Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Selective high adsorption capacity for Congo red dye of a new 3D supramolecular complex and its magnetic hybrid

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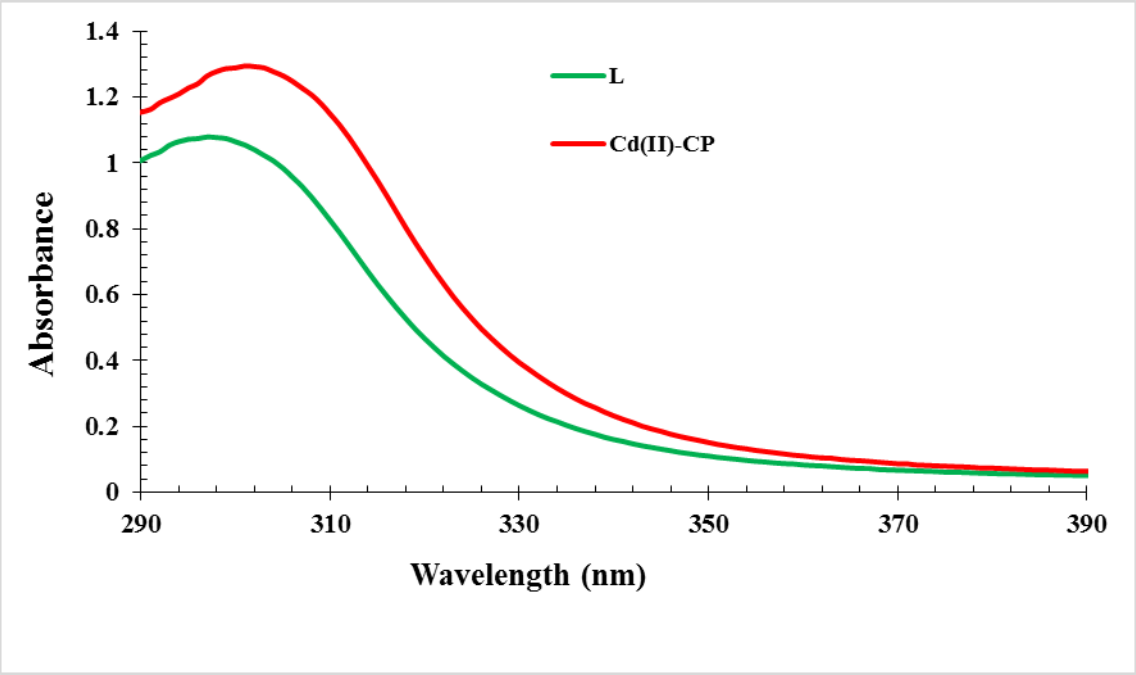


Fig.S1. Experimental UV-Vis spectra of the considered Cd(II)-CP and **L**.

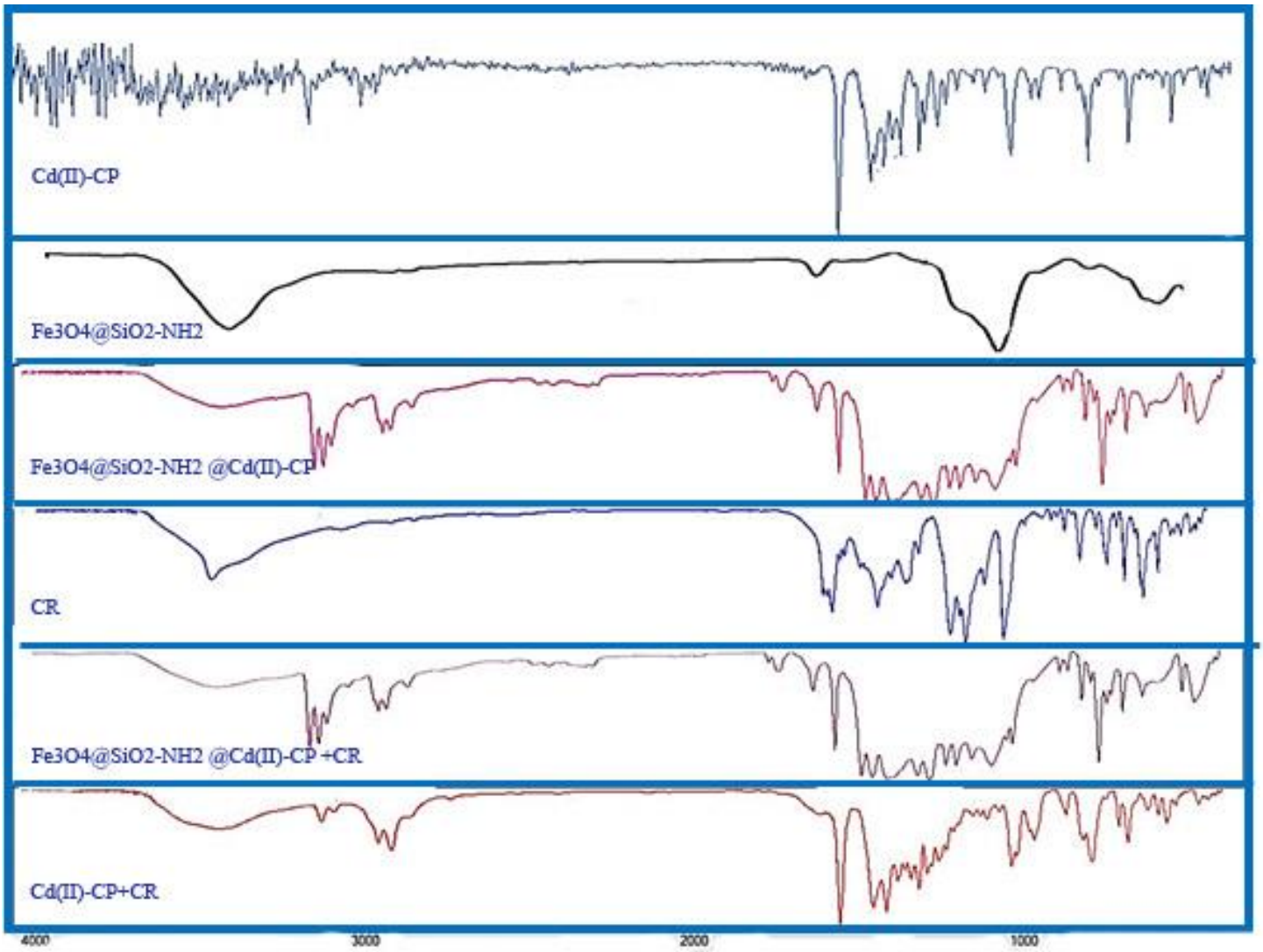


Fig. S2 . Comparison of FT-IR of the materials.

The adsorption of CR onto Cd(II)-CP and magnetic hybrid were affirmed by FT-IR.

XPS results:

Table S1: Binding energies (eV) for carbon, nitrogen, cadmium,oxygen, silicon and chlorine. Standard deviations calculated on three independent measurements is 0.1 eV.

Materials	C1s				Cd 3d	N1s			Cl2p	O1s			Cd M4N45N45	Si2p	α′
	1	aliphatic	3	4	3d5/2 3d3/2	-NH-Cd and N=N (*)	-N-Cd |	- N-C |		1	2	3			
Cd(II)-CP	283.4	285.0	286.4	287.8	406.5 413.2	--	400.9	402.5	198.7		532.1	534.0	1107.2	...	785.9
Magnetic hybrid	283.3	285.0	286.2	287.6	406.3 413.0	399.7-	400.4	401.7	198.9	529.9	531.7	533.1	1107.2	103.1	785.7
Cd(II)-CP-CR	283.5	285.0	286.3	287.7	406.5 413.2	399.6(*)	401.0	401.7	199.1		531.6	533.6	1107.2	...	785.9
Magnetic hybrid-CR	283.4	285.0	286.3	287.7	406.7 413.4	399.8(*)	401.3	402.2	199.3	530.3	531.9	533.6	1107.5	102.8	785.8

Fig.S3 shows the survey spectra of all examined compounds. Only expected elements from stoichiometry are present. Table S1 shows the XPS results obtained on the four samples (ie before and after sorption test). The Carbon C 1s signal shows four components; their binding energy values are constant for all the samples. The binding energy of the Cd 3d signal does not show significant variations among the samples, as well as the Cl 2p signal and, when present, the Si 2p signal. On the contrary, N 1s showed several differences among the different samples (Figure 2). The N 1s – Cd 3d overlap has to be taken into account during data processing. In the Cd-CP sample N 1s showed the presence of two components at 400.9 eV and at 402.5 eV due to the nitrogen atom bound to Cd and to the other nitrogen present in the molecule, respectively; their intensity ratio is 1:1. In the other samples a third signal appears at about 399.6 ±0.1 eV due to the bond between NH and Cd in the Fe_3O_4 @ SiO_2-NH-Cd (II)-CP and due to the presence of the N = N in Congo Red. The relative peak intensities of the N 1s components (see figure S3) are in good agreement with the stoichiometry. The differences in the BE values observed for all the N 1s components are due to differences in the electronic density among the different samples. O 1s shows two components at 529.9 eV and 531.7 eV due to Fe_3O_4 and SiO_2 respectively for magnetic Cd(II)-CP and at 530.3 eV and 531.9 eV due to Fe_3O_4 and SiO_2 respectively for magnetic Cd-CP-CR. A signal at about 533.6 eV due to water was also present in all samples. The Auger parameter α′ calculated for cadmium ($\alpha' = BE_{Cd\ 3d5/2} + KE_{Cd\ M4N45N45}$) and reported in Table 1, is in agreement with the values expected for cadmium atoms surrounded by chlorine and/or nitrogen.

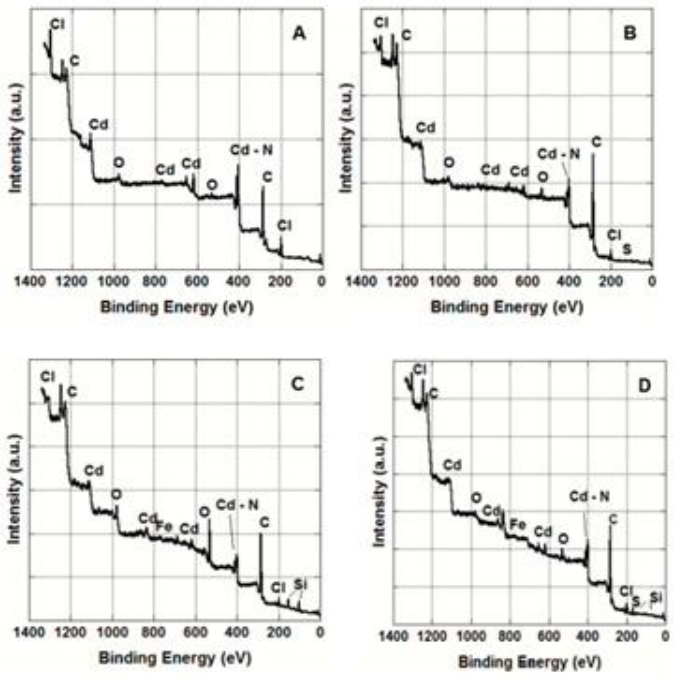


Fig.S3. Survey spectra of: Cd(II)CP (A), Cd(II)CP-CR (B), Magnetic hybrid (C) and Magnetic hybrid-CR (D).

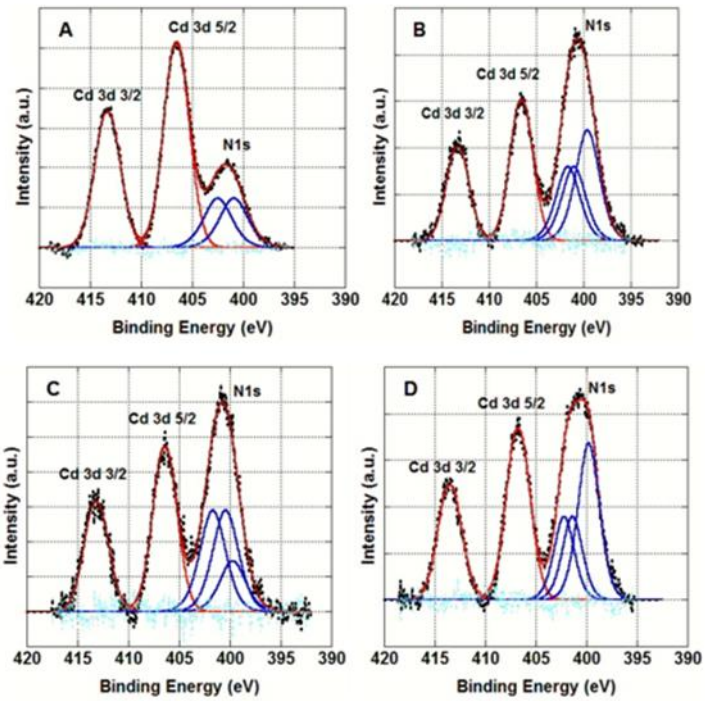


Fig. S3. Cd 3d, N 1s region. **A**: Cd(II)CP; two N1s signals with ratio 1:1. **B**: Cd(II)CP-CR sample; three N 1s signals with ratio 3:2:2. **C**: Magnetic hybrid ; three N 1s signals with ratio 1:2:2. **D**: Magnetic hybrid-CR ; three N 1s signals with ratio 2:1:1.

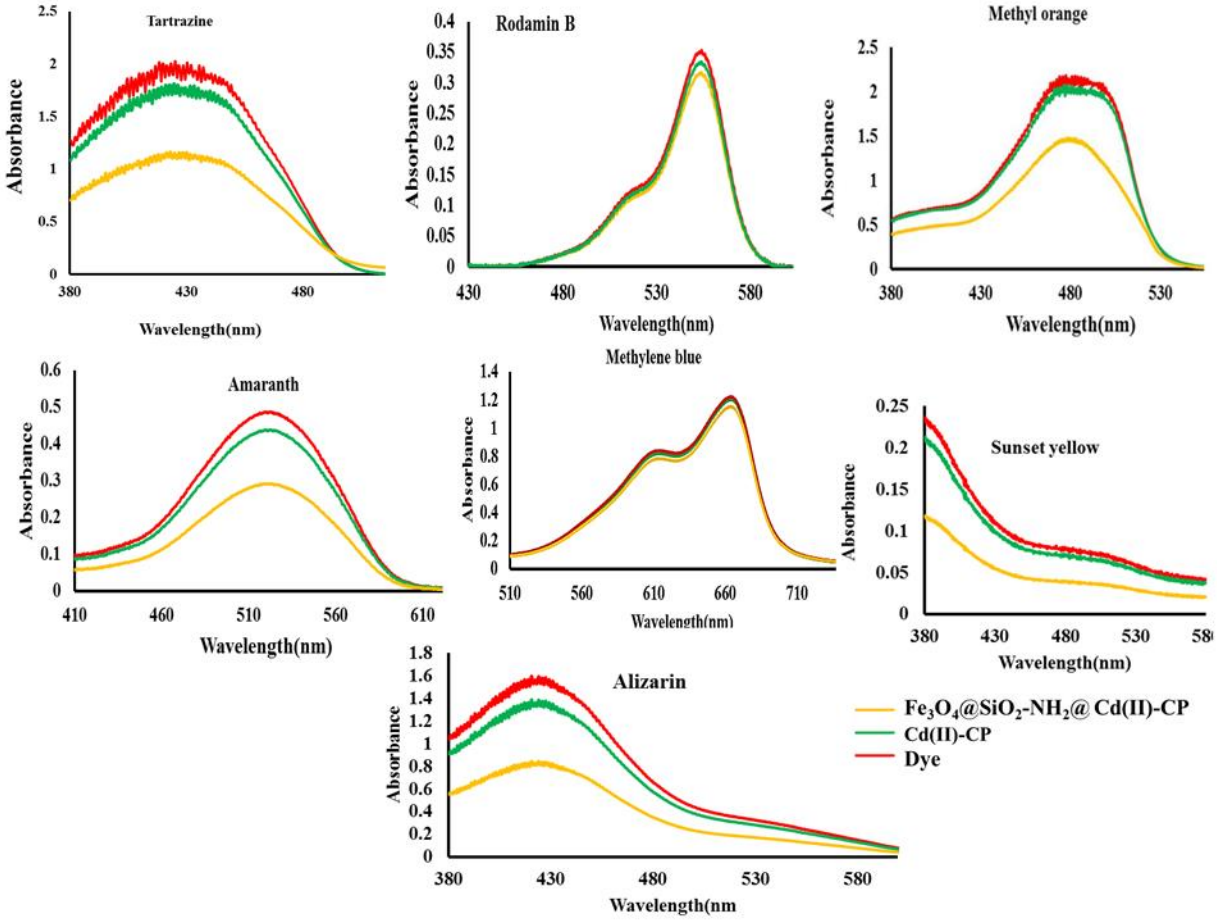


Fig. S4. The Dye adsorption capability of Cd(II)-CP and its magnetic hybrid.

Table S2. Comparison of the adsorption capacities of **CR** onto some typical adsorbents.

Entry	CP		Adsorption of CR mg/g	Selectivity of CR	Ligand	Refrences
1	$[Cd_2(oba)_2(4\text{-}bpdb)_2]_n(DMF)_x$ [2]	3D	-	No	1,4-bisIJ4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb)and 4,4′-bipyridine (4,4′-bipy)	89
2	$[Cd(oba)(4,4'\text{-}bipy)]_n(DMF)_y$	3D	-	No		89
3	$[Co_3(tib)_2(H_2O)_{12}](SO_4)_3$	2D	4923.7	Selective	1,3,5-tris(1-imidazolyl) benzene	90
4	{[Ag(μ3abtz)](NO3)(0.125H2O)}n		823.3		1-(4-aminobenzyl)-1,2,4-triazole (abtz)	91
5	[Cd(oba)(4-bpdh)]n.1DMF	3D	97		H2oba (4,4-oxybisbenzoic acid), and, 4-bpdh (2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene)	92
6	MOF-5	3D	-	No		93
7	$[Cd(C_{10}H_8N_2)(H_2O)_2(S_2O_3)]\_{2}H_2O$	3D	-	No		94
8	$[Cd_2(C_{10}H_8N_2)_3(S_2O_3)_2]$	3D	-	No		94
9	$[Cd2(C_{10}H_8N_2)_2.5(S_2O_3)_2]$	3D	-	No		94
10	MIL-68	3D	1204			95
11	$[CdCl(NCS)L]_n$	1D	84.87	Selective	1, 1-(1,4-butanediyl) bis(1,3-dihydro-3-methyl-1H-imidazole- 2-thione)	96
12	$\{[Cd_2I_4(L)_2]\cdot H_2O\cdot DMF\}n$	1D	58.29	Selective	1, 1-(1,4-butanediyl) bis(1,3-dihydro-3-methyl-1H-imidazole- 2-thione)	96
13	$[CdCl_2L]_n$	1D	-	Selective	L = 1,1-(1,6-hexanediyl)bis(1,3-dihydro-3-methyl-1H-imidazole-2-thione)	97
14	[Zn(L)(*rctt*-tpcb)0.5(H2O)]	2D	-	NO	4,4'-((1,2 phenylenebis (methylene) bis(oxy))dibenzoic acid; (regio *cis*, *trans*, *trans*)-tpcb = tetrakis(4-pyridyl)cyclobutane)	98

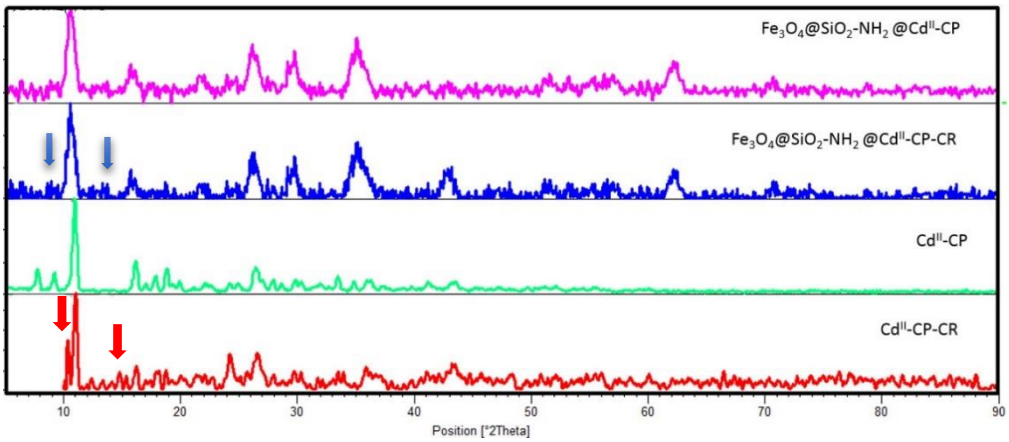
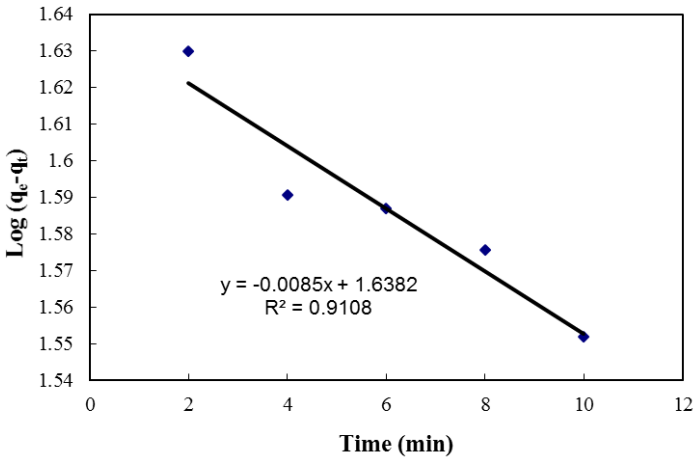
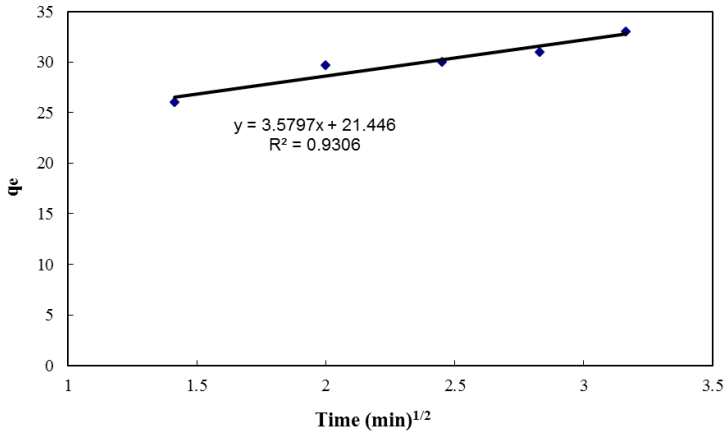
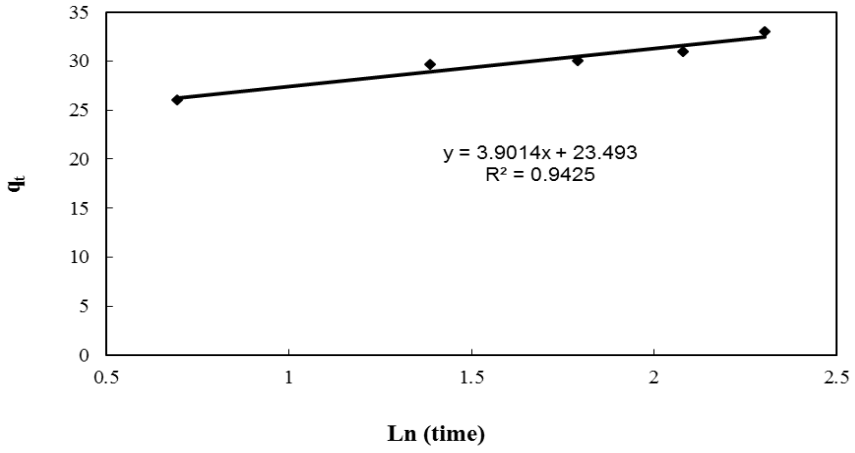
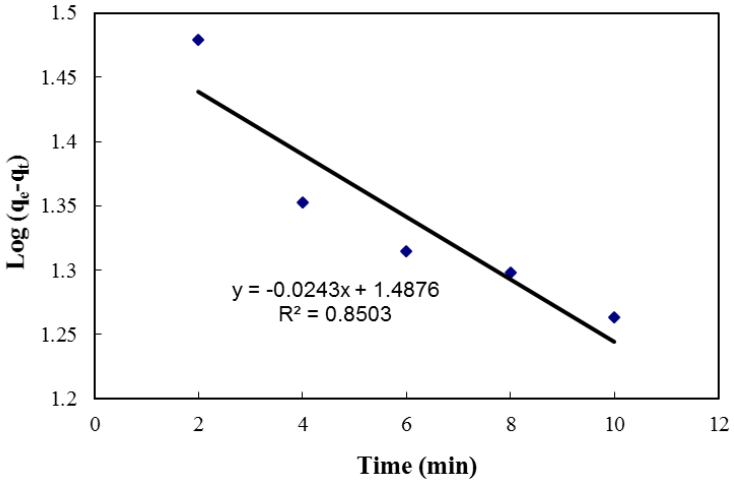


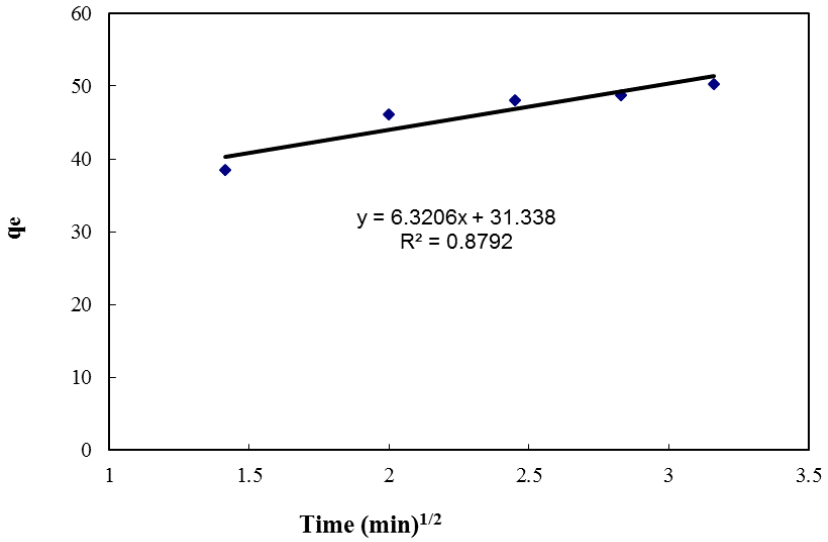
Fig. S5 Comparison of XRD patterns of the Cd(II)-CP and its magnetic hybrid before and after adsorption.

A spectra comparison between XRD spectrum of Cd(II)-CP with its CR-Cd(II)pattern, clearly show an extra peaks at 2Θ = 9 and 25 [1]which is a good sign for the presence of Congo red dye in the structure of Cd(II)-CP. In the case of magnetic hybrid, it was detect a sign for the presence of Congo red as clear as the one observed for Cd(II)-CP.

Cd(II)-CP	
	**First-order kinetic**
	**Intraparticle diffusion:**
	**Elovich**
Magnetic hybrid	



First-order kinetic



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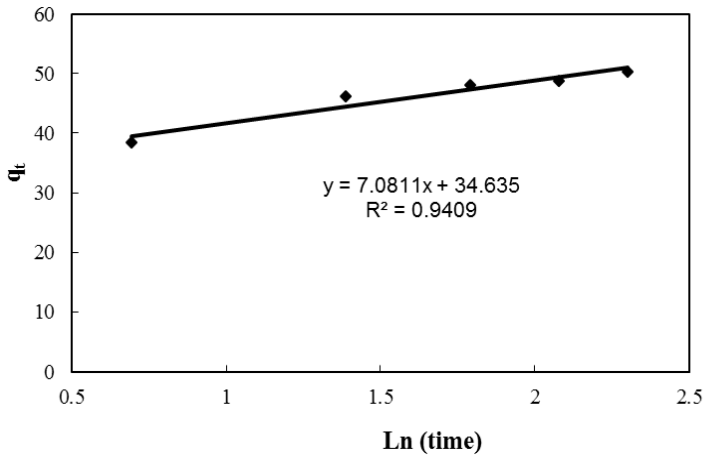
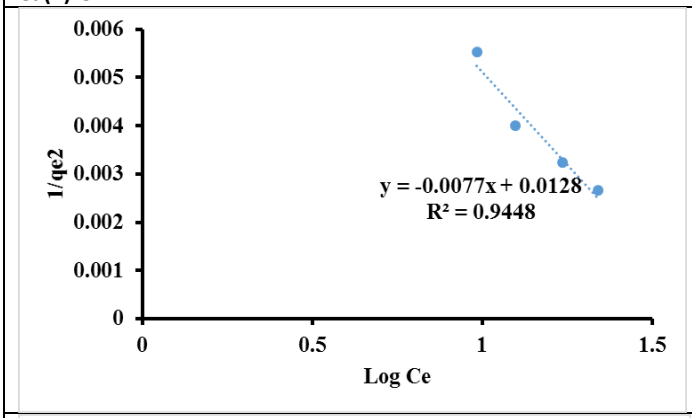
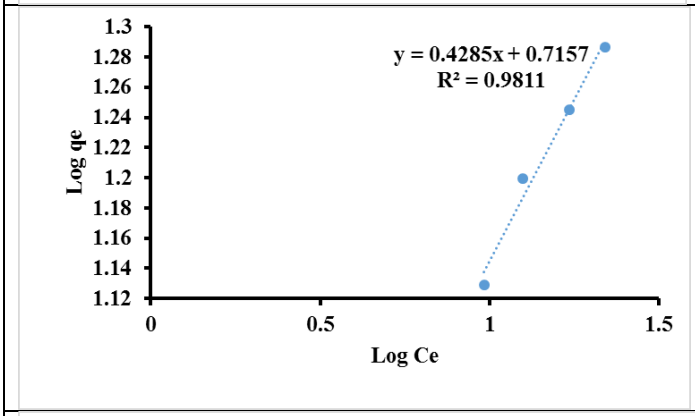
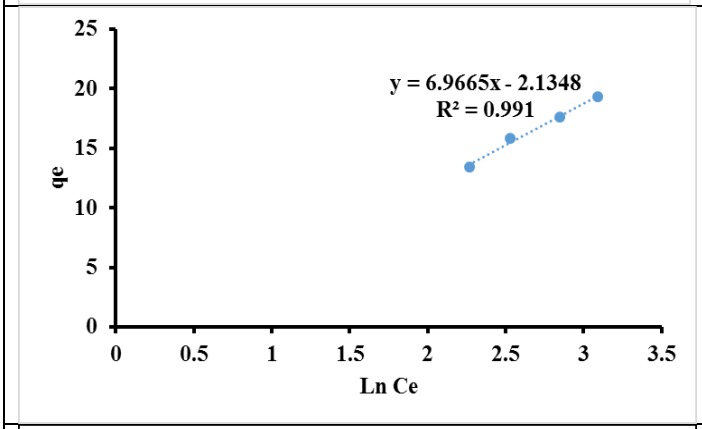
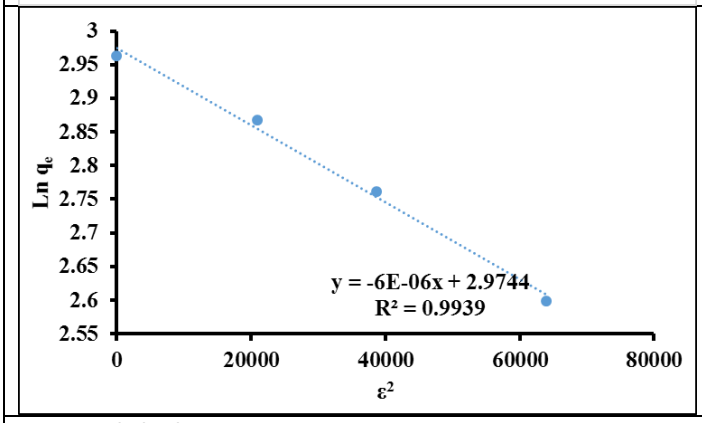


Elovich

Fig. S*6*. . The adsorption kinetics of CR from aqueous solution onto Cd(II)–CP and its magnetic hybrid at room temperature.

Cd(II)-CP		
		**H-J**
		**Freundlich**
		**Temkin**
		**D-R**
Magnetic hybrid		

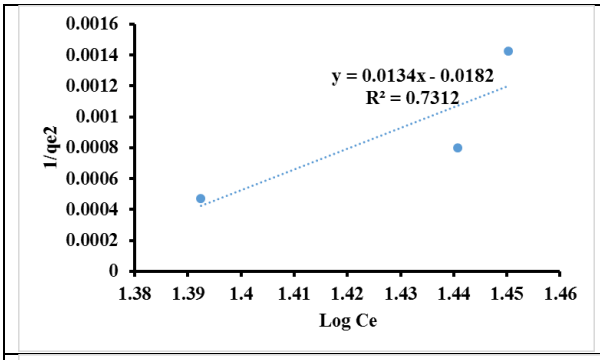
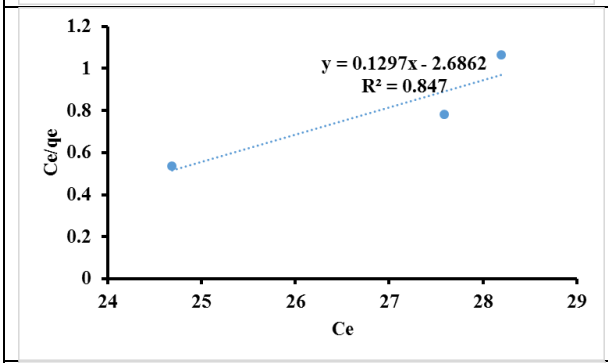
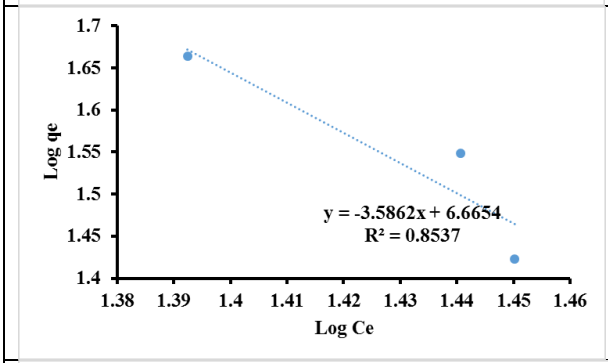
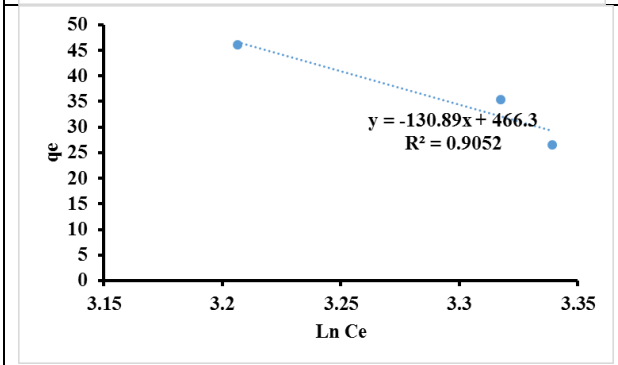
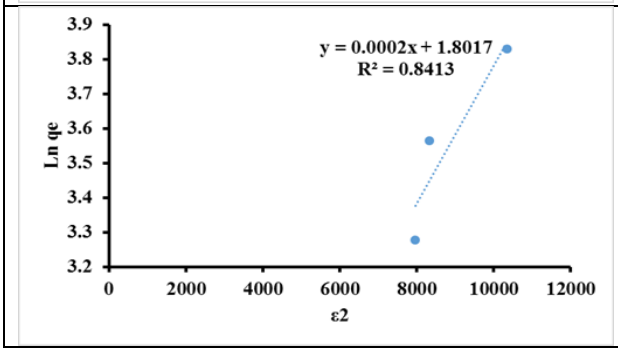
		**H-J**
		**Langmuir**
		**Freundlich**
		**Temkin**
		**D-R**

Fig.S7. The adsorption isotherms of CR from aqueous solution onto onto Cd(II)–CP and its magnetic hybrid at room temperature.

References

1. X. Cai, B. Han, S. Deng, Y. Wang, C. Dong, Y. Wang, I. Djerdj, *CrystEngComm,*2014 ,16(33), 7761-7770.