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Synthesis and characterization of halloysite-cyclodextrin nanosponges for enhanced dyes adsorption

Marina Massaro,[‡] Carmelo G. Colletti,[‡] Giuseppe Lazzara,^{,§} Susanna Guernelli,^{||} Renato Noto[‡] and Serena Riela^{*,‡}*

[‡]Dipartimento STEBICEF, Sez. Chimica, Università degli Studi di Palermo, Viale delle Scienze, Ed. 17, 90128 Palermo, Italy; e-mail: serena.riela@unipa.it.

[§]Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze, Ed. 17, 90128 Palermo, Italy, e-mail: giuseppe.lazzara@unipa.it.

^{||}Dipartimento di Chimica “G. Ciamician”, Università degli Studi di Bologna, Via S. Giacomo 11, 40126 Bologna, Italy.

KEYWORDS. Halloysite, nanosponges, cyclodextrin, bioremediation.

ABSTRACT Inorganic-organic nanosponges hybrids based on halloysite clay and organic cyclodextrin derivatives (HNT-CDs) were developed by means of microwave irradiations in solvent free conditions. The HNT-CDs nanomaterials characterized by FT-IR, TGA, BET, TEM, SEM, DLS and ζ -potential have showed an hyper-reticulated network which possesses both HNT and cyclodextrin peculiarities. The new HNT-CDs nanosponges hybrids were employed as

nano-adsorbents, first choosing Rhodamine B as dye model, furthermore for the removal of some cationic and anionic dyes, under different pH values (1.0, 4.54 and 7.4). The collected results showed that the pH solution as well as the electrostatic interactions affect the adsorption process. Factors controlling the adsorption process were discussed. The experimental adsorption equilibrium and kinetic data were best described by Freundlich isotherm model. Excellent adsorption efficiency for cationic dyes were observed respect to anionic ones. The results suggest that HNT-CDs nanosponges hybrids are a good nano-adsorbent for selective adsorption of cationic dyes with respect to the anionic ones from aqueous solutions.

Introduction

In the last years mesoporous materials are becoming attractive due to their peculiar chemical characteristics such as moderate pore size (within 2–50 nm diameter) and large specific surface area, that increase their applications in several fields such as adsorption, catalysis and so on.¹ The interest for these kinds materials is mainly due to the fact that they generally are low cost, environmental-friendly and available in large scale since them are recovered from natural sources. In this context nanoporous minerals such as zeolite, bentonite, montmorillonite²⁻³ have shown good perspective to replace the common used mesoporous materials.

Halloysite nanotubes (HNTs) are alumino-silicate clay with a predominantly hollow tubular structure in the submicron range. Compared to other nanoparticles such as organic carbon nanotubes, this kind of inorganic tube is naturally occurring, cheap, abundantly available, bio⁴⁻⁵ and eco-compatible.⁶ Chemically, HNTs are constituted by siloxane groups on the external surface, while the aluminol groups are located in the inner lumen.⁷ Thanks to this peculiar

chemical composition, the external surface of halloysite is easily functionalized by covalent grafting of silane groups that increases HNT application fields; moreover the positive charged inner lumen allows to encapsulate negative or electron-rich molecules.⁸ HNTs have been used as filler for polymer⁹ or hydrogel matrices,¹⁰ drug carrier¹¹⁻¹² and delivery,¹³⁻¹⁴ catalyst support¹⁵⁻¹⁶ as well as absorbents.¹⁷⁻¹⁸

Recently, composite materials constituted by inorganic–organic hybrids have attracted considerable attention since they combine the organic and inorganic characteristics within a single molecular-scale composite.¹⁹ Generally, the organic moieties of the hybrids possess toughness, good elasticity, low density and formability, whereas the inorganic components are stiff, hard and thermally stable. Therefore, based on the combination of organic and inorganic properties, the hybrid nanomaterials are employed in a wide range of applications, such as removal of environmental pollutants.²⁰

Up to now several materials are employed as adsorbent for organic dyes, such as bentonite, kaolin, titania, as well as cyclodextrin nanosponges.²¹⁻²⁴

Herein we report a new class of inorganic-organic nanosponges hybrids obtained by the combination of the inorganic halloysite clay and organic cyclodextrin derivatives (HNT-CDs) with potentially complementary binding ability and additional nanochannels formed by the crosslink between CDs and HNT (Figure 1). The new nanosponges hybrids were extensively characterized by FT-IR spectroscopy, thermogravimetric and BET analyses, TEM and SEM investigations, dynamic light scattering and ζ -potential measurements. Thanks to these techniques we deduce that the formation of hyper-reticulated network which possesses both HNT peculiarities and cyclodextrin characteristics. Finally, the performance of HNT-CDs

nanosponges applied in organic dyes adsorption from aqueous medium was evaluated choosing Rhodamine B (RB) as dye model. Furthermore the scope and feasibility of the hybrid with a wide range of organic dyes was also investigated. The method put forward the application of halloysite composite materials in the development of future efficient absorbents.

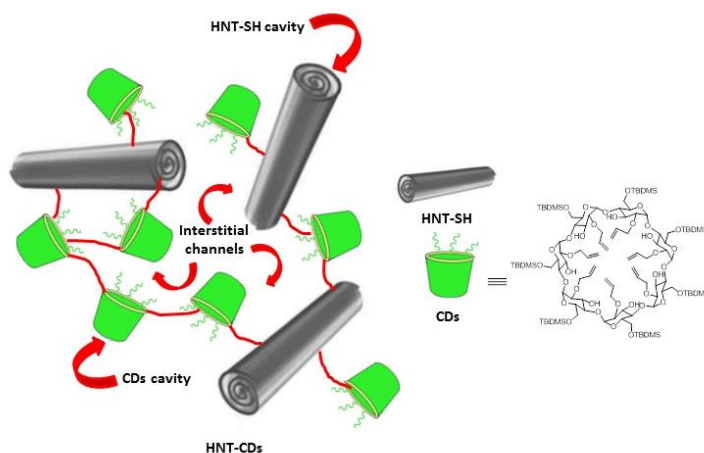


Figure 1. Cartoon representation of HNT-CDs nanosponge hybrids.

Results and Discussion

The starting scaffolds HNT-SH and β CDs can be prepared by means procedures reported elsewhere.²⁵ As previously reported,²⁶ halloysite nanotubes were reacted with an excess of 3-mercaptopropyltrimethoxysilane in solvent free conditions under microwave irradiation, affording HNT-SH, which represents a versatile starting point for subsequent functionalization. After work-up, the amount of organic moiety grafted on HNT external surface was, estimated by TGA, ca. 1 ± 0.1 wt%. The synthesis of HNT-CDs was carried out by AIBN-catalyzed polymerization of heptakis-6-(tert-butyl dimethylsilyl)-2-allyloxy- β -cyclodextrin to HNT-SH by means of a thiol-ene reaction (Scheme 1).

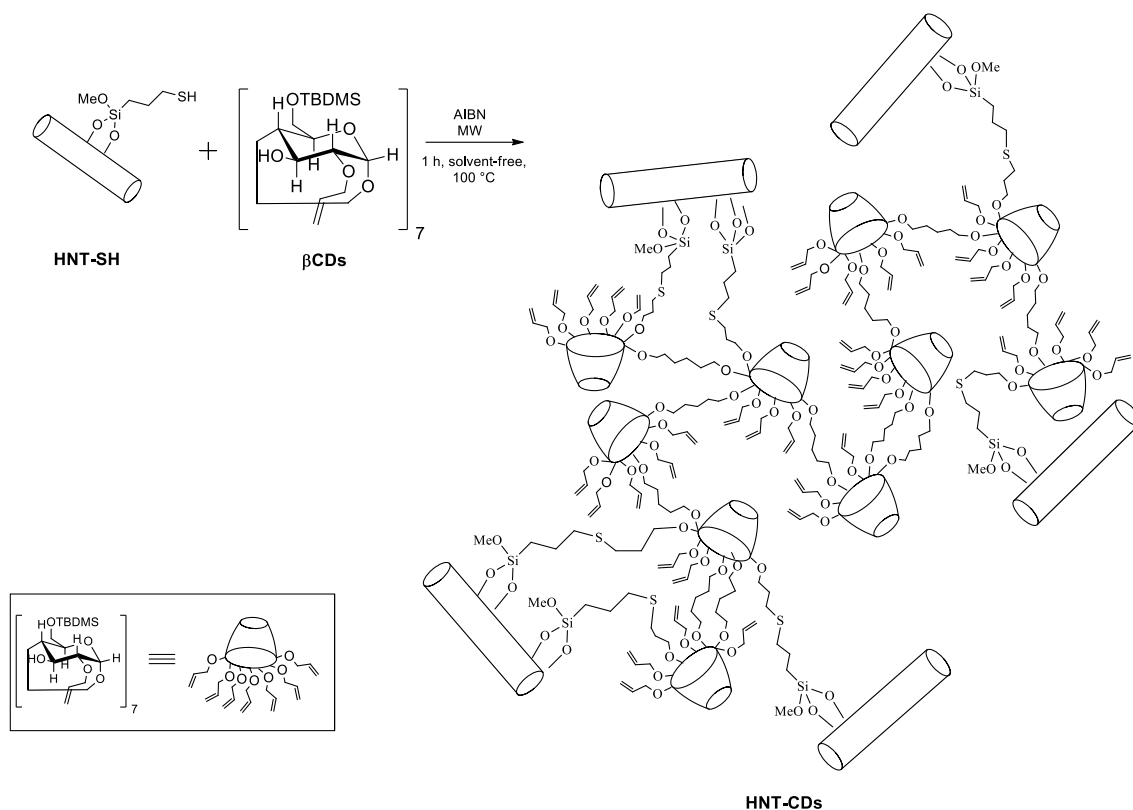
For this synthesis, the reactants were mixed in different proportions (Table 1) and the different percentage of CDs in the obtained composite materials was determined by TGA from the residual mass upon degradation (Table 1).²⁵ Since the cyclodextrin is added in excess relative to the moles of -SH groups, the double bonds that do not react in the thiol–ene reaction can undergo a self-addition reaction, leading to the formation of a cyclodextrin cross-linked network. Therefore, due to the peculiar reticulated structure of the hybrid materials so obtained, constituted by a network of supramolecular host units joined by means of suitable cross-linkers, the hybrid polymer obtained could be considered a sort of nanosponges.²⁷⁻²⁹

Based on the stoichiometric ratios, it should be considered that an excess of unreacted allyloxy groups could be present and they could be able to undergo further functionalizations. The polymerization was carried out in a microwave oven, for an irradiation time of 1 h at 100 °C, in solvent free conditions. Then, the obtained nanomaterials were isolated by subsequent washings with CH₂Cl₂ and CH₃OH, in order to remove the catalyst and some residual unreacted reagents.

Table 1. Reactant ratios and mass yields for HNT-CDs nanosponges hybrids.

Reactants	HNT-CDs products	
HNT (mg)	200	200
CD (mg)	300	150
HNT:CD ratio	1:1.5	1.5:1
% Loading (CD on HNT) ^a	40	20

^aestimated by TGA.



Scheme 1. Schematic representation of the synthesis of HNT-CDs nanosponges hybrid.

Hereinafter the two different HNT-CD nanosponge hybrids are indicated as HNT-CD (20%) or HNT-CD (40%) respectively.

Compared to pristine HNT,²⁵ HNT-CDs (40%) nanosponge hybrid exhibits the vibration bands for C–H stretching of methylene groups around 2980 cm^{-1} and a broad and wide band around 3000 cm^{-1} due to the –OH groups of cyclodextrin (see Figure S.1). These findings provide evidence for the presence of organic moieties in the new material. Moreover, it is interesting to notice that little signals at ca. 1700 cm^{-1} and 1418 cm^{-1} are still present in the spectrum, indicating that not all the reactive functional groups in the starting reactants actually happened to react. This may be a consequence of the hyper-reticulated nature of the hybrid polymers

obtained. Steric hindrances and strains, indeed, might prevent some of the reacting groups to achieve the minimum arrangement requirements needed for the polymerization process to occur. Thermogravimetric analysis evidenced a peculiar pyrolysis process of CDs nanosponges in the presence of HNT. Namely, the organic material degraded almost completely in a single step at ca. 327 °C that is coincident with the degradation temperature of β -CD,³⁰ the presence of HNT generates a two-steps degradation pattern with maximum degradation rates at 265 and 360 °C, respectively. It should also be noted that the degradation at lower temperature is enhanced in the presence of larger HNT amounts (Figure 2). These findings can be explained by involving a change in the degradation mechanism of CDs nanosponges being it split into two consecutive or parallel reactions.³¹ To clarify the effect of HNTs on the CDs degradation mechanism, heating rate was changed for the HNT-CDs (40 %) (see SI) sample and the obtained results indicate that HNTs generate a two steps degradation mechanism rather than a catalytic degradation alternative pattern.

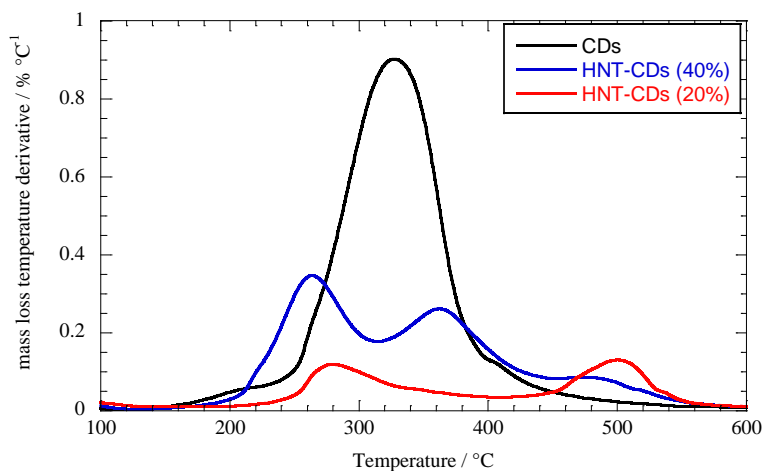


Figure 2. Differential thermal analysis curves for HNT-CD hybrid and CD polymers.

SEM images of HNT-CDs (40%) nanosponge are given in Figure 3a. As known pristine HNTs (p-HNTs) show long-fibrous morphology with a length of 0.5–1 μm and outer diameter of about 100 nm (see SI).³² After functionalization it seems clear that the tubular shape of halloysite is preserved and HNT-CDs hybrid presented a different morphology as compared with p-HNTs. HNT-CDs hybrid still shows a long-range rod-shape with the diameter increasing to about 170 nm. Moreover, the hybrid shows a rather compact structure where the HNT seems glued together with a smooth surface that indicated the presence of an organic layer.

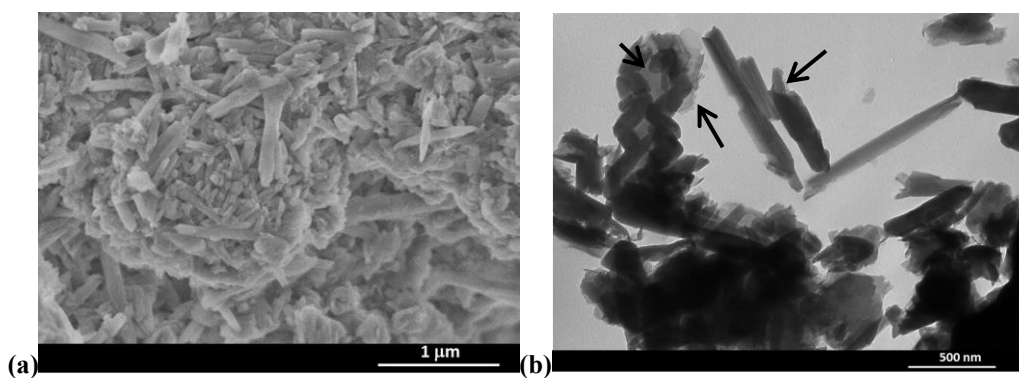


Figure 3. (a) SEM and (b) TEM images of HNT-CDs (40%) nanosponge hybrid

According to the TEM images (Figure 3b), HNT-CDs hybrid (40%) shows the typical nanorod-shaped structure of HNTs. The hybrid exhibits the characteristic hollow tubular structure of halloysite as shell with a cyclodextrin core (indicated by arrows in the Figure 3b).³³ The increased thickness of the hybrid with respect to pristine nanotubes takes into account the formation of the network after the reaction.³⁴

To confirm the formation of the reticulated structure, the diffusion dynamics in water of the HNT-CDs (40%) nanosponge hybrid was characterized by dynamic light scattering (DLS).

Measurements of the particle size using DLS reveal a translational average diffusion coefficient

of the HNT-CDs nanosponges of $3.24 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ that is smaller than the value for p-HNTs in water ($9.4 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$); this result is consistent with the formation of a polymer-like network where HNT are incorporated after the reaction with cyclodextrin units. Although the diffusion behavior is strongly altered, the surface charge in the hybrid is not significantly altered as expected for non-ionic functionalization (ζ -potential= $-25 \pm 1 \text{ mV}$).³⁴

The morphological properties of HNT-CDs (40%) hybrid in terms of specific surface area (BET), mean pore size distribution (BJH) and cumulative pore volume, were determined by N₂ adsorption/desorption measurements and are listed in Table 2. The HNT-CDs nanosponge hybrid shows a surface area of $19.9 \text{ m}^2 \text{ g}^{-1}$ slightly smaller than that of starting pristine halloysite ($22.1 \text{ m}^2 \text{ g}^{-1}$).³⁴ The slight decrease in the specific surface area, observed for the new polymeric hybrid, takes into account the small degree of organosilane loading on HNT surface. Pore size of HNT-CDs hybrid is greater than that of p-HNT as a result of the formation of reticulated structure that could form additional channel in the hybrid polymer mesh.³⁵ The porous structure makes the hybrid polymer a promising material that could act as nanosponge for dye adsorption.

Table 2. Textural parameters determined by N₂ adsorption/desorption measurements for p-HNT and HNT-CD nanosponge hybrid.

	Surface area, S _{BET} (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore size (nm)
p-HNT ³⁴	22.1	0.06	9.3
HNT-CDs	19.9	0.29	85.2

Swelling properties of HNT-CD nanosponge hybrid.

Since swelling provides more specific surface area for adsorption, hence wettability and swelling are presumed to facilitate the adsorption of target molecules or ions. Therefore, it is essential to

measure swelling of a polymer in aqueous medium before its application as adsorbent. The swelling ratio of the HNT-CDs (40%) nanosponge hybrid is $91.2 \pm 1.6 \%$. The reduction of swelling ratio in comparison with some previously reported cyclodextrin polymers³⁶ could be due to the presence of HNT that increased crosslinking density through formation of covalent bonding within the cyclodextrin; as a consequence, HNTs could make the hybrid polymer network denser, blocking the passage of water from entering in the polymer.

Adsorption measurements

The adsorption capacity of the new hybrid nanomaterials were evaluated by adsorption isotherm experiments using rhodamine B (RB) as dye model. In Figure 4 is reported the equilibrium amount of dye adsorbed into the clay (Q_e , mol g⁻¹) as a function of the equilibrium dye concentration in solution (C_e , mol L⁻¹). First of all, it can be observed that the amount of adsorbed dye increases on increasing the equilibrium dye concentration and it is considerably lower at the higher pH (Figure 4). This could be explained as follow: HNT presents a negative outer surface in a wide pH range, therefore, in acidic pH media an electrostatic attraction between the negatively charged nanosponge hybrid and positively charged RB would take place; on the contrary for pH values up to 7.4, RB mainly exists in zwitterion forms forming dimers³⁷ which are unable to interact with the HNT surfaces and therefore the dye can be encapsulated mainly into CD cavities decreasing the adsorption efficiency.

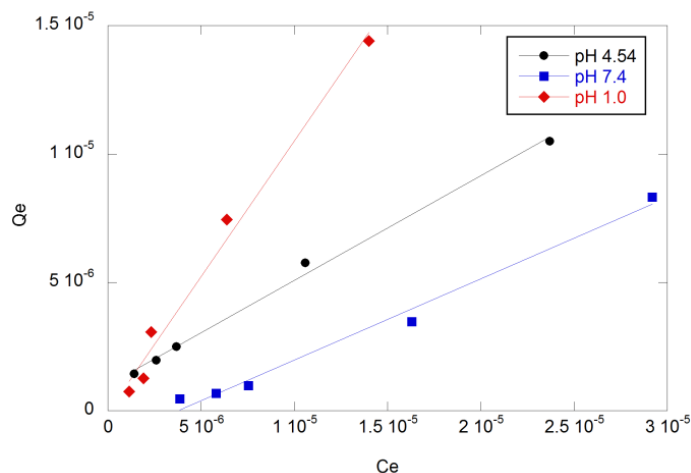


Figure 4. Adsorption isotherms of RB on HNT-CD nanosponge hybrid in HCl 0.1 N, acetate buffer pH 4.54 and phosphate buffer pH 7.4.

Both the Langmuir and the Freundlich models were used to analyze the experimental data. The obtained results are reported in Table 3. As it is possible to note the adsorption data are better fitted by the Freundlich model suggesting the heterogeneity of the polymer and multi-molecular layer adsorption. The value of n is larger than 1 in acidic solution, which indicates the favorable nature of adsorption and a physical process; while the n value less than 1 obtained in a neutral medium indicates that the adsorption bond becomes weak; unfavorable adsorption takes place, as a result of the decrease in adsorption capacity.³⁸

For comparison we studied the adsorption of RB on pristine HNT (p-HNT). In all cases we observed a decrease in the RB adsorption efficiency with respect to the HNT-CD hybrids (see SI). In addition, the adsorption data are better fitted by Langmuir model at pH 7.4; furthermore both models are not applicable for data at pH 4.54.

Table 3. Parameters of Langmuir and Freundlich isotherm models for RB adsorption on HNT-CDs nanosponges hybrids.

pH		Langmuir			Freundlich		
		Q_m (mol g ⁻¹)	K_L (L mol ⁻¹)	R^2	K_F (mol g ⁻¹ (mol L ⁻¹) ^{1/n})	n	R^2
1.00	HNT-CDs (20%)	(2.7±1.5)×10 ⁻⁵	(7±6) ×10 ⁵	0.965	0.08±0.06	1.3±0.1	0.996
	HNT-CDs (40%)	(2.0±0.1)×10 ⁻⁵	(3±2) ×10 ⁵	0.964	0.3±0.1	1.01±0.03	0.977
4.54	HNT-CDs (20%)	(2.5±0.4)×10 ⁻⁵	(3±1) ×10 ⁵	0.994	0.05±0.01	1.26±0.05	0.997
	HNT-CDs (40%)	(6±4)×10 ⁻⁵	(8±6) ×10 ⁴	0.991	0.10±0.06	1.13±0.07	0.994
7.40	HNT-CDs (20%)	na	na	na	86±40	0.65±0.02	0.999
	HNT-CDs (40%)	na	na	na	2.2±1.9	0.80±0.05	0.994

^{na} Langmuir model is not successful.

To well-understand the adsorption mechanisms, kinetics of Rhodamine B adsorption onto HNT-CDs nanosponge hybrids, in the best pH conditions, were investigated (see SI). It was found that the adsorption amount increases rapidly in first 100 min, and then slows down until the sorption reached equilibrium. The beginning rapid adsorption of RB is due to the existence of a large number of sorption sites on the surface of HNT-CDs nanosponge hybrids (HNT and CDs cavities, interstitial channels). As the surface active sites are occupied, the adsorption rates slow down and finally reached the adsorption equilibrium.

The kinetic data were fitted by first-order, second-order, intraparticle diffusion models and double exponential (DEM) (see Table S.1). It was found that the experimental data are better fitted by DEM model (Table 4). According to the literature the DEM mode describes a process where the adsorbent offers two different types of adsorption sites.³⁹ Therefore, it could be possible that rapid adsorption equilibration occurs within a few minutes onto HNT external surface, whereas on inner cyclodextrin core, adsorption is more slowly.

Table 4. Adsorption kinetic parameters of RB onto HNT-CDs nanosponge hybrids.

DEM				
$Q_t = Q_e' (1 - e^{-k't}) + Q_e'' (1 - e^{-k''t})$				
Q_e' (10 ⁻⁶ M)	k' (min ⁻¹)	Q_e'' (10 ⁻⁶ M)	k'' (min ⁻¹)	R^2

20%	3.91±0.02	0.083±0.003	1.61±0.02	(3.4±0.01)×10 ⁻³	0.994
40%	3.73±0.02	0.8±0.1	1.61±0.02	(1.35±0.03)×10 ⁻²	0.981

Finally, in order to determine the effect of temperature on RB adsorption, experiments were conducted at 277, 298, 310 and 331 K, respectively. The adsorption process was favorable at lower temperature and RB molecules were orderly adsorbed on the surface of HNT-CDs nanosponge and into CD cavities. The thermodynamic parameters were calculated by means of the van't Hoff equation and listed in Table 5. The obtained data further confirm that the material shows better adsorption efficiency in acidic medium with respect to the neutral one.

Table 5. Thermodynamic parameters at different temperatures.

pH	T (K)	$\Delta G^{\circ,a}$ (KJ mol ⁻¹)	ΔH (KJ mol ⁻¹)	ΔS (J mol ⁻¹)
4.54	277	-88.31	-100.71	-44.76
	298	-87.37		
	310	-86.83		
	331	-85.89		
7.40	277	1.87	-37.19	-141

^a, obtained from Langmuir model.

In order to evaluate the performance of the obtained HNT-CD hybrid polymers, additional adsorption experiments were performed to determine the adsorption capacity of the hybrid for six cationic and anionic dyes (see SI), under different pH values, namely 1.0, 4.54 and 7.4 (Figure 5). In general the synthesized materials show higher adsorption capacity than p-HNT (see Figure S.8 and Table S.2) as a consequence of the introduction of CD moieties and the formation of network.

It was found that HNT-CDs hybrids, in all pH values investigated, showed high adsorption capacity for cationic dyes. In particular methylene blue (MB) and toluidine blue (TB) are quantitatively adsorbed, while only 70% of RB is adsorbed at the best pH value. These differences could be due to the small steric hindrance of MB and TB with respect to RB.

Anionic dyes are poorly adsorbed from the polymer, probably due to the presence of electrostatic repulsions between the negatively charged halloysite external surface and the dyes. The small amount of these dye adsorbed could selectively interact with positively charged HNT lumen. However, in these cases the best adsorption is obtained at pH 4.54. The anionic dyes, indeed, turns from a neutral to a largely delocalized anionic form at around pH 4, therefore they can interact with the nanomaterial in their partly cationic form.⁴⁰

Surprisingly, the nanomaterial showed good adsorption capacity for the anionic dye congo rubin (CR) at acidic pH values. This could be explained by a difference in binding mechanism of halloysite to the anionic dyes and a strong interaction between CR and HNT.⁴¹ In addition, the formation of inclusion complexes between CR and β -CD occurs.⁴² At lower pH, the sulfonate ions of CR can be neutralized and the complexing effect between neutral CR and the cavity of β -CD is strengthened, thereby promoting adsorption of CR.

The obtained results show that HNT-CDs nanosponge hybrids could be used as a good nanoadsorbent for selective adsorption of cationic dyes with respect to the anionic ones in a wide pH range.

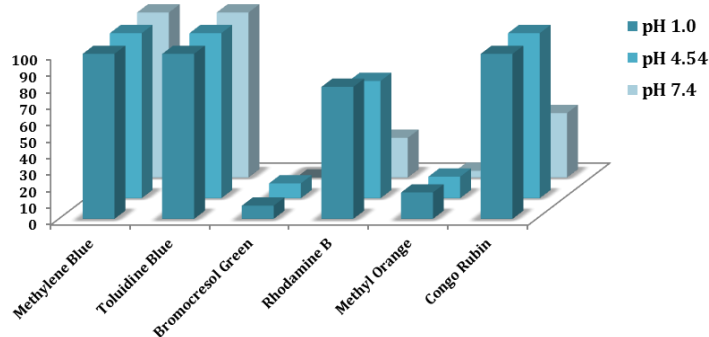


Figure 5. Adsorption capacities of HNT-CD hybrid polymer for the different dyes at pH 1, 4.54 and 7.4.

For comparison in Table 6 are reported the adsorption capacities of MB on HNT-CD (40%) hybrid and that obtained with other adsorbents.

Table 6. Adsorption capacities of MB for some adsorbent.

Adsorbent	Adsorption capacity (mg g⁻¹)	Ref.
p-HNT	84.32	43
Titania	5.98	23
Zeolite	16.37	24
NaOH-treated kaolin	20.49	22
Titanate nanotubes	133.30	44
β -cyclodextrin cross-linked by citric acid	105.00	45
HNT-CD (40%) hybrid	226	this work

The results demonstrated that the HNT-CD hybrid nanosponges could be employed as promising adsorbents for removal of organic dyes from wastewater.

Conclusions

New hybrid organic-inorganic nanosponges based on halloysite nanotubes and cyclodextrins were successfully synthesized by microwave irradiation in solvent free conditions. In particular combining the starting scaffolds in different ratio it was possible to obtain two nanosponges with different amount of organic moieties that possess some non-reacted allyl groups that can be subjected to further functionalizations. The structure and morphology of the hybrid materials were extensively investigated by means of several techniques such as thermogravimetric analysis, TEM and SEM investigation, DLS and ζ -potential measurements and FT-IR spectroscopy. BET measurements and swelling investigations highlighted the presence of hyper-reticulated network and the possible presence of interstitial channel that could be useful for future applications. The feasibility of the material as decontaminant of wastewater was

investigated by studying its adsorption capacity towards an organic dye, rhodamine B. Adsorption experiments evidenced that the adsorption capacity is strictly influenced by the pH of the medium, and the presence of cyclodextrin in the hybrid enhances the adsorption ability of halloysite. The performance of the hybrid nanosponge was also evaluated towards different cationic and anionic dyes and the obtained results showed that HNT-CDs nanosponge hybrids are good nanoadsorbent for selective adsorption of cationic dyes with respect to the anionic ones in a wide pH range. In conclusion we think that the nanomaterial prepared combines the properties of both halloysite and cyclodextrin and therefore it put forward the use of halloysite in the bioremediation field.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Experimental details, N₂ adsorption/desorption isotherm, adsorption isotherms, adsorption kinetics and kinetic parameters, temperature dependent adsorption, structure of the investigated dyes and adsorption capacities of p-HNT (PDF).

AUTHOR INFORMATION

Corresponding Author

*serena.riela@unipa.it; giuseppe.lazzara@unipa.it

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

1. Ma, T.-Y.; Liu, L.; Yuan, Z.-Y. Direct Synthesis of Ordered Mesoporous Carbons. *Chem. Soc. Rev.* **2013**, *42* (9), 3977-4003.
2. Salem, S.; Salem, A.; Agha Babaei, A. Preparation and Characterization of Nano Porous Bentonite for Regeneration of Semi-Treated Waste Engine Oil: Applied Aspects for Enhanced Recovery. *Chem. Eng. J.* **2015**, *260*, 368-376.
3. Bakare, I. A.; Muraza, O.; Taniguchi, T.; Tago, T.; Nasser, G.; Yamani, Z. H.; Masuda, T. Steam-Assisted Catalytic Cracking of N-Hexane over La-Modified Mtt Zeolite for Selective Propylene Production. *J. Anal. Appl. Pyrolysis* **2015**, *116*, 272-280.
4. Fakhrullina, G. I.; Akhatova, F. S.; Lvov, Y. M.; Fakhrullin, R. F. Toxicity of Halloysite Clay Nanotubes in Vivo: A Caenorhabditis Elegans Study. *Environ. Sci.: Nano* **2015**, *2* (1), 54-59.
5. Kryuchkova, M.; Danilushkina, A.; Lvov, Y.; Fakhrullin, R. Evaluation of Toxicity of Nanoclays and Graphene Oxide: In Vivo a Paramecium Caudatum Study. *Environ. Sci.: Nano* **2016**, *3* (2), 442-452.
6. Bellani, L.; Giorgetti, L.; Riela, S.; Lazzara, G.; Scialabba, A.; Massaro, M. Ecotoxicity of Halloysite Nanotube-Supported Palladium Nanoparticles in Raphanus Sativus L. *Environ. Toxicol. Chem.* **2016**, *35* (10), 2503-2510.
7. Lvov, Y.; Wang, W.; Zhang, L.; Fakhrullin, R. Halloysite Clay Nanotubes for Loading and Sustained Release of Functional Compounds. *Adv. Mater.* **2016**, *28* (6), 1227-1250.
8. Lvov, Y. M.; DeVilliers, M. M.; Fakhrullin, R. F. The Application of Halloysite Tubule Nanoclay in Drug Delivery. *Expert Opin. Drug Deliv.* **2016**, *13* (7), 977-986.
9. Biddeci, G.; Cavallaro, G.; Di Blasi, F.; Lazzara, G.; Massaro, M.; Milioto, S.; Parisi, F.; Riela, S.; Spinelli, G. Halloysite Nanotubes Loaded with Peppermint Essential Oil as Filler for Functional Biopolymer Film. *Carbohydr. Polym.* **2016**, *152*, 548-557.
10. Fan, L.; Zhang, J.; Wang, A. In Situ Generation of Sodium Alginate/Hydroxyapatite/Halloysite Nanotubes Nanocomposite Hydrogel Beads as Drug-Controlled Release Matrices. *J. Mater. Chem. B* **2013**, *1* (45), 6261-6270.

11. Liu, M.; Chang, Y.; Yang, J.; You, Y.; He, R.; Chen, T.; Zhou, C. Functionalized Halloysite Nanotube by Chitosan Grafting for Drug Delivery of Curcumin to Achieve Enhanced Anticancer Efficacy. *J. Mater. Chem. B* **2016**, *4* (13), 2253-2263.
12. Massaro, M.; Piana, S.; Colletti, C. G.; Noto, R.; Riela, S.; Baiamonte, C.; Giordano, C.; Pizzolanti, G.; Cavallaro, G.; Milioto, S.; Lazzara, G. Multicavity Halloysite-Amphiphilic Cyclodextrin Hybrids for Co-Delivery of Natural Drugs into Thyroid Cancer Cells. *J. Mater. Chem. B* **2015**, *3* (19), 4074-4081.
13. Massaro, M.; Riela, S.; Baiamonte, C.; Blanco, J. L. J.; Giordano, C.; Lo Meo, P.; Milioto, S.; Noto, R.; Parisi, F.; Pizzolanti, G.; Lazzara, G. Dual Drug-Loaded Halloysite Hybrid-Based Glycocluster for Sustained Release of Hydrophobic Molecules. *RSC Adv.* **2016**, *6* (91), 87935-87944.
14. Massaro, M.; Amorati, R.; Cavallaro, G.; Guernelli, S.; Lazzara, G.; Milioto, S.; Noto, R.; Poma, P.; Riela, S. Direct Chemical Grafted Curcumin on Halloysite Nanotubes as Dual-Responsive Prodrug for Pharmacological Applications. *Coll. Surf. B.* **2016**, *140*, 505-513.
15. Massaro, M.; Riela, S.; Cavallaro, G.; Colletti, C. G.; Milioto, S.; Noto, R.; Parisi, F.; Lazzara, G. Palladium Supported on Halloysite-Triazolium Salts as Catalyst for Ligand Free Suzuki Cross-Coupling in Water under Microwave Irradiation. *J. Mol. Catal. A: Chem.* **2015**, *408*, 12-19.
16. Massaro, M.; Schembri, V.; Campisciano, V.; Cavallaro, G.; Lazzara, G.; Milioto, S.; Noto, R.; Parisi, F.; Riela, S. Design of PNIPAAm Covalently Grafted on Halloysite Nanotubes as a Support for Metal-Based Catalysts. *RSC Adv.* **2016**, *6* (60), 55312-55318.
17. Peng, Q.; Liu, M.; Zheng, J.; Zhou, C. Adsorption of Dyes in Aqueous Solutions by Chitosan-Halloysite Nanotubes Composite Hydrogel Beads. *Microp. Mesop. Mater.* **2015**, *201* (C), 190-201.
18. Massaro, M.; Riela, S.; Cavallaro, G.; Colletti, C. G.; Milioto, S.; Noto, R.; Lazzara, G. Eco-compatible Halloysite/Cucurbit[8]uril Hybrid as Efficient Nanosponge for Pollutants Removal. *ChemistrySelect* **2016**, *1* (8), 1773-1779.
19. Shao, X.; Li, C.; Chen, S.; Yao, K.; Yao, M. Functional Two-Dimensional Organic-Inorganic Hybrid Materials with Regular Peptides. *Coll. Surf. A* **2013**, *424*, 66-73.
20. Mahmoud, M. E.; Hafez, O. F.; Osman, M. M.; Yakout, A. A.; Alrefaay, A. Hybrid Inorganic/Organic Alumina Adsorbents-Functionalized-Purpurogallin for Removal and Preconcentration of Cr(II), Fe(II), Cu(II), Cd(II) and Pb(II) from Underground Water. *J. Hazard. Mater.* **2010**, *176* (1-3), 906-912.
21. Liang, X.; Lu, Y.; Li, Z.; Yang, C.; Niu, C.; Su, X. Bentonite/Carbon Composite as Highly Recyclable Adsorbents for Alkaline Wastewater Treatment and Organic Dye Removal. *Microp. Mesop. Mater.* **2017**, *241*, 107-114.
22. Ghosh, D.; Bhattacharyya, K. G. Adsorption of Methylene Blue on Kaolinite. *Appl. Clay Sci.* **2002**, *20* (6), 295-300.
23. Fetterolf, M. L.; Patel, H. V.; Jennings, J. M. Adsorption of Methylene Blue and Acid Blue 40 on Titania from Aqueous Solution. *J. Chem. Eng. Data* **2003**, *48* (4), 831-835.
24. Han, R.; Zhang, J.; Han, P.; Wang, Y.; Zhao, Z.; Tang, M. Study of Equilibrium, Kinetic and Thermodynamic Parameters About Methylene Blue Adsorption onto Natural Zeolite. *Chem. Eng. J.* **2009**, *145* (3), 496-504.

25. Massaro, M.; Riela, S.; Lo Meo, P.; Noto, R.; Cavallaro, G.; Milioto, S.; Lazzara, G. Functionalized Halloysite Multivalent Glycocluster as a New Drug Delivery System. *J. Mater. Chem. B* **2014**, *2* (44), 7732-7738.
26. Massaro, M.; Riela, S.; Cavallaro, G.; Gruttadauria, M.; Milioto, S.; Noto, R.; Lazzara, G. Eco-Friendly Functionalization of Natural Halloysite Clay Nanotube with Ionic Liquids by Microwave Irradiation for Suzuki Coupling Reaction. *J. Organomet. Chem.* **2014**, *749*, 410-415.
27. Liang, W.; Yang, C.; Zhou, D.; Haneoka, H.; Nishijima, M.; Fukuhara, G.; Mori, T.; Castiglione, F.; Mele, A.; Caldera, F.; Trotta, F.; Inoue, Y. Phase-Controlled Supramolecular Photochirogenesis in Cyclodextrin Nanosponges. *Chem. Commun.* **2013**, *49* (34), 3510-3512.
28. Wei, X.; Liang, W.; Wu, W.; Yang, C.; Trotta, F.; Caldera, F.; Mele, A.; Nishimoto, T.; Inoue, Y. Solvent- and Phase-Controlled Photochirogenesis. Enantiodifferentiating Photoisomerization of (Z)-Cyclooctene Sensitized by Cyclic Nigerosyl-nigerose-Based Nanosponges Crosslinked by Pyromellitate. *Org. Biomol. Chem.* **2015**, *13* (10), 2905-2912.
29. Lo Meo, P.; Lazzara, G.; Liotta, L.; Riela, S.; Noto, R. Cyclodextrin-Calixarene Copolymers as a New Class of Nanosponges. *Polymer Chemistry* **2014**, *5* (15), 4499-4510.
30. Riela, S.; Lazzara, G.; Lo Meo, P.; Guernelli, S.; D'Anna, F.; Milioto, S.; Noto, R. Microwave-Assisted Synthesis of Novel Cyclodextrin-Cucurbituril Complexes. *Supramol. Chem.* **2011**, *23* (12), 819-828.
31. Lazzara, G.; Milioto, S. Dispersions of Nanosilica in Biocompatible Copolymers. *Polym. Degrad. Stab.* **2010**, *95* (4), 610-617.
32. Massaro, M.; Riela, S.; Guernelli, S.; Parisi, F.; Lazzara, G.; Baschieri, A.; Valgimigli, L.; Amorati, R. A Synergic Nanoantioxidant Based on Covalently Modified Halloysite-Trolox Nanotubes with Intra-Lumen Loaded Quercetin. *J. Mater. Chem. B* **2016**, *4* (13), 2229-2241.
33. Del Buffa, S.; Grifoni, E.; Ridi, F.; Baglioni, P. The Effect of Charge on the Release Kinetics from Polysaccharide-Nanoclay Composites. *J. Nanopart. Res.* **2015**, *17* (3), 146.
34. Pasbakhsh, P.; Churchman, G. J.; Keeling, J. L. Characterisation of Properties of Various Halloysites Relevant to Their Use as Nanotubes and Microfibre Fillers. *Appl. Clay Sci.* **2013**, *74*, 47-57.
35. Massaro, M.; Cina, V.; Labbozzetta, M.; Lazzara, G.; Lo Meo, P.; Poma, P.; Riela, S.; Noto, R. Chemical and Pharmaceutical Evaluation of the Relationship between Triazole Linkers and Pore Size on Cyclodextrin-Calixarene Nanosponges Used as Carriers for Natural Drugs. *RSC Adv.* **2016**, *6* (56), 50858-50866.
36. Jalalvandi, E.; Cabral, J.; Hanton, L. R.; Moratti, S. C. Cyclodextrin-Polyhydrazine Degradable Gels for Hydrophobic Drug Delivery. *Mater. Sci. Eng. C* **2016**, *69*, 144-153.
37. Yang, C.; Wu, S.; Cheng, J.; Chen, Y. Indium-Based Metal-Organic Framework/Graphite Oxide Composite as an Efficient Adsorbent in the Adsorption of Rhodamine B from Aqueous Solution. *J. Alloys Compd.* **2016**, *687*, 804-812.
38. Gereli, G.; Seki, Y.; Murat Kuşoğlu, İ.; Yurdakoç, K. Equilibrium and Kinetics for the Sorption of Promethazine Hydrochloride onto K10 Montmorillonite. *J. Coll. Interf. Sci.* **2006**, *299* (1), 155-162.
39. Qiu, H.; Lv, L.; Pan, B.-c.; Zhang, Q.-j.; Zhang, W.-m.; Zhang, Q.-x. Critical Review in Adsorption Kinetic Models. *J Zhejiang Univ-Sci A* **2009**, *10* (5), 716-724.

40. Russo, M.; Saladino, M. L.; Chillura Martino, D.; Lo Meo, P.; Noto, R. Polyaminocyclodextrin Nanosponges: Synthesis, Characterization and Ph-Responsive Sequestration Abilities. *RSC Adv.* **2016**, *6* (55), 49941-49953.
41. Chen, H.; Zhao, J.; Wu, J.; Yan, H. Selective Desorption Characteristics of Halloysite Nanotubes for Anionic Azo Dyes. *RSC Adv.* **2014**, *4* (30), 15389-15393.
42. Yu, L.; Xue, W.; Cui, L.; Xing, W.; Cao, X.; Li, H. Use of Hydroxypropyl-B-Cyclodextrin/Polyethylene Glycol 400, Modified Fe₃O₄ Nanoparticles for Congo Red Removal. *Int. J. Biol. Macromol.* **2014**, *64*, 233-239.
43. Zhao, M.; Liu, P. Adsorption Behavior of Methylene Blue on Halloysite Nanotubes. *Microp. Mesop. Mater.* **2008**, *112* (1-3), 419-424.
44. Xiong, L.; Yang, Y.; Mai, J.; Sun, W.; Zhang, C.; Wei, D.; Chen, Q.; Ni, J. Adsorption Behavior of Methylene Blue onto Titanate Nanotubes. *Chem. Eng. J.* **2010**, *156* (2), 313-320.
45. Zhao, D.; Zhao, L.; Zhu, C.-S.; Huang, W.-Q.; Hu, J.-L. Water-Insoluble B-Cyclodextrin Polymer Crosslinked by Citric Acid: Synthesis and Adsorption Properties toward Phenol and Methylene Blue. *J. Incl. Phenom. Macro. Chem.* **2009**, *63* (3), 195-201.

Table of Content

Synthesis and characterization of halloysite-cyclodextrin nanosponges for enhanced dyes adsorption

Marina Massaro, Carmelo G. Colletti, Giuseppe Lazzara, Susanna Guernelli, Renato Noto and
Serena Riela

HNT-CD hybrids has been developed by covalently linking biocompatible cyclodextrin on natural halloysite nanotubes, thus obtaining nanosponges for water purification.

