

Engineered SrSnFe₂O₄@ δ -MnO₂/Activated Biochar Heterocomposite with a Porous Surface for Efficient o-Nitrophenol Removal

Ahmed M. Abdelfatah^{1,*}, Mohamed E. El-Khouly², Abdelazeem S. Eltaweil³, Manal Fawzy¹

¹ Green Technology Group, Environmental Sciences Department, Faculty of Science, Alexandria University, Alexandria 21511, Egypt.

² Institute of basic and applied sciences Egypt-Japan University of Science and Technology, Egypt.

³ Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt.

*Corresponding author: AhmedMohamedFatah@alexu.edu.eg (A. M. Abdelfatah), ORCID ID: [0000-0002-3361-8320](https://orcid.org/0000-0002-3361-8320)

Text S1

Chemicals

Deionized water with a resistivity of 18.2 M Ω /cm, obtained from a Milli-Q system (Arioso Power II, Korea), was employed for the preparation of all aqueous solutions used throughout the experimental procedures. Ferric nitrate (Fe(NO₃)₃·9H₂O, > 98%), anhydrous tin chloride (SnCl₂, > 99.5%), Manganese sulfate (MnSO₄·4H₂O, 99.5%), strontium chloride (SrCl₂·6H₂O, > 99.5%), Potassium hydroxide (KOH, > 99.5%), and ortho nitrophenol (C₆H₅NO₃, > 99.5%) were purchased from Sigma-Aldrich Corporation, St. Louis, MO, USA. Sodium hydroxide (NaOH, 97%), ethanol (C₂H₅OH, 99.9%), and hydrochloric acid (HCl, 37%) were purchased from Merck, USA.

Text S2

Characterization of biochar nanocomposites

The prepared hybrid adsorbents were characterized by characterized by Scanning Electron Microscopy (SEM-S4800, Hitachi), X-ray Diffractometer (XRD-MAC Science M03XHF), Fourier Transform Infrared Spectrometer (FTIR-JASCO spectrometer over the range 4000-600 cm⁻¹), X-ray Photoelectron Spectroscopy (XPS-Thermoscientific ESCALAB 250Xi VG), Energy Dispersive X-ray Spectroscopy (EDX-JEOL model JSM-IT100), Zeta Potential analyzer

(Zetasizer Nano ZS Malvern), and Vibrating Sample Magnetometer (VSM; Lakeshore). The thermogravimetric properties of the biochar nanocomposites were carried out by thermogravimetry analyzer TGA SD600 with a Q500 TA software, (complies with UL 3101-1 CSA C22.2 number 1010.1, USA). The surface area and pore characteristics of the biochar nanocomposites were determined by nitrogen adsorption at 77 K using Accelerated Surface Area and Porosimetry System (Model: ASAP 2020, Norcross, GA, USA). Prior to the analysis, the samples were degassed at a temperature of 250 °C for 3 h, and Vibrating Sample Magnetometer (VSM; Lakeshore).

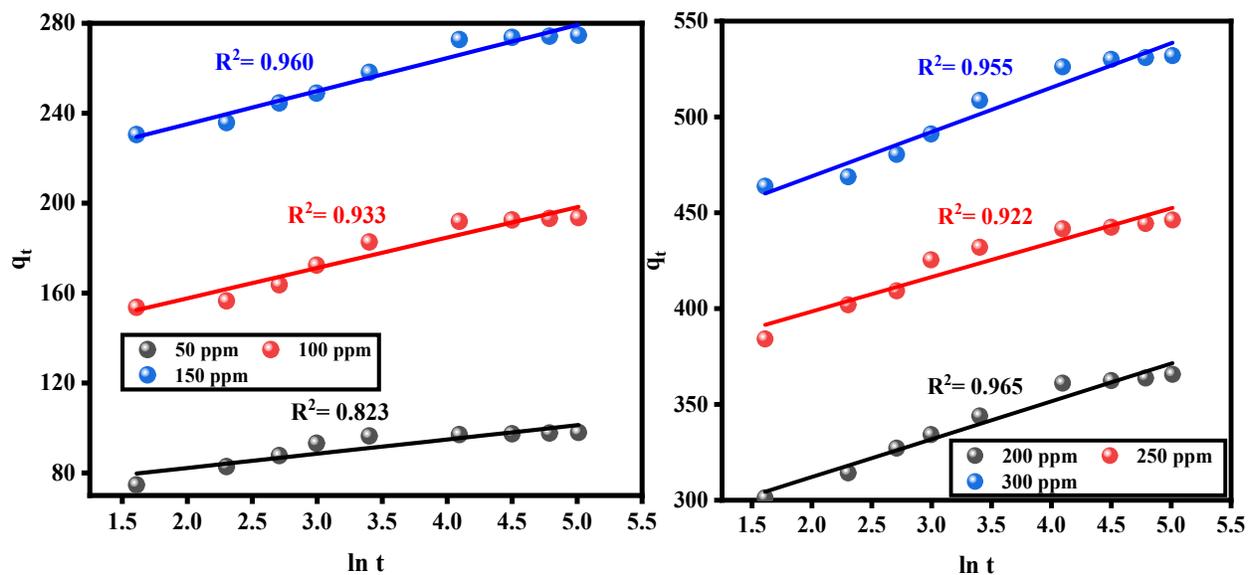


Fig. S1. Elovich model.

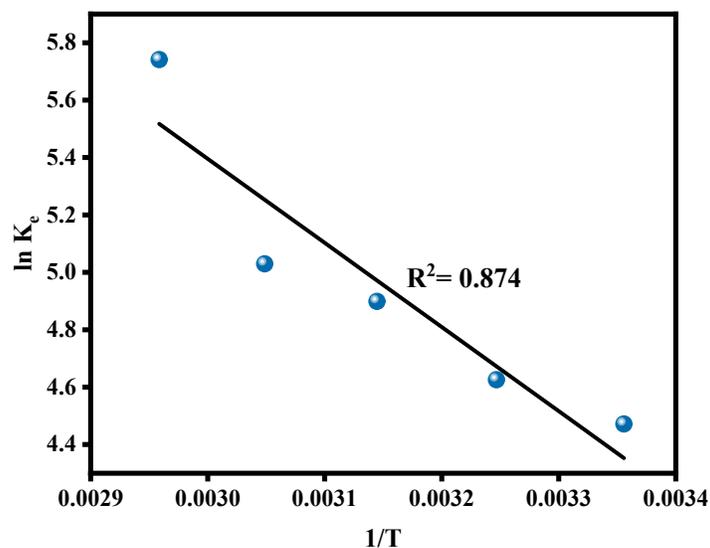


Fig. S2 . Van't Hoff's plot for adsorption of o-NP on SrSnFe₂O₄@σ-MnO₂/BC_{KOH} nanocomposite.

Table S1. XPS Peak-Fitting Parameters for Element Fe, Sn, Sr, and Mn.

Peak assignment	Binding energy (eV)	FWHM (eV)	Area (P) CPS. eV	Atomic %
Fe 2P _{3/2} (Fe ²⁺)	710	0.68	84.18	4.82
Fe 2P _{3/2} (Fe ³⁺)	711.5	3.37	408.7	23.41
Fe 2P ¹ / ₂ (Fe ²⁺)	724.8	3.37	361.82	20.95
Fe 2P ¹ / ₂ (Fe ³⁺)	725.9	3.37	408.7	18.1
Satellite 1	~719 eV	3.37	312.69	17.99
Sn 3d _{5/2} (Sn ²⁺)	486.85	3.28	88.14	10.6
Sn 3d _{5/2} (Sn ⁴⁺)	485.87	2.18	523.48	62.79
Sn 3d _{3/2} (Sn ²⁺)	495.56	1.29	188.39	22.71
Sn 3d _{3/2} (Sn ⁴⁺)	494.34	0.52	32.45	3.91
Sr 3d _{5/2} (Sr ²⁺)	131.97	0.9	165.89	14.87

Sr 3d _{5/2} (Sr ²⁺)	133.06	1.2	462.34	43.66
Sr 3d _{3/2} (Sr ²⁺)	134.18	2.54	486.48	41.47
Mn 2p _{3/2} (Mn ³⁺)	641.2	2.63	11473.5	42.67
Mn 2p _{3/2} (Mn ⁴⁺)	643.64	3.37	3647.35	13.59
Mn 2p _{1/2} (Mn ³⁺)	652.93	3.37	8247	30.92
Mn 2p _{1/2} (Mn ⁴⁺)	654.82	3.37	1089.92	4.08
Satellite	647	3.37	2338.58	8.74

Table S2. Equations of the applied adsorption kinetic models

Kinetic Model	Equation
PFO	$\ln (q_e - q_t) = \ln q_e - k_1 (t)$
PSO	$t/q_t = 1/k_2 q_e^2 + 1/q_e(t)$
Elovich model	$q_t = \frac{1}{\beta} \ln (\alpha\beta) + \frac{1}{\beta} \ln (t)$
Goodness of adsorption (Chi-square)	$\chi^2 = \sum \frac{(q_e, exp - q_e, cal.)^2}{q_e, cal}$

Where, q_t and q_e are the amount of the adsorbed phosphate ions at time t and equilibrium, respectively. k_1 and k_2 are the rate constants of PFO and PSO, respectively. α and β are Elovich coefficients that represent the initial adsorption rate and the desorption coefficient, respectively, also related to the extent of surface coverage and activation energy for chemisorption.

Table S3. Equations of the applied adsorption isotherm models

Model	Equation
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$
Temkin	$q_e = B \ln A + B \ln C_e$
D-R	$\ln q_e = \ln q_s - K_{ad} \varepsilon^2, \quad \varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$

Where, q_e and C_e are the adsorption capacity and the concentration of the un-adsorbed phosphate ions at equilibrium, respectively. q_m and K_L are the monolayer adsorption capacity and Langmuir constant, respectively. n and K_F are Freundlich constants. A is the equilibrium binding constant and $B = \frac{RT}{b}$, b is Temkin constant related to heat of adsorption. R is the gas constant (8.314 J/mol.K) and T is the absolute temperature. q_s is the saturation capacity, ε is the Polanyi potential and K_{ad} is a constant related to the mean free energy of adsorption per mole of the adsorbate.

Table S4. The summarized parameters of thermodynamic

Thermodynamic parameters	$\ln K_{e=}$ $\frac{\Delta S}{R} - \frac{\Delta H}{RT}$ $\Delta G = \Delta H - T\Delta S$
--------------------------	---

Where, $K_e = \frac{C_{Ae}}{C_e}$ is the thermodynamic equilibrium constant; C_e and C_{Ae} are the concentration of o-NP in the bulk solution and onto the surface of SrSnFe₂O₄@ σ -MnO₂/BC_{KOH} at equilibrium, respectively. R and RT are the gas constant and adsorption temperature, respectively.