

### Supplementary information for

## Zn<sup>2+</sup> removal from the aqueous environment using Polydopamine/Hydroxyapatite/Fe<sub>3</sub>O<sub>4</sub> magnetic composite under ultrasonic waves

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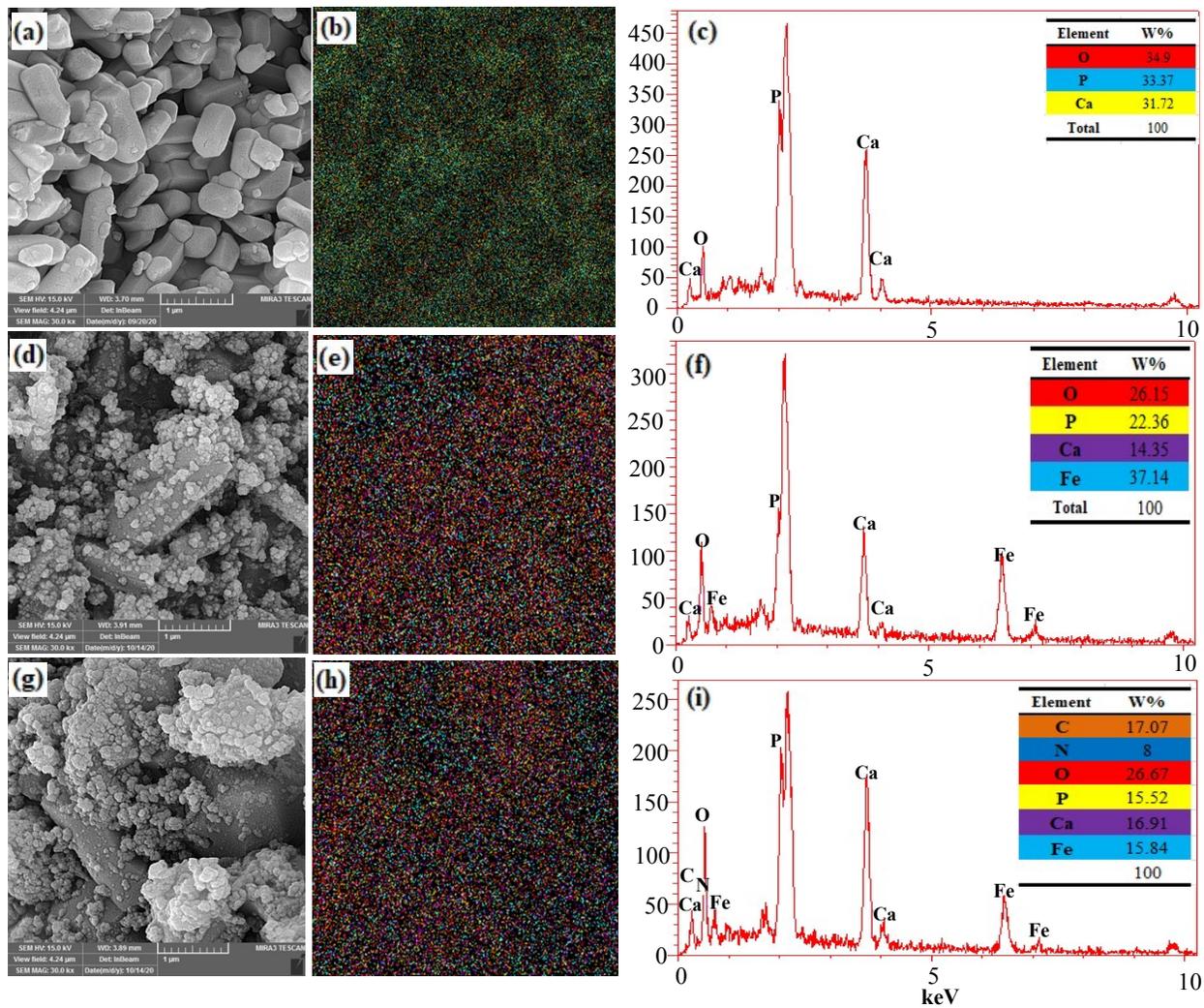
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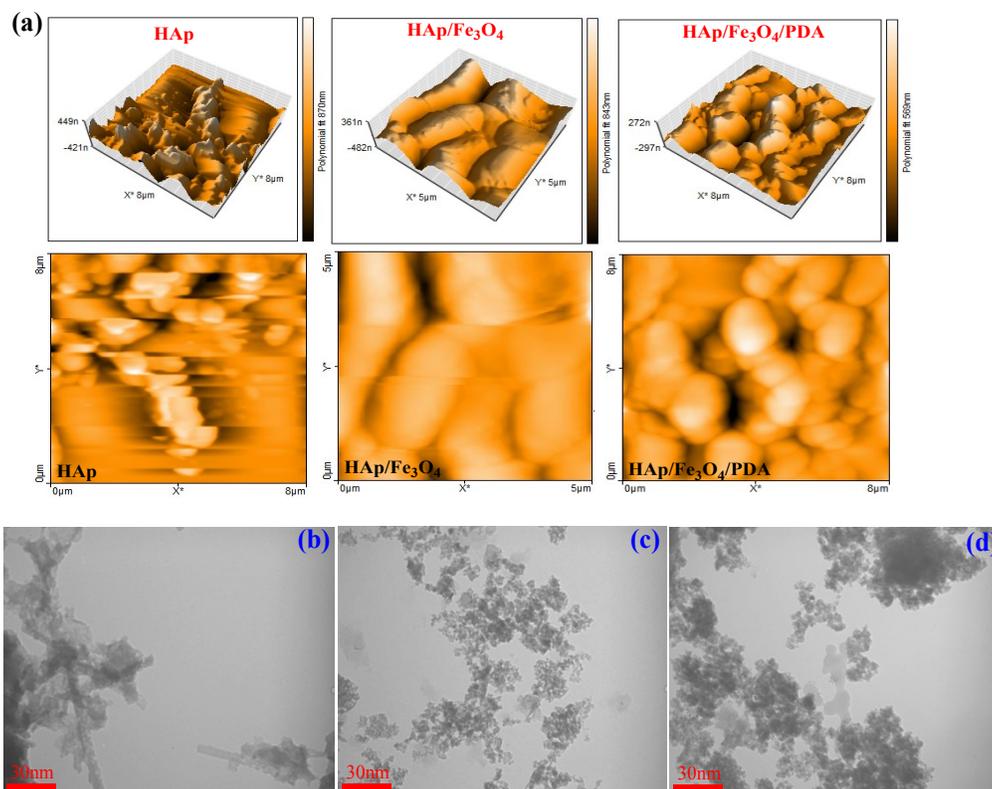
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### Content:

- SEM images and Map-EDX results.
- AFM and TEM images of HAp, HAp/Fe<sub>3</sub>O<sub>4</sub>, and HAp/Fe<sub>3</sub>O<sub>4</sub>/PDA magnetic composites.
- Independent variables in the Zn<sup>2+</sup> ions adsorption, actual removal percentage, predicted removal percentage, and the difference between them.
- ANOVA for Zn<sup>2+</sup> ions adsorption using RSM-CCD.
- Nonlinear relationship of PFO, PSO, and Elovich for Zn<sup>2+</sup> ions adsorption using PDA/HAp/Fe<sub>3</sub>O<sub>4</sub> magnetic composite, HAp/Fe<sub>3</sub>O<sub>4</sub> magnetic composite, and HAp.
- Linear relationship of intraparticle diffusion model for Zn<sup>2+</sup> adsorption process using adsorbents.
- Nonlinear relationship of isotherm models for Zn<sup>2+</sup> adsorption process using PDA/HAp/Fe<sub>3</sub>O<sub>4</sub> magnetic composite, HAp/Fe<sub>3</sub>O<sub>4</sub> magnetic composite, and HAp.
- Effect of Na<sup>+</sup> ion and effect of the number of adsorption/desorption steps on the efficiency of Zn<sup>2+</sup> ions adsorption process using produced adsorbents.



**Fig. S1.** SEM images and Map-EDX results of (a-c) HAP, (d-f) HAP/Fe<sub>3</sub>O<sub>4</sub> and (g-i) PDA/HAP/Fe<sub>3</sub>O<sub>4</sub> magnetic composites.



**Fig. S2.** (a) AFM and TEM images of (b) HAp, (c) HAp/Fe<sub>3</sub>O<sub>4</sub>, and (d) HAp/Fe<sub>3</sub>O<sub>4</sub>/PDA magnetic composites.

**Table S1.** Independent variables in the Zn<sup>2+</sup> ions adsorption, actual removal percentage, predicted removal percentage, and the difference between them.

Run	Factors					Adsorption Zn <sup>2+</sup> (%)			Run	Factors					Adsorption Zn <sup>2+</sup> (%)		
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	Exp. <sup>a</sup>	Pred. <sup>b</sup>	Res. <sup>c</sup>		X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	Exp. <sup>a</sup>	Pred. <sup>b</sup>	Res. <sup>c</sup>
1	200	4	10	30	0.8	90.73	91.02	-0.294	24	150	5	25	40	1	92.71	91.7	1.01
2	200	4	20	30	0.8	79.51	78.49	1.02	25	250	3	25	40	0.6	74.69	74.1	0.5891
3	250	3	15	20	1	85.94	84.47	1.47	26	150	5	15	20	0.6	82.81	82.77	0.0434
4	200	2	20	30	0.8	62.25	63.81	-1.56	27	200	4	20	30	0.8	78.13	78.49	-0.3633
5	250	3	15	40	0.6	83.37	82.75	0.6191	28	150	5	15	20	1	86.28	86.04	0.2391
6	250	5	15	40	1	98.68	99.86	-1.18	29	150	3	25	20	1	72.93	72.89	0.0446
7	150	3	15	40	1	84.58	84.43	0.1479	30	250	3	25	40	1	82.93	82.86	0.0674
8	200	4	20	10	0.8	79.15	80.14	-0.991	31	250	3	25	20	1	76.32	75.82	0.4991
9	150	5	15	40	1	94.52	93.08	1.44	32	150	3	25	40	0.6	71.36	71.17	0.1946
10	200	4	20	30	0.8	79.47	78.49	0.9767	33	250	5	15	40	0.6	93.72	93.59	0.1286
11	250	3	15	20	0.6	79.63	79.01	0.6234	34	150	5	25	20	0.6	82.44	81.39	1.05

12	250	5	15	20	1	93.86	93.12	0.7386	35	150	3	25	20	0.6	66.42	67.42	-1
13	150	3	15	40	0.6	75.52	75.67	-0.1504	36	200	4	20	50	0.8	89.28	90.93	-1.65
14	200	4	20	30	0.8	80.68	78.49	2.19	37	250	5	15	20	0.6	90.37	89.85	0.5229
15	150	3	15	20	0.6	72.86	71.93	0.9339	38	250	5	25	40	0.6	89.38	88.07	1.31
16	250	3	15	40	1	90.83	91.51	-0.6826	39	250	5	25	20	1	88.76	87.6	1.16
17	150	3	25	40	1	82.18	79.93	2.25	40	150	5	25	40	0.6	85.84	85.13	0.7091
18	100	4	20	30	0.8	80.38	81.38	-0.996	41	150	3	15	20	1	76.28	77.39	-1.11
19	250	3	25	20	0.6	71.61	70.36	1.25	42	200	4	20	30	1.2	82.79	84.51	-1.72
20	200	4	30	30	0.8	78.65	80.99	-2.34	43	250	5	25	40	1	94.67	94.64	0.0319
21	250	5	25	20	0.6	83.39	84.32	-0.9321	44	200	6	20	30	0.8	85.34	86.42	-1.08
22	200	4	20	30	0.4	70.38	72.48	-2.1	45	300	4	20	30	0.8	89.75	91.39	-1.64
23	150	5	25	20	1	83.74	84.66	-0.9209	46	150	5	15	40	0.6	86.26	86.51	-0.2509

<sup>a</sup> Experimental data    <sup>b</sup> Predicted value    <sup>c</sup> Residual

**Table S2.** ANOVA for Zn<sup>2+</sup> ions adsorption using RSM-CCD.

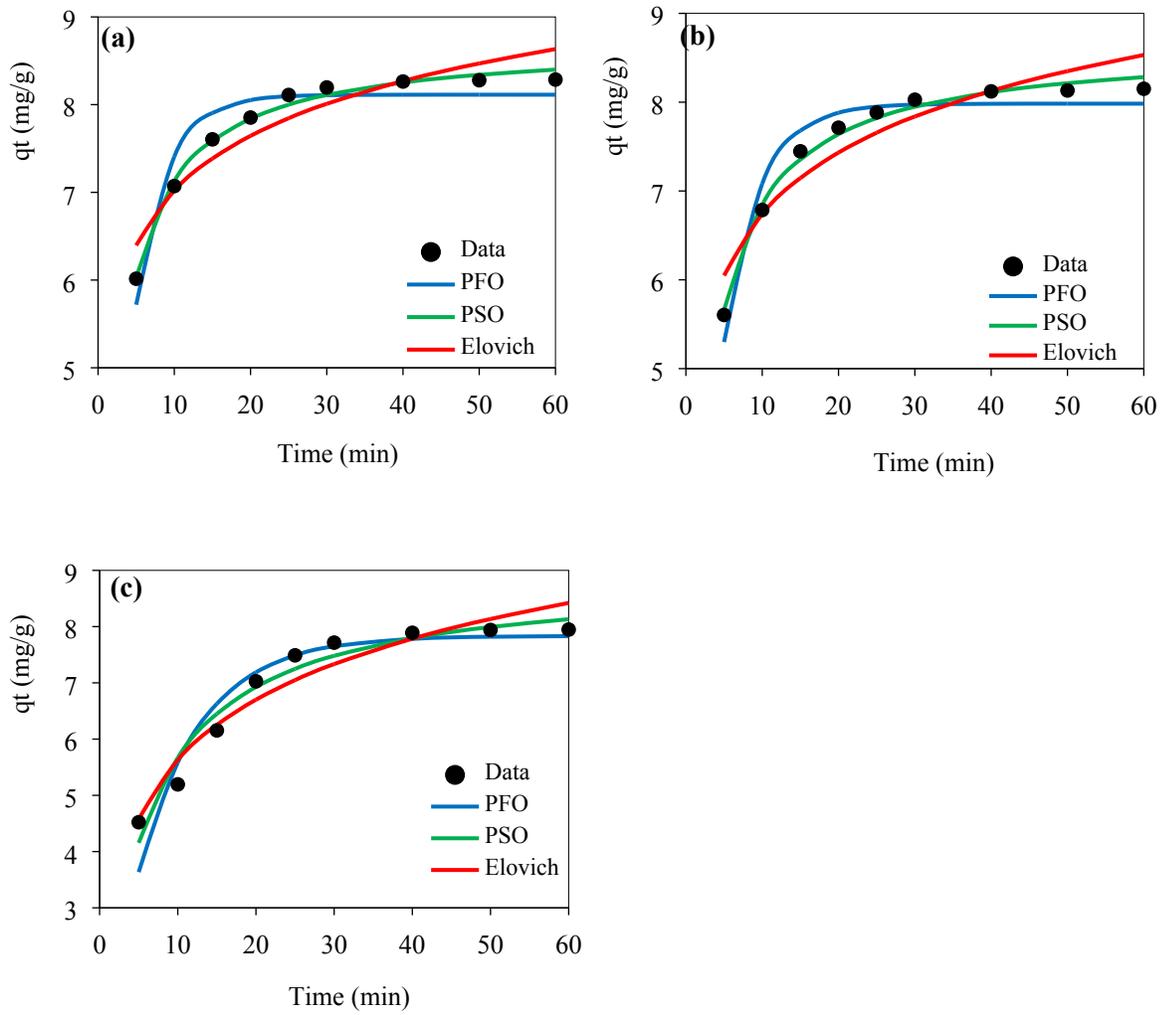
Source	Df <sup>a</sup>	Zn (II) Removal (%)				Source	Df <sup>a</sup>	Zn <sup>2+</sup> Removal (%)			
		SS <sup>b</sup>	MS <sup>c</sup>	F-value	P-value			SS <sup>b</sup>	MS <sup>c</sup>	F-value	P-value
Model	13	2810.83	216.22	138.61	< 0.0001	X <sub>4</sub> X <sub>5</sub>	1	21.75	21.75	13.94	0.0007
X <sub>1</sub>	1	250.8	250.8	160.78	< 0.0001	X <sub>1</sub> <sup>2</sup>	1	104.38	104.38	66.91	< 0.0001
X <sub>2</sub>	1	1278.71	1278.71	819.74	< 0.0001	X <sub>2</sub> <sup>2</sup>	1	22.61	22.61	14.49	0.0006
X <sub>3</sub>	1	231.84	231.84	148.63	< 0.0001	X <sub>3</sub> <sup>2</sup>	1	122.03	122.03	78.23	< 0.0001
X <sub>4</sub>	1	290.84	290.84	186.45	< 0.0001	X <sub>4</sub> <sup>2</sup>	1	82.58	82.58	52.94	< 0.0001
X <sub>5</sub>	1	362.16	362.16	232.17	< 0.0001	Residual	32	49.92	1.56		
X <sub>1</sub> X <sub>3</sub>	1	34.36	34.36	22.03	< 0.0001	Lack of Fit	29	46.66	1.61	1.48	0.4258
X <sub>2</sub> X <sub>3</sub>	1	19.53	19.53	12.52	0.0013	Pure Error	3	3.26	1.09		
X <sub>2</sub> X <sub>5</sub>	1	9.59	9.59	6.15	0.0186	Cor Total	45	2860.75			
Model Statistics											
Std. Dev. (SD): 1.25						R <sup>2</sup> : 0.9826					
Coefficient of Variance (C.V. %): 1.51						Adj-R <sup>2</sup> : 0.9755					
Adequate precision (Ap): 52.9839						Pred-R <sup>2</sup> : 0.9602					

<sup>a</sup> Degree of freedom

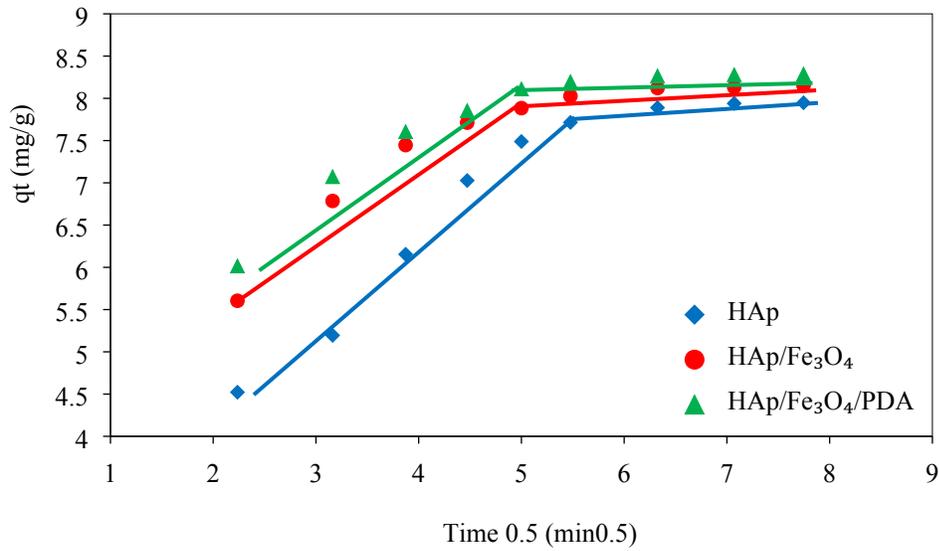
<sup>b</sup> Sum of Square

<sup>c</sup> Mean of Square

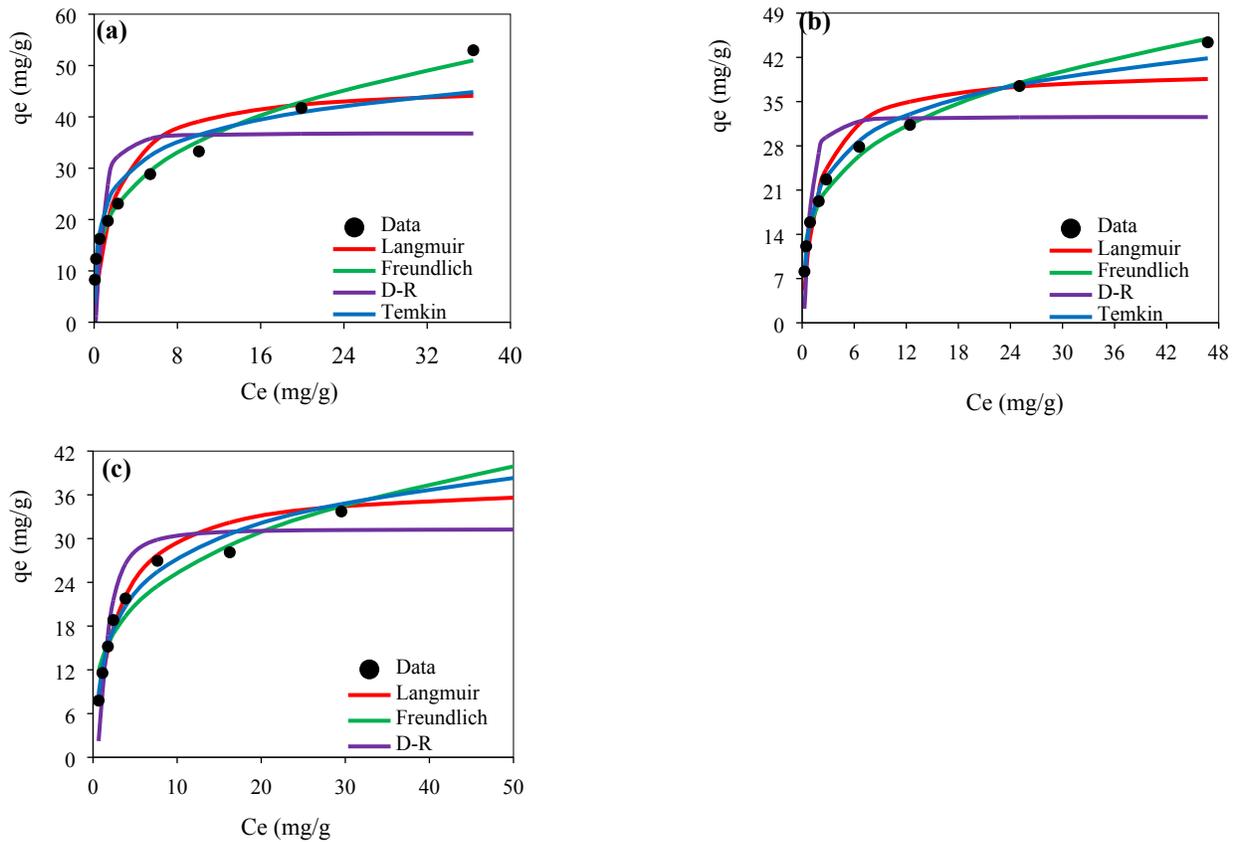
<sup>d</sup> Adequate precision



**Fig.S3.** Nonlinear relationship of PFO, PSO, and Elovich for Zn<sup>2+</sup> ions adsorption using (a) PDA/HAp/Fe<sub>3</sub>O<sub>4</sub> magnetic composite, (b) HAp/Fe<sub>3</sub>O<sub>4</sub> magnetic composite, and (c) HAp.



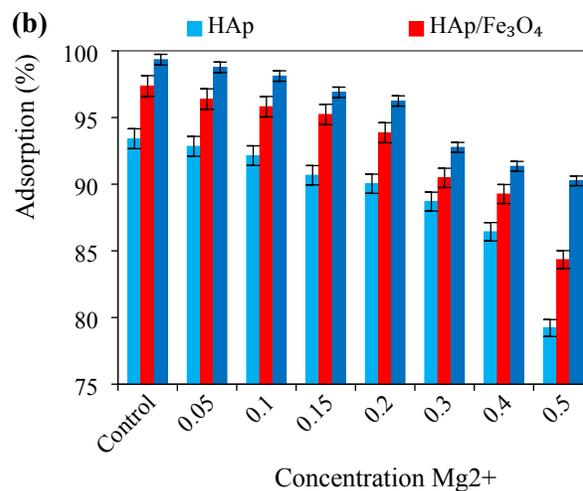
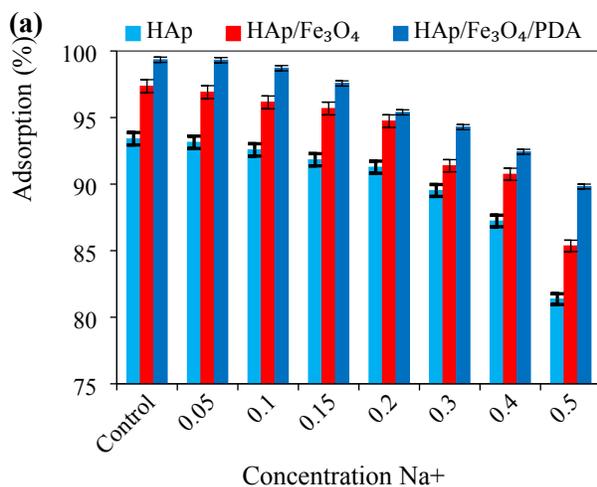
**Fig. S4.** Linear relationship of intraparticle diffusion model for  $Zn^{2+}$  adsorption process using adsorbents.

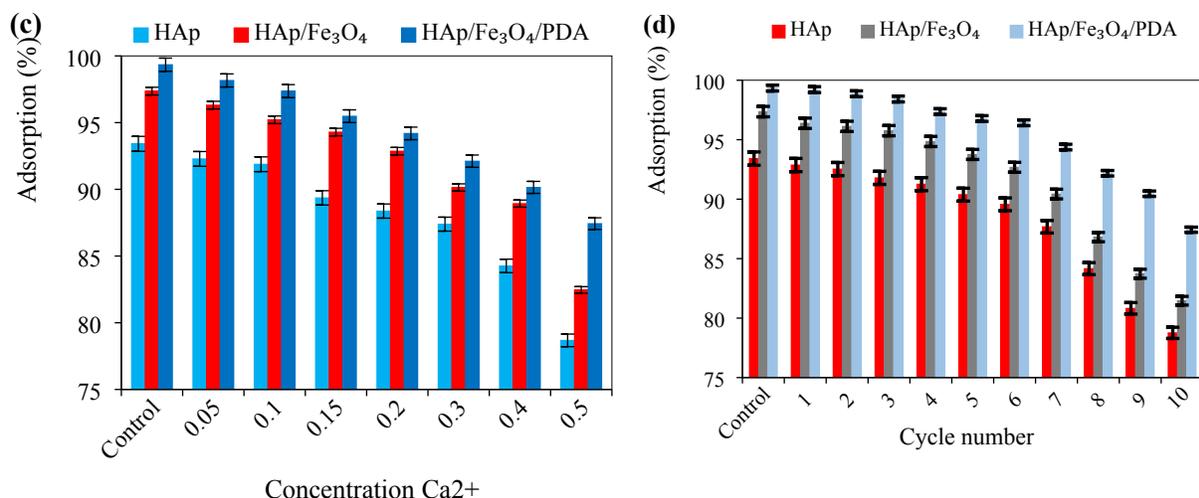


**Fig. S5.** Nonlinear relationship of isotherm models for  $Zn^{2+}$  adsorption process using (a) PDA/HAp/Fe<sub>3</sub>O<sub>4</sub> magnetic composite, (b) HAp/Fe<sub>3</sub>O<sub>4</sub> magnetic composite, and (c) HAp.

**Table S3.** Comparison of adsorption capacity of investigated adsorbents with other adsorbents used for Zn<sup>2+</sup> adsorption.

Adsorbent	q <sub>max</sub> (mg/g)	Reference
Chitosan/Hydroxyapatite/nano-Magnetite composite	6.497	1
watermelon rind	52.816	2
CSH-Mt	16.74	3
SiO <sub>2</sub>	9.107	4
MnFe <sub>2</sub> O <sub>4</sub> @CS-SiO <sub>2</sub> microsphere	60.13	5
muskmelon peel biochar	72.99	6
modified water hyacinth ( <i>Eichhornia crassipes</i> ) fibers	18.9	7
Li-Al HTlc	20.5-49.9	8
Bentonite clay	2.1	9
Mesoporous silica particles functionalized triethylenetetramine	13.6	10
waste-reclaimed material	0.106	11
Fe <sub>2</sub> O <sub>3</sub> @SBA-15 – CS – APTMS	100.47	12
granules prepared using sludge	1.23	13
HAp	37.57	Present work
HAp/Fe <sub>3</sub> O <sub>4</sub>	40.07	Present work
HAp/Fe <sub>3</sub> O <sub>4</sub> /PDA	46.37	Present work





**Fig. S6.** (a) Effect of Na<sup>+</sup> ion sand (b) effect of the number of adsorption/desorption steps on the efficiency of Zn<sup>2+</sup> ions adsorption process using produced adsorbents.

## References

1. A. Pooladi and R. Bazargan-Lari, *Journal of Materials Research and Technology*, 2020, **9**, 14841-14852.
2. Z. M. Shakor, H. H. Mahdi, F. Al-Sheikh, G. M. Alwan and T. Al-Jadir, *Materials Today: Proceedings*, 2021, **42**, 2502-2509.
3. G. Wang, H. Xiao, J. Zhu, H. Zhao, K. Liu, S. Ma, S. Zhang and S. Komarneni, *Environmental Research*, 2021, **201**, 111496.
4. M. Ahmed, M. Elektorowicz and S. W. Hasan, *Journal of Water Process Engineering*, 2019, **31**, 100815.
5. Z. Liu, G. Chen, F. Hu and X. Li, *Journal of Environmental Management*, 2020, **263**, 110377.
6. T. A. Khan, A. A. Mukhlif and E. A. Khan, *Egyptian Journal of Basic and Applied Sciences*, 2017, **4**, 236-248.
7. J. B. Neris, F. H. M. Luzardo, P. F. Santos, O. N. de Almeida and F. G. Velasco, *Journal of Environmental Chemical Engineering*, 2019, **7**, 102885.
8. L.-X. Zhao, J.-L. Liang, N. Li, H. Xiao, L.-Z. Chen and R.-S. Zhao, *Science of The Total Environment*, 2020, **716**, 137120.
9. M. Vhahangwele and G. W. Mugeru, *Journal of Environmental Chemical Engineering*, 2015, **3**, 2416-2425.
10. J. I. Lachowicz, G. R. Delpiano, D. Zanda, M. Piludu, E. Sanjust, M. Monduzzi and A. Salis, *Journal of Environmental Chemical Engineering*, 2019, **7**, 103205.
11. Y.-H. Jo, S.-H. Do and S.-H. Kong, *Journal of Environmental Chemical Engineering*, 2014, **2**, 619-625.

12. S. J. Mousavi, M. Parvini and M. Ghorbani, *Journal of the Taiwan Institute of Chemical Engineers*, 2018, **84**, 123-141.
13. X. Du, S. Cui, X. Fang, Q. Wang and G. Liu, *Journal of Environmental Chemical Engineering*, 2020, **8**, 104530.