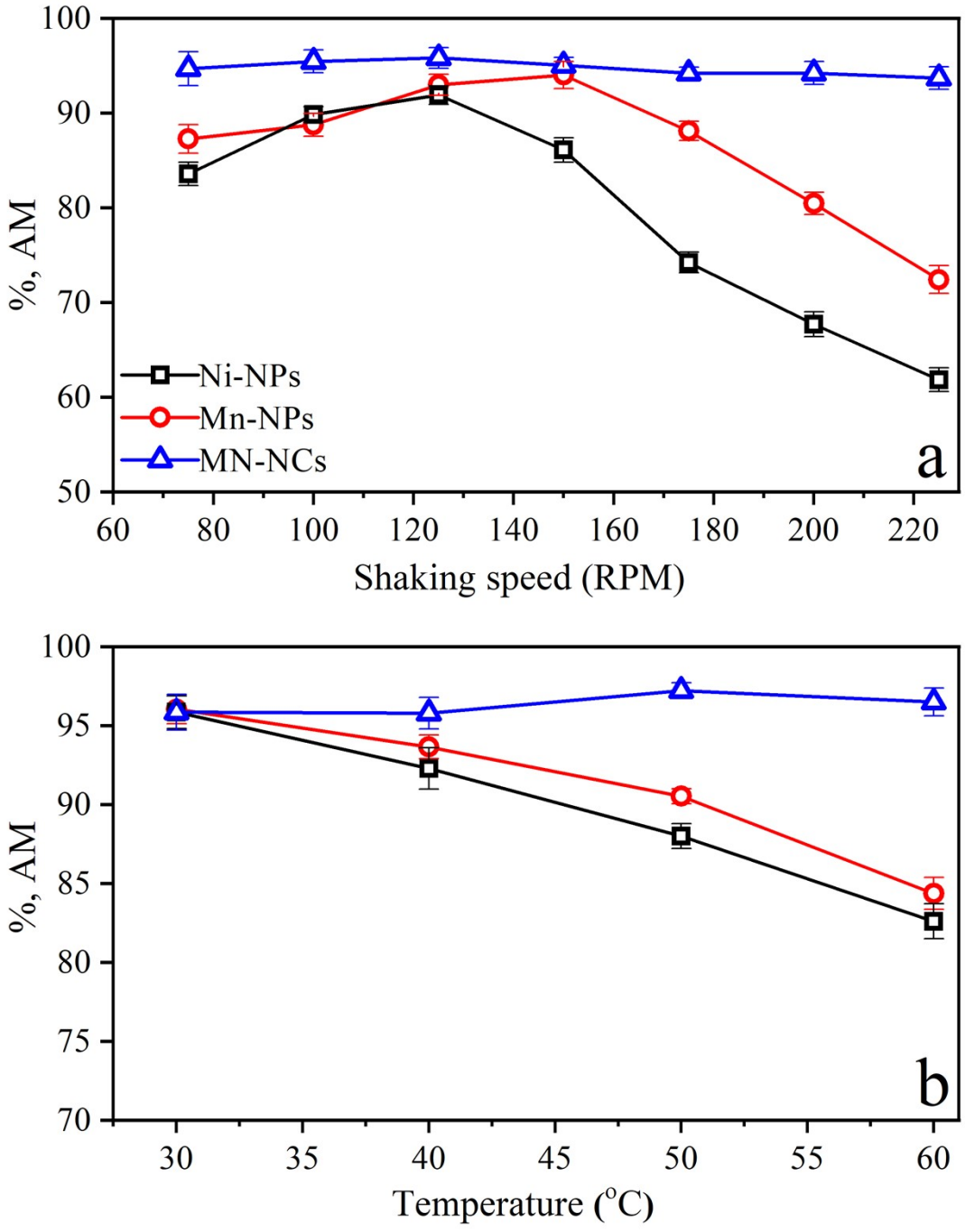

Figure S1. Effect of (a) shaking speed and (b) temperature on AM removal onto Ni-NPs, Mn-NPs, and MN-NCs

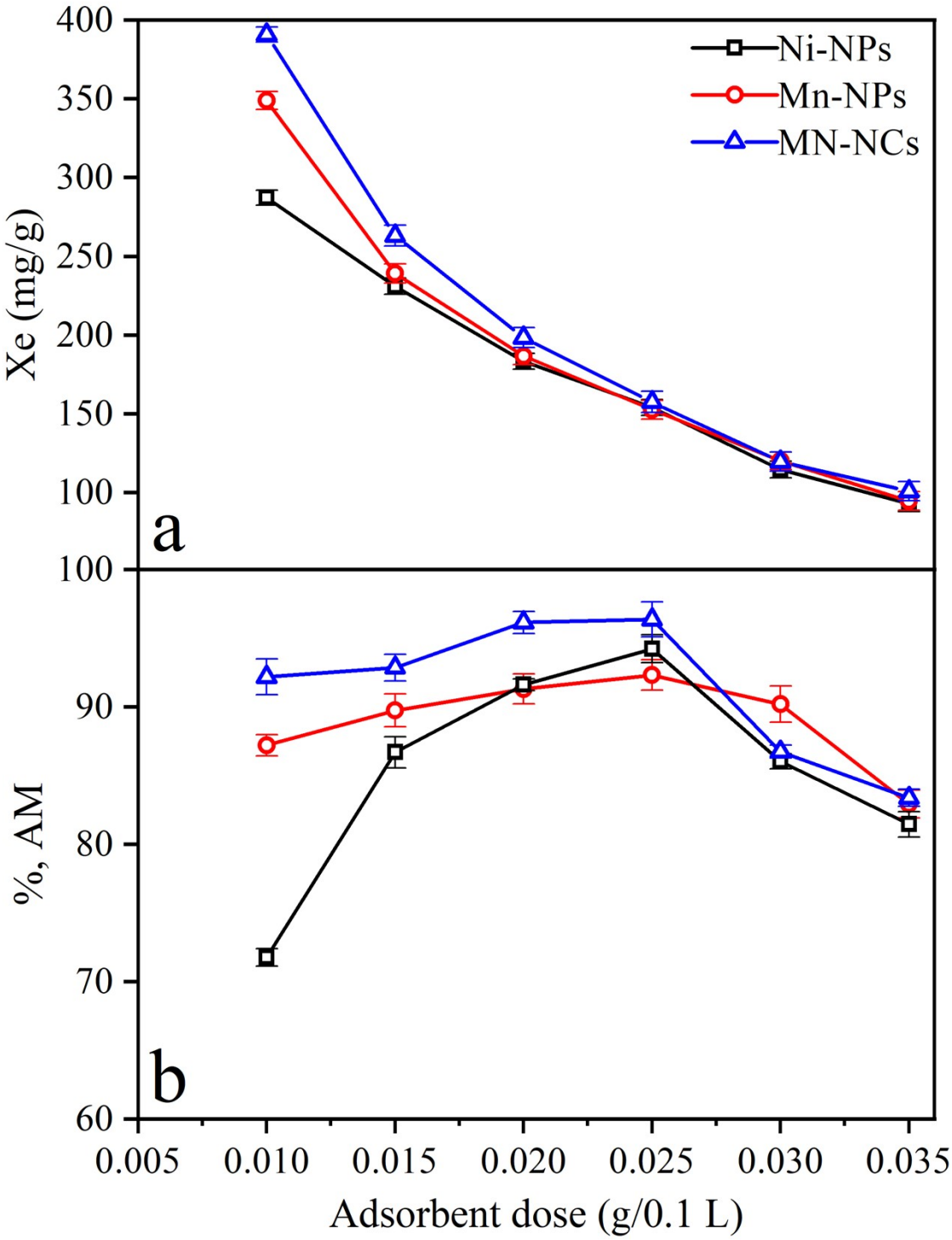

Figure S2. Effect of adsorbent dosage on AM removal onto Ni-NPs, Mn-NPs, and MN-NCs [(a) adsorption capacity and (b) %, AM removal]

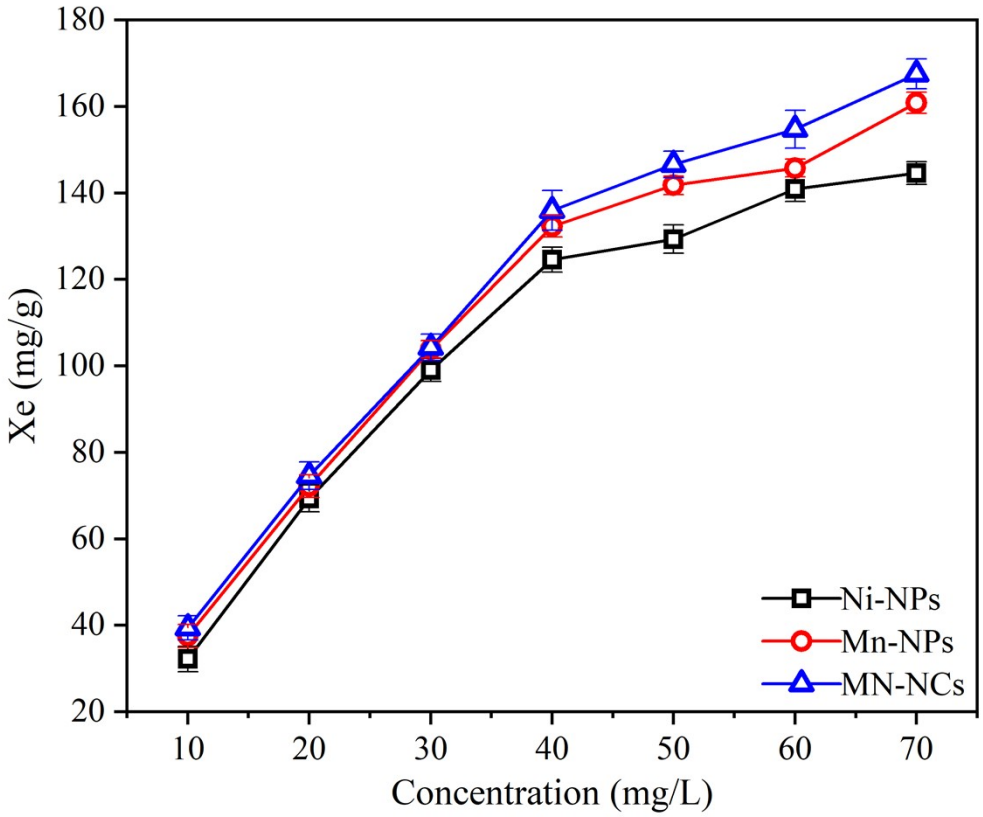

Figure S3. Effect of AM initial concentration on AM removal onto Ni-NPs, Mn-NPs, and MN-NCs

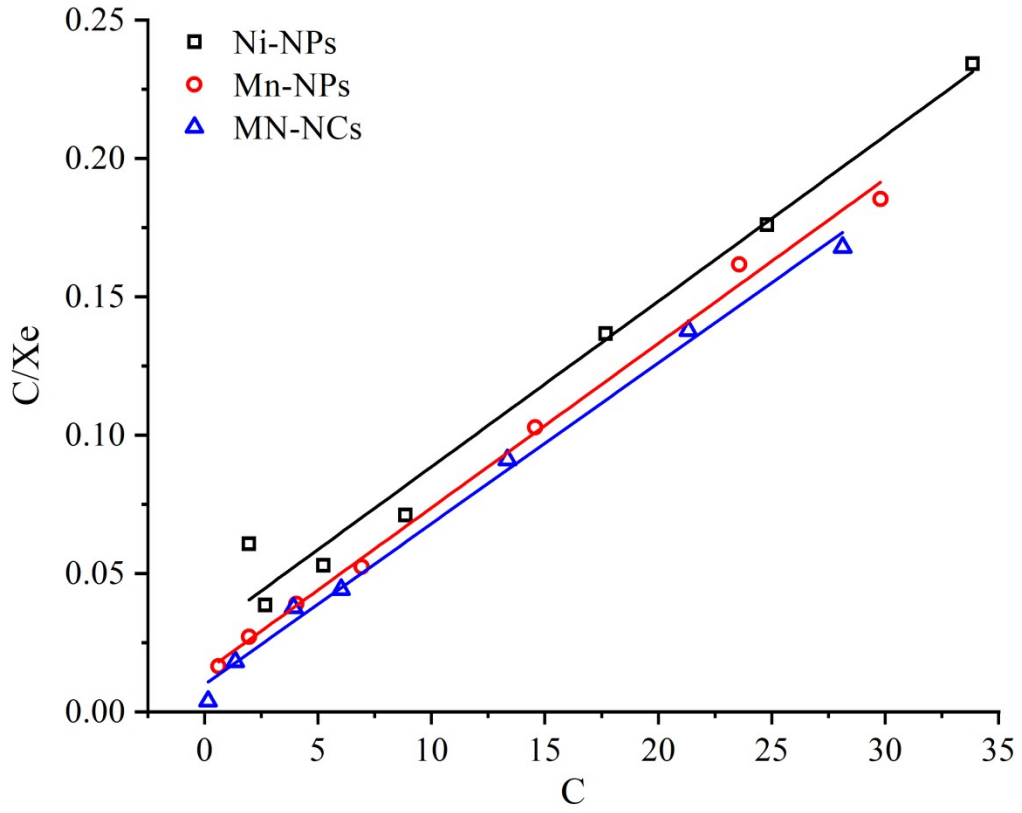

Figure S4. Langmuir isotherm model for AM removal onto Ni-NPs, Mn-NPs, and MN-NCs

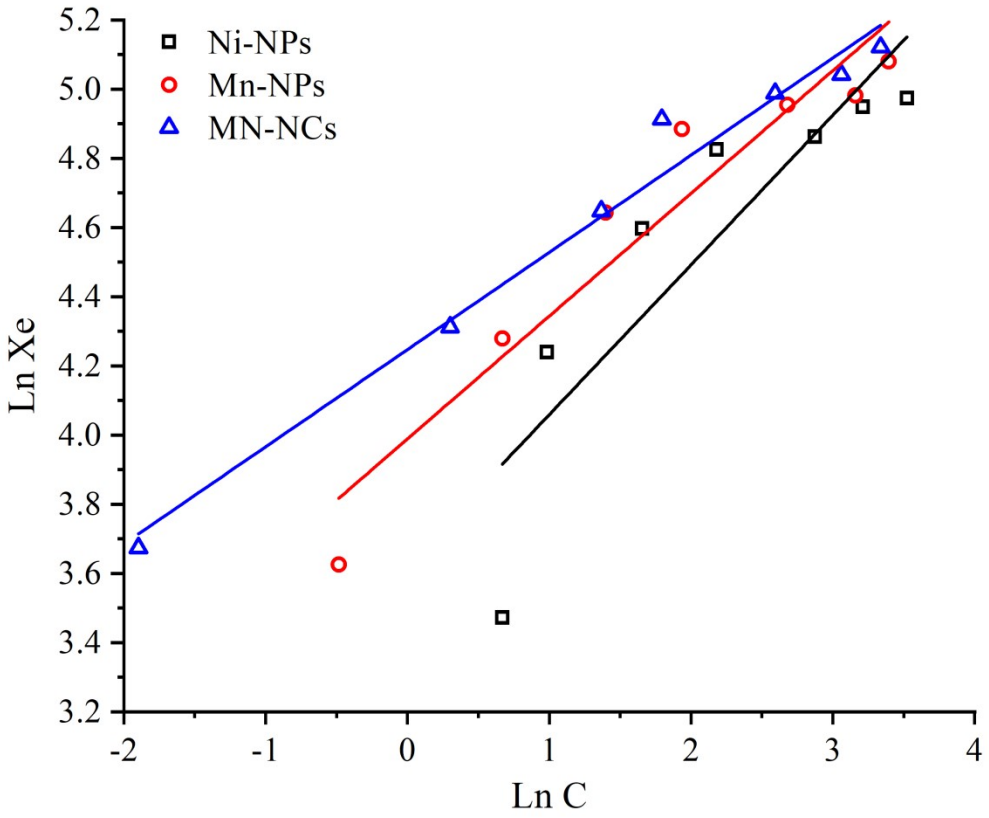

Figure S5. Freundlich isotherm model for AM removal onto Ni-NPs, Mn-NPs, and MN-NCs

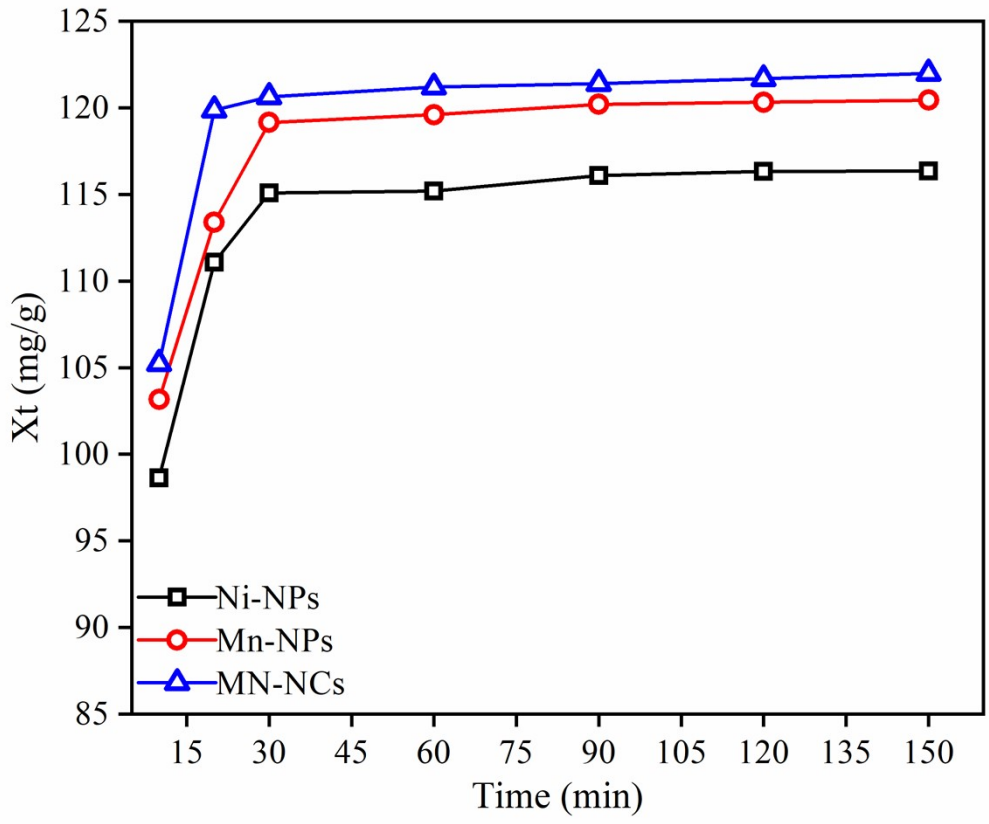

Figure S6. Effect of time on AM removal onto Ni-NPs, Mn-NPs, and MN-NCs

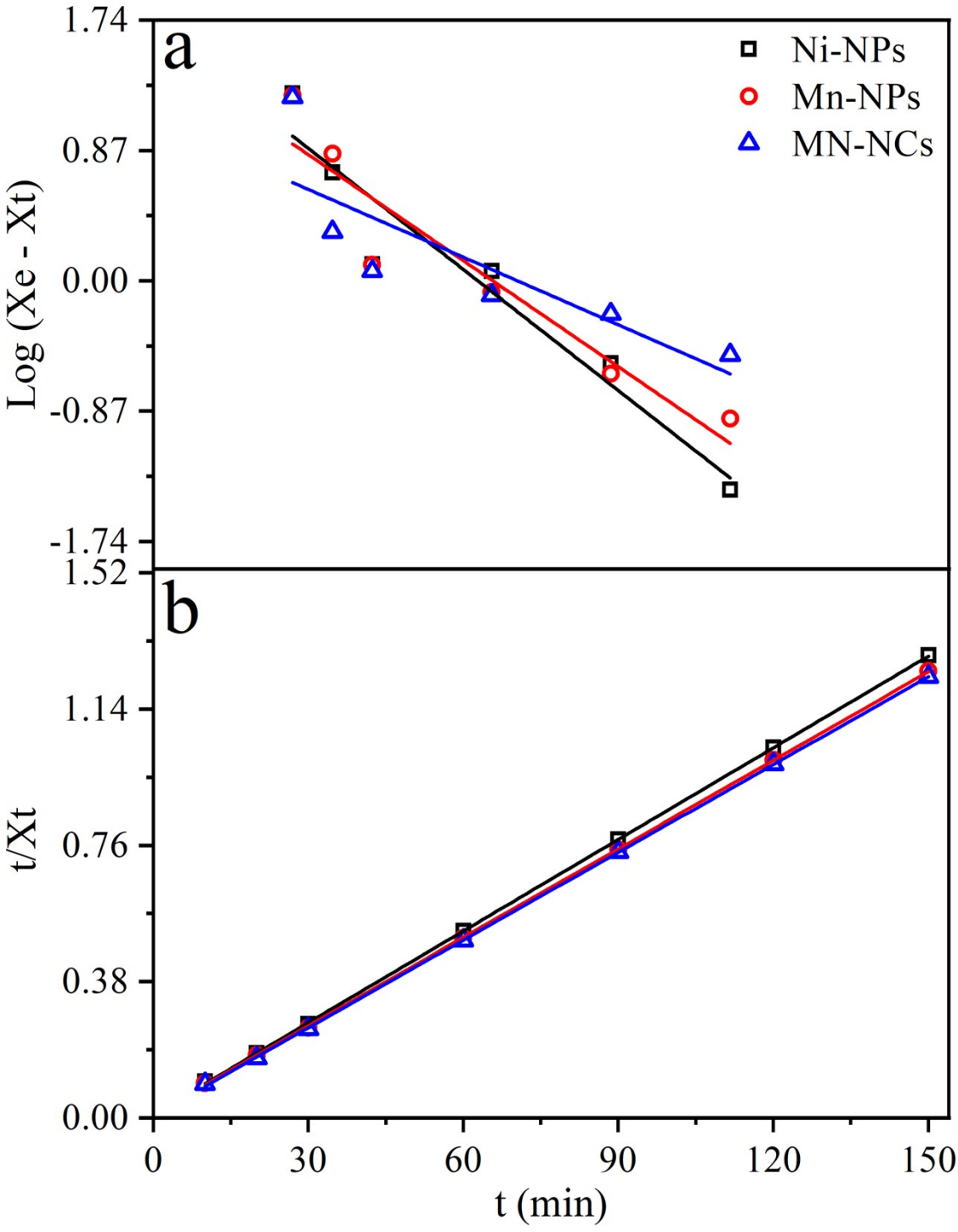

Figure S7. Pseudo first order (a), and pseudo second order (b) model for AM removal onto Ni-NPs, Mn-NPs, and MN-NCs

Section S1. DFT methodology

The geometry optimization and excited-state calculations were performed by B3LYP-D3(BJ) level exchange-correlation functional with the def2-tzvp basis set based on ORCA 5.0.3. Frequency calculations were performed to ensure that the stable configuration has no imaginary frequencies.

In addition, **AM** are both synthesized in water solution. Therefore, the SMD model, a continuum solvation model based on the quantum mechanical charge density of a solute molecule interacting with a continuum description of the solvent, is adopted to take water effects into account.

All structures and isosurfaces were visualized by VMD 1.9.3. Fukui function is an important concept in the conceptual density functional theory (CDFT),5which has been widely used to predict the regioselectivity of electrophilic, nucleophilic, and radical attack.6 Therefore, Hirshfeld charges, condensed Fukui functions of nucleophilic (f+), electrophilic (f-), radical attack (f0) and condensed dual descriptors (CDD), the HOMO, the LUMO and surface electrostatic potential (ESP) of 2-MBT were calculated with Multiwfn 3.8 at B3LYP/6-31G(d) level and drawn by VMD (1.9.3 version).7Specifically, Fukui function is defined as:

$$f(r) = [\frac{\partial \mu}{\partial v(r)}]_N = [\frac{\partial \rho(\mathrm{r})}{\partial N}]_{v(r)}$$

where ρ(r) is the electron density at a point r in space, N is the number of electrons and the constant term ν in the partial derivative is the external potential. The f $^{-}$, f +, f 0 and CDD can be calculated by:

Nucleophilic attack: $f_{\mathrm{A}}^{+} = q_N^{\mathrm{A}} - q_{N+1}^{\mathrm{A}}$

Electrophilic attack: $f_{\mathrm{A}}^{-} = q_{N-1}^{\mathrm{A}} - q_N^{\mathrm{A}}$

Radical attack: $f_{\mathrm{A}}^{0} = \left(q_{N-1}^{\mathrm{A}} - q_{N+1}^{\mathrm{A}}\right)/2$

Condensed dual descriptor:where qA is the atom charge of atom A at the corresponding state.

Table S1. Structural properties of all atoms in AM in reference of their electrophlicity, nucleophilicity, and CDD values

Atom	q(N)	q(N+1)	q(N-1)	f-	F+	F 0	CDD
1(C)	-0.0283	-0.0690	0.0148	0.0431	0.0407	0.0419	-0.0024
2(C)	-0.0024	-0.0151	0.0112	0.0136	0.0127	0.0132	-0.0008
3(C)	-0.0028	-0.0210	0.0112	0.0140	0.0182	0.0161	0.0041
4(C)	0.0287	-0.0005	0.0671	0.0384	0.0292	0.0338	-0.0092
5(C)	-0.0363	-0.0872	0.0174	0.0537	0.0509	0.0523	-0.0028
6(C)	-0.0293	-0.0572	0.0050	0.0243	0.0280	0.0261	0.0037
7(C)	-0.0450	-0.0584	-0.0108	0.0342	0.0135	0.0238	-0.0207
8(C)	-0.0384	-0.0616	-0.0027	0.0358	0.0232	0.0295	-0.0125
9(C)	-0.0358	-0.0520	-0.0078	0.0280	-0.0163	0.0221	-0.0117
10(C)	-0.0507	-0.0677	-0.0131	-0.0376	0.0170	0.0273	-0.0207
11(S)	0.4347	0.4240	0.4435	0.0088	0.0107	0.0098	0.0020
12(O)	-0.3586	-0.3679	-0.3484	0.0102	0.0093	0.0097	-0.0009
13(O)	-0.4041	-0.4188	-0.3870	0.0170	0.0147	0.0159	-0.0023
14(O)	-0.3678	-0.3796	-0.3543	0.0135	0.0119	0.0127	-0.0016
15(Na)	0.6695	0.6627	0.6764	0.0069	0.0068	0.0069	-0.0002
16(N)	-0.0787	-0.1824	-0.0028	0.0759	0.1037	0.0898	0.0278
17(N)	-0.0374	-0.1304	0.0287	0.0662	0.0929	0.0796	0.0268
18(C)	0.0077	-0.0183	0.0498	0.0420	0.0260	0.0340	-0.0160
19(C)	0.0912	0.0464	0.1308	0.0396	0.0448	0.0422	0.0052
20(C)	-0.0439	-0.0652	-0.0319	0.0120	0.0214	0.0167	0.0094
21(C)	-0.0031	-0.0650	0.0354	-0.0386	0.0619	0.0502	0.0233
22(C)	-0.0003	-0.0164	0.0131	0.0133	0.0162	0.0148	0.0029
23(C)	0.0095	-0.0139	0.0220	0.0125	0.0234	0.0180	0.0109
24(C)	-0.0374	-0.0524	-0.0159	0.0215	0.0150	0.0183	-0.0065
25(C)	-0.0249	-0.0491	-0.0045	0.0204	0.0242	0.0223	0.0039
26(C)	-0.0364	-0.0482	-0.0211	0.0153	0.0118	0.0135	-0.0035
27(C)	-0.0210	-0.0392	-0.0028	0.0182	0.0182	0.0182	-0.0000
28(O)	-0.1957	-0.2298	-0.1556	0.0400	0.0341	0.0371	-0.0060
29(S)	0.4435	0.4369	0.4484	0.0048	0.0066	0.0057	0.0018
30(S)	0.4269	0.4231	0.4311	0.0042	0.0038	0.0040	-0.0005
31(O)	-0.3456	-0.3554	-0.3378	0.0078	0.0097	0.0088	0.0019
32(O)	-0.3465	-0.3551	-0.3392	0.0073	0.0087	0.0080	0.0014
33(O)	-0.3789	-0.3835	-0.3739	0.0050	0.0045	0.0048	-0.0005
34(O)	-0.3992	-0.4041	-0.3934	0.0058	0.0049	0.0054	-0.0008
35(O)	-0.3785	-0.3830	-0.3734	0.0051	0.0045	0.0048	-0.0006
36(O)	-0.3647	-0.3733	-0.3579	0.0068	0.0086	0.0077	0.0017
37(Na)	0.6794	0.6727	0.6839	0.0045	0.0067	0.0056	0.0022
38(Na)	0.6638	0.6606	0.6670	0.0032	0.0032	0.0032	-0.0000
39(H)	0.0530	0.0282	0.0765	0.0235	0.0248	0.0242	0.0014
40(H)	0.0519	0.0381	0.0651	0.0132	0.0138	0.0135	0.0006
41(H)	0.0357	0.0251	0.0508	0.0150	0.0106	0.0128	-0.0044

42(H)	0.0540	0.0435	0.0694	0.0154	0.0105	0.0130	-0.0049
43(H)	0.0552	0.0469	0.0685	0.0134	0.0083	0.0108	-0.0051
44(H)	0.0298	0.0220	0.0435	0.0137	0.0078	0.0107	-0.0059
45(H)	0.0676	0.0447	0.0816	0.0141	0.0229	0.0185	0.0088
46(H)	0.0419	0.0293	0.0544	0.0125	0.0126	0.0125	0.0002
47(H)	0.0642	0.0540	0.0730	0.0088	0.0103	0.0095	0.0015
48(H)	0.0536	0.0445	0.0621	0.0085	0.0091	0.0088	0.0007
49(H)	0.1292	0.1180	0.1421	0.0129	0.0112	0.0120	-0.0017

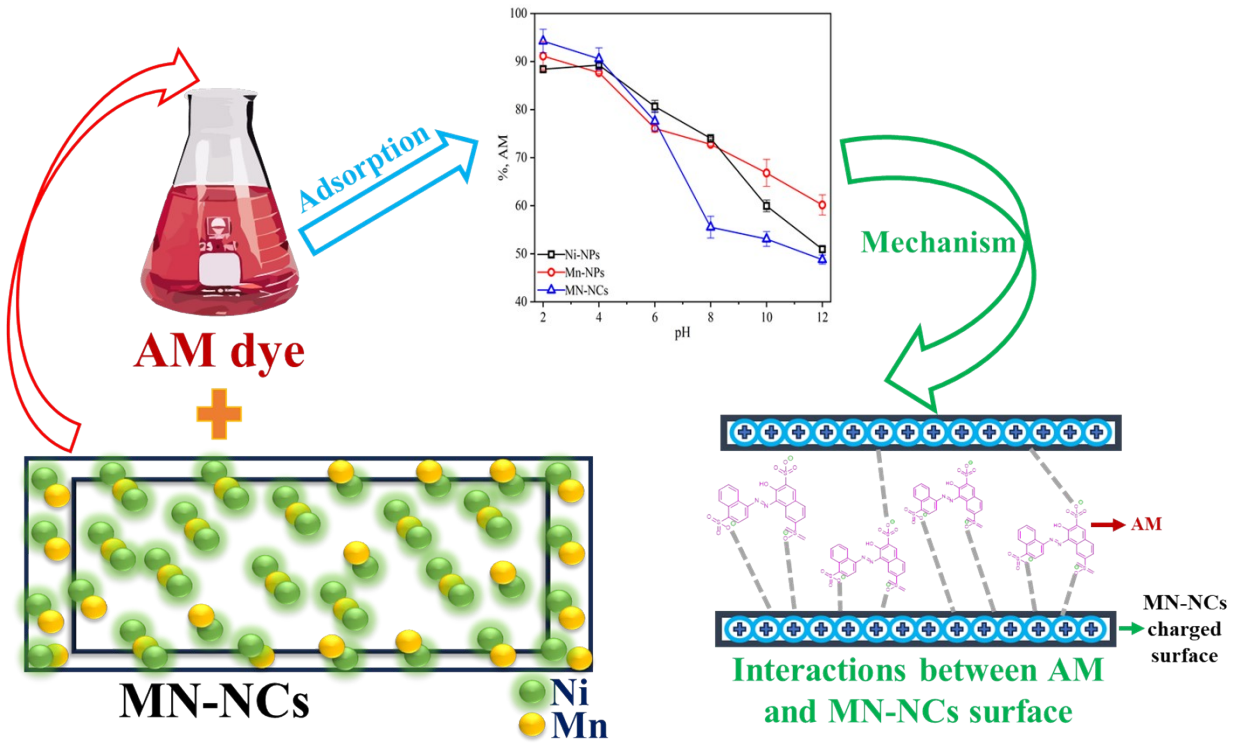

Figure S8. Possible adsorption mechanism of AM removal by MN-NCs