Synthesis of Sustainable Guar gum-g-(Acrylic Acid-co-Acrylamide-co-3-Acrylamido Propanoic Acid) Interpenetrating Polymer Network via *in situ* Attachment of 3-Acrylamido Propanoic Acid for Analyzing Superadsorption Mechanism of Pb(II)/Cd(II)/Cu(II) and Dyes: Comparative Studies of Microstructures

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Fig. S1 ¹H-NMR of (a) AM, (c) AA and (e) MBA and ¹³C-NMR of (b) AM, (d) AA and (f) MBA

Adsorption isotherm models

Adsorption isotherm data were fitted to the following isotherm models

$$q_e = q_{\max} \frac{k_L C_e}{1 + k_L C_e}$$
(S1)

$$q_e = k_F C_e^{1/n} \tag{S2}$$

$$q_{e} = q_{BET} \frac{k_{1}C_{e}}{(1 - k_{2}C_{e})(1 - k_{2}C_{e} + k_{1}C_{e})}$$
(S3)

Here, k_L , k_F , k_1 and k_2 are the corresponding isotherm constants and q_{max} , n and q_{BET} are the corresponding isotherm parameters.

Adsorption kinetics study

Adsorption kinetics data were fitted to the following pseudosecond and pseudofirst order kinetics models.

$$q_t = q_e \left(1 - \frac{1}{1 + k_2 q_e t} \right) \tag{S4}$$

$$q_t = q_e [1 - \exp(-k_1 t)] \tag{S5}$$



Fig. S2 (a) Langmuir fitting for Pb(II), Cd(II), Cu(II) and (b) SF and (c) BET isotherm fitting for MB



Fig. S3 In k_2 vs. 1/T for (a) MB and SF and In k_d vs. 1/T plots for (b) SF and (c) MB



Fig. S4 Full scan kinetics data of MO adsorption at $pH_i = 2$

Dyes/M(II)	Name of the adsorbents	Adsorption capacities (mg g^{-1}) /pH/C ₀ (mg L ⁻¹)/temperature (K)	Ref.
MB	PNIPAAm ^a	8.50/6.5-6.7/10-50/298	S1
	PNIPAAm/IA ^b	17.52/6.5-6.7/10-50/298	S1
	PNIPAAm/IA/pumice	22.18/6.5-6.7/10-50/298	S1
	Cu-BTC ^c	15.28*/7.0/1–10#/298	S2
	BC-PM ^d microparticles	25/6.5/500/298	S3
	IPNS ^e	16.97/11.0/5-30/303	S4
	IPNS ^e	137.43/11.0/200-300/303	S4
	MIL-53(A1)-NH ₂ ^f	45.20/7.0/5/-	S5
	Br/Mo heterostructures	54.82/4.0/30-70/-	S6
	MCGO ^g	70.03/1.5-12.0/70/298	S7
	h-XG/SiO ₂ ^h	497.50/8.0/400/323	S8
	GGAAAMAPA	27.06/9.0/5-25/303	TS^
SF	AC ^j	1.32/5.0/25/298	S9
	Hydrogels prepared with sodium	9.45/-/10/-	S10
	polyacrylate and 6 wt. % of CM		
	CO ₂ neutralized activated red mud	9.77/8.3/37.3/302	S11
	Native SBP ^k	17.90/10.0/100/293	S12
	AC ^j	19.01/6.0/10/-	S13
	Pinapple peels	21.70/6.0/60/302	S14
	Cu-NWs-AC ¹	34.00/5.5/15/-	S15
	NaOH-treated rice husk	37.97/8.0/10/303	S16
	CuO-NPs ^m	53.67/12.0/154/303	S17
	PDA@SBP ⁿ	54.00/10.0/100/293	S12
	HDTMA ^o -modified Spirulina sp.	54.05/2.0/300/-	S18
	MIL-101(Cr)-SO₂H	70.80/6.2/50/-	S19
	Al-Mont-EnPILC ^p	76.13/10.0/100/295	S20
	SDS/RM ^q	89.40/4.0/50/308	521
	MDMLG ^r	137.53/12.0/105/-	S22
	GGAAAMAPA ⁱ	39.35/9.0/5–25/303	TS [^]
Pb(II)	Bare Malachite Nanoparticle	7.2/5.0–6.0/10–100/–	\$23
	Kaolinite	11.50/5.7/10–50/303	S24
	Jordanian kaolinite	13.32/5.0/50-400/295	S25
	Montmorillonite	31.10/5.7/10–50/303	S24
	Lemon peel	37.87/5.0/100–300/301	S26
	IPNS ^e	54.86/7.0/5-30/303	54
	APAN ^s	60.6/4.0/40–1000/303	S27
	GGAAAMAPA ⁱ	41.98/7.0/5–25/303	TS [^]
Cd(II)	RGO ^t -Fe(O)/Fe₂O₄	1.91/7.0/2-6/298	S28
	Dithiocarbamated-sporopollenin	7.09/7.0/15/293	529
	Dead T. viride	10.95/6.0/26/320	530
	BiOBr microsphere	11.70/7.0/29/298	S31
	Polyaniline grafted chitosan	12.87/6.0/20-40/303	S32
	GO ^u	14.90/5.6/-/-	533
	Garden grass	17 60/4 0/50/303	534
	Functionalized granhene (GNS ^{C8P})	30.05/6.2/-/-	535 535
	Si-DTC ^V	43 47/7 0/100/298	536
	GO-TIO	72 80/5 6/_/_	232
		12.00/3.0/-/-	222

	Functionalized graphene (GNS ^{PF6})	73.42/6.2/–/–	S35
	Dithiocarbamate-anchored	82.20/7.0/50/293	S37
	polymer/organosmectite composites		
	MGO ^w	91.29/6.0/200/298	S38
	Biomass of nonliving, dried brown	100.00/3.5/100/-	S39
	marine algae Sargassum natans,		
	Fucus vesiculosus, and Ascophyllum		
	nodosum		
	Polyvinyl alcohol-chelating sponge CS-co-MMB-co-PAA ^x GO ^u	125.11/5.5/560/293	S40
		135.51/4.5–5.5/300/–	S41
		167.50/6.0/-/333	S42
	Mesoporous MCM-41	210.96/7.0/250/298	S43
	ANMP derived from PCBs ^y	230.06/3.5/450/293	S44
	GGAAAMAPA ⁱ	40.55/7.0/5–25/303	TS^
Cu(II)	Copper-imprinted polymethacrylate	2.00/6.5/5-100/298	S45
	porous beads		
	Bare Malachite Nanoparticle	3.20/5.0-6.0/10-100/-	S23
	Cu(II) ion-imprinted poly(methacrylic	15.04/6.2/10/-	S46
	acid/vinyl pyridine) micro-particles		
	P(NIPAM-MA-VI) ^z	21.10/5.0/-/333	S47
	Cu(II)-imprinted poly(methacrylic	22.40/7.0/2.5-70/298	S48
	acid/vinyl pyridine) polymer		
	Fe ₃ O ₄ @SiO ₂ -Cu(II)-imprinted	24.20/7.0/80/298	S49
	polymer		
	Cu(II)-imprinted	35.20/1.0-6.0/40/298	S50
	poly(chitosan/attapulgite)		
	IPNS ^e	53.86/7.0/5-30/303	S4
	Lemon peel	70.92/5.0/100–300/301	S26
	GGAAAMAPA ⁱ	39.42/7.0/5–25/303	TS^

^apoly(N-isopropylacrylamide) hydrogel, ^bpoly (N-isopropylacrylamide)/itaconic acid composite hydrogel, ^cmetal-organic framework (MOF) based on copper-benzenetricarboxylate, ^dbiochar microparticles derived from pig manure, ^emetal-organic framework, ^finterpenetrating network superadsorbent, ^gmagnetic cellulose/graphene oxide composite, ^hHydrolyzed polyacrylamide grafted xanthan gum and its nanosilica composite, ⁱguar gum-g-(acrylic acid-co-acrylamide-co-3-acrylamido propanoic acid)^jactivated carbon, ^ksea buckthornbranchpowder, ⁱcopper nanowires loaded on activated carbon, ^msodium dodecyl sulphate/red mud, ⁿpolydopamine coated sea buckthornbranch powder, ^ohexadecyltrimethylammonium bromide, ⁿMulti-walled carbon nanotubes, ^qsodium dodecyl sulphate/red mud, ^rMgO decked multi-layered graphene, ^saminated polyacrylonitrile, ^treduced graphene oxide, ^ugraphene oxide, ^xsilica-supported dithiocarbamate adsorbent, ^wMagnetic graphene oxide, ^xa chitosan-based hydrogel, ^yactivated non-metallic Powder derived from printed circuit boards, ^zpoly(N-isopropylacrylamide-*co*maleic acid-*co*-1-vinylimidazole), [#]µ mol L⁻¹, ^{*}µ mol g⁻¹ and ^{*}this study.

REFERENCES

S1. B. Taşdelen, D. I. Çifçi and S. Meriç, Colloid Surface A, 2017, 519, 245–253.

S2. S. Lin, Z. Song, G. Che, A. Ren, P. Li, C. Liu and J. Zhang, Micropor. Mesopor. Mater., 2014, 193, 27-34.

S3. L. Lonappan, T. Rouissi, R. K. Das, S. K. Brar, A. A. Ramirez, M. Verma, R. Y. Surampalli and J. R. Valero, *Waste Manage.*, 2016, **49**, 537–544.

S4. N. R. Singha, M. Karmakar, M. Mahapatra, H. Mondal, A. Dutta, C. Roy and P. K. Chattopadhyay, *Polym. Chem.*, 2017, **8**, 3211–3237.

S5. C. Li, Z. Xiong, J. Zhang and C. Wu, J. Chem. Eng. Data, 2015, 60, 3414–3422.

- S6. D. Wang, H. Shen, L. Guo, C. Wang and F. Fu, ACS Omega, 2016, 1, 566–577.
- S7. H. Shi, W. Li, L. Zhong and C. Xu, Ind. Eng. Chem. Res., 2014, 53, 1108–1118.
- S8. S. Ghorai, A. Sarkar, M. Raoufi, A. B. Panda, H. Schönherr and S. Pal, ACS Appl. Mater. Interfaces, 2014, 6, 4766–4777.
- S9. M. Ghaedi, S. Haghdoust, S. Nasiri Kokhdan, A. Mihandoost, R. Sahraie and A. Daneshfar, *Spectrosc. Lett.*, 2012, **45**, 500–510.
- S10. B. Mandal and S. K. Ray, J. Taiwan Inst. Chem. E., 2015, 60, 1–15.
- S11. M. K. Sahu, U. K. Sahu and R. K. Patel, RSC Adv., 2015, 5, 42294–42304.
- S12. X. Xu, B. Bai, H. Wang and Y. Suo, J. Phys. Chem. Solids, 2015, 87, 23-31.
- S13. F. Nasiri Azad, M. Ghaedi, K. Dashtian, S. Hajati, A. Goudarzi and M. Jamshidi, *New J. Chem.*, 2015, **39**, 7998–8005.
- S14. M. A. Mohammed, A. Ibrahim and A. Shitu, Int. J. Environ. Monit. Anal., 2014, 2, 128–133.
- S15. M. Roosta, M. Ghaedia and A. Asfaram, RSC Adv., 2015, 5, 57021–57029.
- S16. S. Chowdhury, R. Mishra, P. Kushwaha and P. Saha, Asia-Pac. J. Chem. Eng., 2012, 7, 236–249.
- S17. R. Wahab, F. Khan, N. K. Kaushik, J. Musarrat and A. A. Al-Khedhairy, Sci. Rep., 2017, 7, 1–15.
- S18. U. A. Guler, M. Ersan, E. Tuncel and F. Dügenci, Process Saf. Environ., 2016, 99, 194–206.
- S19. X. Zhao, K. Wang, Z. Gao, H. Gao, Z. Xie, X. Du and H. Huang, Ind. Eng. Chem. Res., 2017, 56, 4496–4501.
- S20. R. Tovar-Gómez, D. A. Rivera-Ramírez, V. Hernández-Montoya, A. Bonilla-Petriciolet, C.J. Durán-Valle and M. A.
- Montes-Morán, J. Hazard. Mater., 2012, 199-200, 290-300.
- S21. M. K. Sahu and R. K. Patel, *RSC Adv.*, 2015, **5**, 78491–78501.
- S22. N. K. Rotte, S. Yerramala, J. Boniface and V. V. S. S. Srikanth, Chem. Eng. J., 2014, 258, 412–419.
- S23. B. Saha, S. Chakraborty and G. Das, J. Phys. Chem. C, 2010, 114, 9817-9825.
- S24. S. S. Gupta and K. G. Bhattacharyya, J. Environ. Manag., 2008, 87, 46–58.
- S25. M. Al-Harahsheh, R. Shawabkeh, A. Al-Harahsheh, K. Tarawneh, M. M. Batiha, Appl. Surf. Sci., 2009, 255, 8098–8103.
- S26. M. Thirumavalavan, Y. Lai, L. Lin and J. Lee, J. Chem. Eng. Data, 2010, 55, 1186–1192.
- S27. P. Kampalanonwat, P. Supaphol, ACS Appl. Mater. Interfaces, 2010, 2, 3619–3627.
- S28. P. Bhunia, G. Kim, C. Baik and H. Lee, Chem. Commun., 2012, 48, 9888–9890.
- S29. N. Ünlü and M. Ersoz, Sep. Purif. Technol., 2007, 52, 461–469.
- S30. R. M. Hlihor, M. Diaconu, F. Leon, S. Curteanu, T. Tavares and M. Gavrilescu, N. biotechnol., 2015, 32, 358–368.
- S31. X. Wang, W. Liu, J. Tian, Z. Zhao, P. Hao, X. Kang, Y. Sang and H. Liu, J. Mater. Chem. A, 2014, 2, 2599–2608.
- S32. R. Karthik and S. Meenakshi, Chem. Eng. J., 2015, 263, 168–177.
- S33. Y. C. Lee and J. W. Yang, J. Ind. Eng. Chem., 2012, 18, 1178–1185.
- S34. A. H. Sulaymon, A. A. Mohammed and T. J. Al-Musawi, Int. J. Chem. Reac. Eng., 2014, 12, 477–486.
- S35. X. Deng, L. Lü, H. Li and F. Luo, J. Hazard. Mater., 2010, 183, 923–930.

S36. L. Bai, H. P. Hu, W. Fu, J. Wan, X. Cheng, L. Zhuge, L. Xiong and Q. Chen, *J. Hazard. Mater.*, 2011, **195**, 261–275.
S37. R. Say, E. Birlik, A. Denizli and A. Ersöz, *Appl. Clay Sci.*, 2006, **31**, 298–305.

S38. J. H. Deng, X. R. Zhang, G. M. Zeng, J. L. Gong, Q. Y. Niu and J. Liang, *Chem. Eng. J.*, 2013, **226**, 189–200.

- S39. Z. R. Holan, B. Volesky and I. Prasetyo, *Biotechnol. Bioeng.*, 1993, 41, 819–825.
- S40. C. Cheng, J. Wang, X. Yang, A. Li and C. Philippe, J. Hazard. Mater., 2014, 264, 332–341.

S41. A. T. Paulino, L. A. Belfiore, L. T. Kubota, E. C. Muniz, V. C. Almeida and E. B. Tambourgi, *Desalination*, 2011, **275**, 187–196.

- S42. G. Zhao, J. Li, X. Ren, C. Chen and X. Wang, Environ. Sci. Technol., 2011, 45, 10454–10462.
- S43. Z. Zhen and L. Wei, *RSC Adv.*, 2012, **2**, 5178–5184.
- S44. M. Xu, P. Hadi, G. Chen and G. McKay, J. Hazard. Mater., 2014, 273, 118–123.
- S45. N. T. Hoai and D. Kim, AlchE J., 2009, 55, 3248–3254.
- S46. N. T. Hoai, D. K. Yoo and D. Kim, J. Hazard. Mater., 2010, 173, 462–467.
- S47. J. Cheng, G. Shan and P. Pan, Ind. Eng. Chem. Res., 2017, 56, 1223–1232.
- S48. Y. Jiang and D. Kim, Chem. Eng. J., 2011, 116, 435–444.
- S49. X. Luo, S. Luo, Y. Zhan, H. Shu, Y. Huang and X. Tu, J. Hazard. Mater., 2011, 192, 949–955.
- S50. Y. Shi, Q. Zhang, L. Feng, Q. Xiong and J. Chen, *Korean J. Chem. Eng.*, 2014, **31**, 821–827.