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Metal-inorganic-organic core–shell material as efficient matrices for CO_2 adsorption: Synthesis, properties and kinetic studies

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ABSTRACT

A novel hydrochar-based core–shell material with improved affinity towards CO_2 was synthesized through encapsulation within ZnO shell, followed by chemical grafting to an organic moiety bearing terminal diethanolamino groups and further dispersion of Cu^0 nanoparticles. Characterization through nitrogen adsorption–desorption isotherms with BET and BJH models, SEM, TEM, zeta potential measurements, FTIR spectroscopy, DSC and XPS analyses revealed a strong influence of the modification procedure on the performance of each material in CO_2 adsorption. The resulting metal-inorganic-organic-core–shell (MIOCS) displayed compacted structure with a wide pore size distribution that imposes intraparticle diffusion as a kinetic-controlling step. Cu-MIOCS showed an appreciable CO_2 retention capacity of 5.42 mmol/g compared to many adsorbents reported so far. This affinity towards CO_2 was explained in terms of physical and non-stoichiometric CO_2 condensation. This finding is of great importance, because it demonstrates that judicious modifications of vegetal-deriving wastes such as woods and other biomasses give rise to added-value materials as low cost and efficient gas adsorbents with high affinity towards CO_2.

1. Introduction

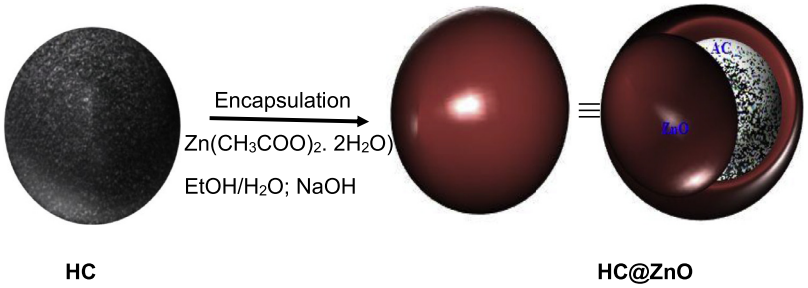
Global warming and climate changes turn out to arise from high concentrations of greenhouse gases (GHG), among which carbon dioxide (CO_2) is the most directly related to human activities [1,2]. The persistent use of fossil fuels as the main energy source in designing new technologies clearly demonstrates the lack of a clear strategy for a sustainable development. This makes that GHG and CO_2 emissions from anthropic activities still remain a major environmental issue [3,4]. Clear evidence in this regard is provided by numerous procedures targeting direct CO_2 capture from flue emissions [5,6,7], even if, in most cases, adsorbents regeneration often requires more CO_2-equivalent energy than captured. Amine-based adsorbents display sufficient basicity for retain CO_2 via the formation of carbamates [8,9], but severe thermal regeneration. In the long run, this way of acting is doomed to failure, unless strategies regarding CO_2 as a product, for instance, for further uses in chemistry and in agricultural greenhouses are developed. Such strategies will certainly face a major issue, that of the too low CO_2 concentrations in flue emissions, which impose previous concentration of the captured gas.

A judicious approach in this direction resides in designing new waste-free and non-polluting technologies for CO_2 concentration through a truly reversible gas capture at ambient conditions. Weaker CO_2–adsorbent interactions are an essential requirement in this regard, and can be achieved using materials bearing amphoteric to slightly basic chemical functions such as hydroxyl groups. The latter are known to promote only CO_2 adsorption via weakly bonded carbonate-like association [10–17].

OH-enriched materials containing soya-deriving polyglycerols were already found to show high affinity towards CO_2, and gave

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Scheme 1. Schematic illustration of HC@ZnO core–shell particles.

similar performances as polyol dendrimers [11,12,13,14,15,16,17]. Their affinity improvement was explained in terms of mere incorporation of a vegetal source of OH groups. Unlike complex structure materials such as zeolites, metal-organic frameworks (MOFs) and others tested in CO_2 adsorption [18,19,20], low cost natural materials such as vegetal wastes display low surface acidity and do not require sophisticated modification procedures [21,22]. The structure of any vegetal material should bear terminal hydroxyl groups but does not necessarily exhibit interesting affinity towards CO_2 due to structure constraints such as porosity and/or optimum amphoteric to slightly character.

Vegetal waste modification often turns out to an essential requirement for affinity improvement. Their conversion into hydrochar (HC), followed by suitable modifications could be a judicious route for obtaining highly added-value materials with improved affinity towards CO_2. HCs are also low cost porous materials that display high porosity and specific surface area along with appreciable thermal and chemical stability [23,24]. They may be obtained through pyrolysis, carbonization or hydrothermal conversion of diverse vegetal wastes [25,26]. Their activation in optimal conditions is known to improve the surface properties [27] and affinity towards CO_2 [28].

So far, the behavior of vegetal wastes as host matrices for metal, metal oxides and CO_2 condensation along with the interactions involved still remains barely tackled. This became the main objective of the present paper. Metal oxides, and more particularly zinc oxide (ZnO) are also assumed to exhibit interesting surface properties as adsorbent [29,30] and electronic material [31]. ZnO combination with a diethanolamine-modified cocoa shell-deriving hydrochar already showed interesting surface properties [32–35]. It turned out to act as host matrice for copper-zero dispersion and as effective adsorbent for CO_2 at room temperature like other materials with attenuated basicity [15]. The specific surface area was not an essential requirement, inasmuch as compacted matrices paradoxically displayed higher affinity towards CO_2 than much more expanded and more porous materials [14,36,37]. Hence, a new strategy was rather focused on the preparation of compacted matrices that promote metal stabilization and attenuate CO_2 retention strength. Strong metal: matrice interaction is expected to attenuate the Lewis basicity of the N atom of the organic moiety [35], and, subsequently, CO_2 capture will mainly occur via purely physical gas condensation, that favors with easy release upon forced convection or under lower pressure. The material interactions with both metal particles and CO_2 were deeply examined herein as specific objectives of this work.

Due to their low thermal and chemical stability, vegetal-deriving materials cannot be directly used in CO_2 capture from flue emissions. Previous cooling and water treatments of flue emissions with energy recovery with advanced elimination of SO_x, NO_x and volatile organic compounds (VOC) turns out to be essential requirements for a possible sustainable technology. That is why reversible capture of CO_2 appears as an original alternative for a non-thermal gas release for regeneration and further CO_2 utilization. This new concept still remains a difficult challenge, but can be addressed using metal-inorganic-organic core–shell materials (MIOCS) displaying weak basicity. In this regard, our approach resides in correlating Cu^0-matrice and CO_2-matrice interactions with both the surface properties and structural and textural features of the synthesized material. Full characterization of MIOCS by means of diverse techniques allowed achieving deep analysis of the adsorbent affinity towards CO_2 in terms of magnitude and adsorption kinetics. The results will open promising prospects for manufacturing adsorbing materials and membranes that "respire CO_2" under ambient conditions.

2. Experimental

2.1. Chemicals

Zinc acetate dihydrate ($Zn(CH_3COO)_2{,}2H_2O$; 99%); 3-chloropropyltrimethoxysilane ($C_6H_{15}ClO_3Si$; 97%); sodium borohydride ($NaBH_4$; 99%); diethanolamine ($NH(CH_2–CH_2–OH)_2$; 98%); copper(II) sulfate anhydrous ($CuSO_4$; 99.9%); triethylamine ($C_6H_{15}N$; 99.9%) and absolute ethanol (CH_3CH_2OH; 99.9%) were purchased from Sigma-Aldrich and used as received. For all the experiments, ultra-pure water was used (Millipore).

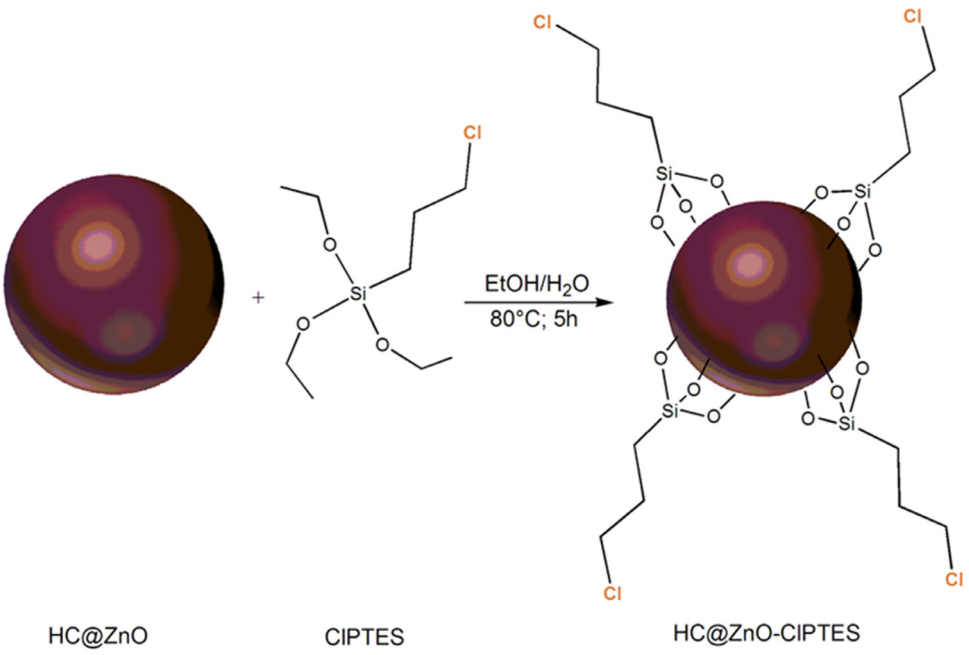
2.2. Materials synthesis

Hydrochar (HC) was produced via hydrothermal conversion of cocoa shell powder (1 g), originating from Cameroon, previously dispersed in deionized water (10 mL), at 240 °C for 24 h in a sealed Teflon lined autoclave (30 mL). The mixture was cooled down to room temperature (RT), and HC was obtained in the form of a white suspension. HC was filtered, repeatedly washed with deionized water and then with ethanol, and finally dried at 80 °C overnight.

HC was then encapsulated into a shell of ZnO in a mixture of aqueous solutions of zinc acetate dihydrate (0.2 M) and sodium hydroxide as precursors, under continuous and vigorous stirring at 60 °C in a 3:1 (V:V) ethanol-water mixture for 15 min. The pH value was previously adjusted at 9.5. HC was added in a proportion of 0.01 wt% and the mixture was heated at 60 °C for 4 h. The resulting grey precipitate of HC@ZnO was filtrated, washed with water/ethanol to remove the unreacted sodium acetate and then dried overnight at 100 °C (Scheme 1). Further, 3-chloropropyltrimethoxysilane (ClPTES) was grafted on HC@ZnO using ethanol/water 3:1 as a solvent at 80 °C during 5 h (Scheme 2). The resulting HC@ZnO–ClPTES sample was washed, filtrated, dried overnight at 80 °C and then prone to chlorine substitution by diethanolamine (DEA) at 50 °C under inert atmosphere for 24 h (Scheme 3).

The final HC@ZnO–Si–$(CH_2)_3$–$N(CH_2–CH_2–OH)_2$ material obtained denoted as HC@ZnO–Si–$N(OH)_2$ was washed, filtrated and

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Scheme 2. Schematic illustration of the ClPTES grafting onto the surface of HC@ZnO.

then dried at 80 °C. Copper nanoparticles (CuNPs) were incorporated in HC@ZnO–Si–$N(OH)_2$ using 0.3 wt% anhydrous copper(II) sulfate ($CuSO_4$) as a precursor in 40 mL toluene in the presence of 0.03 wt% sodium borohydride ($NaBH_4$) as the metal reducing agent after 6 h of stirring at RT. The final HC@ZnO–Si–$N(OH)_2$–Cu material (Scheme 4), denoted as metal-inorganic-organic-core–shell (Cu-MIOCS) was dried overnight at 80 °C and then stored in sealed enclosure containing dried and O_2-free nitrogen.

2.3. Material characterization

HC, HC@ZnO and Cu-MIOCS were characterized through Fourier transform IR spectroscopy (FTIR) using a Tensor 27 (Bruker) spectrometer with a ZnSe ATR crystal equipment. For each spectrum, 20 scans were accumulated with a resolution of 4 cm^{-1}. All samples were drilled before IR analysis and background spectra were recorded on air. Analysis through Scanning Electronic Microscopy (SEM) of samples previously metallized by gold layer (at 18 mA during 360 s with a Biorad E5200 device) was performed by means of a ZEISS EVO 15 electron microscope. The surface morphology was investigated with secondary electrons, while the atomic composition was assessed by an attached Energy Dispersive X-ray Fluorescence (ED-XRF) device. The TEM (transmission electron microscopy) observations were achieved using a FEI TECNAI 20FST instrument on samples ultrasonically dispersed in ethanol and deposited on amorphous holey carbon membranes and then dried.

The specific surface area and porosity were assessed by nitrogen adsorption–desorption isotherms at 77 K, using a Micromeritics Tristar 3000 device. Typically, equivalent BET (Brunauer–Emmett–Teller) surface areas were determined in the relative pressure range P/P0 from 0.01 to 0.04 and equivalent BJH (Barrett–Joyner–Halenda) pore volume were measured at P/P0 > 0.985. The samples were previously degassed at 150 °C for at least 7 h using a Micromeritics Vac Prep 061 degasser. Measurements through differential scanning calorimetry (DSC) were carried out using (DSC-92 Setaram) at a 2 °C/min heating rate from room temperature to 500 °C. XPS analysis was performed using a Shimadzu ESCA-3400 and Al K_{alpha} X-ray source (1486.6 eV), while deconvolution of the XPS patterns was achieved using a nonlinear least-square curve-fitting program (XPS-PEAK software 4.1). The zeta potential of each 2 mg of sample previously dispersed in 10 mL of deionized water and ultrasonicated for 15 min was measured with the phase analysis light scattering (PALS) mode using a Malvern zeta sizer nanoZS setup.

2.4. CO_2 adsorption tests and kinetics

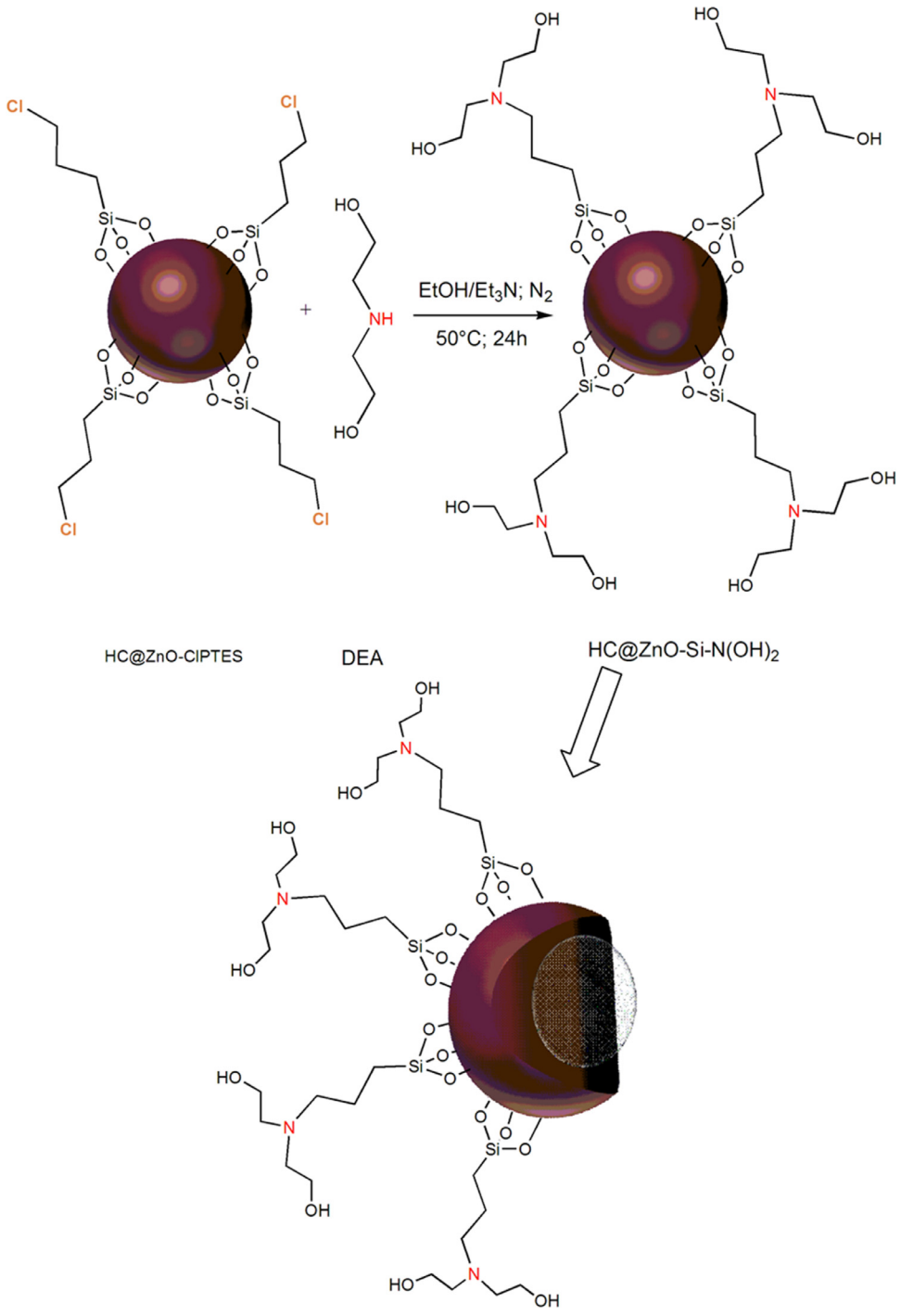
This was achieved using an appropriate device containing dry air-free nitrogen according to a specific procedure fully described elsewhere [35]. Triplicate CO_2 adsorption tests were carried out within a 20 mL sealed enclosure at 292 K and normal pressure. Concisely, 3 mL of pure carbon dioxide previously dried was injected by a syringe in sealed capillary U-shaped manometer (0.25 mm internal diameter) containing dry air-free nitrogen and 0.01 g of dry material samples with a 2.43–5.14 µm particle size. The non-adsorbed CO_2 excess was further purged until the normal pressure is attained in the internal U-shaped manometer. The adsorbed CO_2 amount was periodically measured in time (0.2 min, 0.4 min, 0.6 min, 0.8 min, 1 min etc.) by measuring that of the residual non adsorbed gas. When necessary, complete regeneration for a total CO_2 release from the adsorbents was achieved by slight heating up to 80 °C or by forced convection under strong air stream (15–30 mL/min) until no CO_2 was detected by bubbling into a 0.1 N aqueous NaOH solution. The adsorbent affinity towards CO_2 was examined in terms of contact time and adsorption kinetics using pseudo 1st and 2nd order models [30,38,39].

3. Results and discussion

3.1. Surface morphology and textural properties

Same-scale SEM images (Fig. 1) (20 nm) revealed morphology change from fibrous HC (*a*) to granular HC@ZnO (*b*), suggesting strong HC: ZnO interaction. Much more pronounced changes were noticed after ClPTES (*c*) and diethanolamine grafting (*d*), resulting in aggregates of much smaller particles with particle size not exceeding few micrometers, presumably due to self-condensation of triethoxysilane groups and hydrophobic interaction between grafted chloro-propyl groups.

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Scheme 3. Schematic illustration of the diethanolamine substitution of chloride on grafted ClPTES.

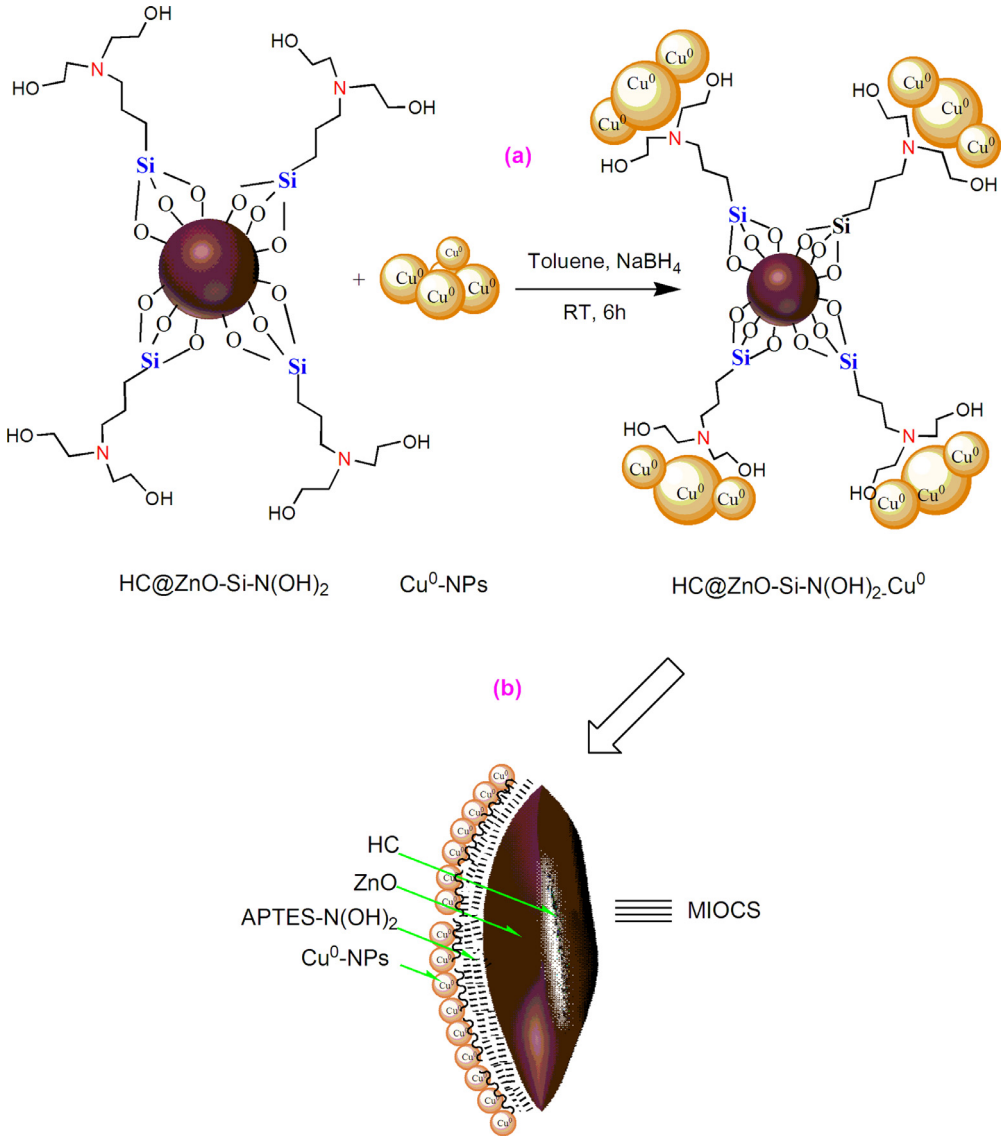
Further SEM images after Cu^0 incorporation (*e*) and close-up (*f*) showed larger aggregates of particles with much smoother external surface, most likely due intra and intergranular entrapment of Cu^0 particles. Here, strong Cu^0:$N(OH)_2$ Lewis-acid-base (LAB) interaction must induce a structure compaction that should reduce porosity, but should promote non-stoichiometric and purely physical condensation of CO_2 on metal sites surrounded by N atoms and hydroxyl groups.

Deeper insights through TEM images (Fig. 2) showed a clear membrane of ZnO shell surrounding aggregates of 0.05–0.1 µm dark stains of HC (*a*), whose aggregation generates interparticle void spaces (*a*). The latter appears to dramatically decrease upon ZnO-coating (*b*). After ClPTES grafting and further functionalization by diethanolamine (*c*), close-up on the clear membrane (*d*) and ED-XRF analysis revealed non uniformly sized 2–20 nm Cu^0 nanoparticles (CuNPs).

The nitrogen adsorption–desorption isotherms recorded were found to be of type IV with an H3-type hysteresis loop for mesoporous materials (Fig. 3). Measurements using the BET and BJH models (Table 1) revealed a structure expansion after ZnO incorporation as supported by the increase of the specific surface area (SSA) from 20 m^2/g for HC to 25 m^2/g for HC@ZnO.

The consecutive SSA decrease down to 21 m^2/g upon ClPTES grafting agrees with our previous statement regarding a possible self-condensation of triethoxysilane groups and a structure compaction as a result hydrophobic interaction between grafted

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Scheme 4. Illustration of CuNPs insertion (a) and close-up on HC@ZnO–Si–$N(OH)_2$–Cu (b).

Table 1
Textural properties of the prepared samples.

Sample	Isotherm	Hysteresis	Specific surface area (m^2/g)	Total pore volume (cc/g)	BJH pore volume (cc/g)
HC	–	–	20	–	–
HC@ZnO	Type II	H3	25	0.17	0.17
HC@ZnO–ClPTES	Type II	H3	21	0.13	0.13
HC@ZnO–Si–$N(OH)_2$	Type II	H3	29	0.20	0.20
Cu-MIOCS	Type II	H3	20	0.12	0.12

chloro-propyl groups. This is also supported by a porosity decay reflected by a pore volume decrease from 0.17 to 0.13 cc/g. Further functionalization with diethanolamine appears to suppress such an interaction, since a marked SSA improvement up to 29 m^2/g was noticed. This must be due the appearance of H-bridges between terminal hydroxyls belonging to both the grafted organic moieties and residual free terminal Cu–OH groups. This is supposed to give rise to additional porosity, as supported by the significant increase in total pore volume from 0.12 to 0.20 cc/g.

Cu^0 particle insertion induced marked decay of the specific surface area and average pore volume down to 20 m^2/g and 0.12 nm, respectively, thereby confirming our previously stated structure compaction. This phenomenon is a special feature of the occurrence of –N:Metal and -O:Metal Lewis-Acid-Base (LAB) interactions, as already reported elsewhere [14,36,40–43].

3.2. Evidence of metal stabilization

The most significant changes were noticed through FTIR analysis in the 750–1700 cm^{-1} and 3000–3500 cm^{-1} regions. These changes were mainly reflected by the rise of an intense absorption band at *ca.* 1065 cm^{-1} and smaller one around 800 cm^{-1} (Figs. 4, S1 and S2) attributed to Si–O–Si and Si–O–C stretching vibrations,

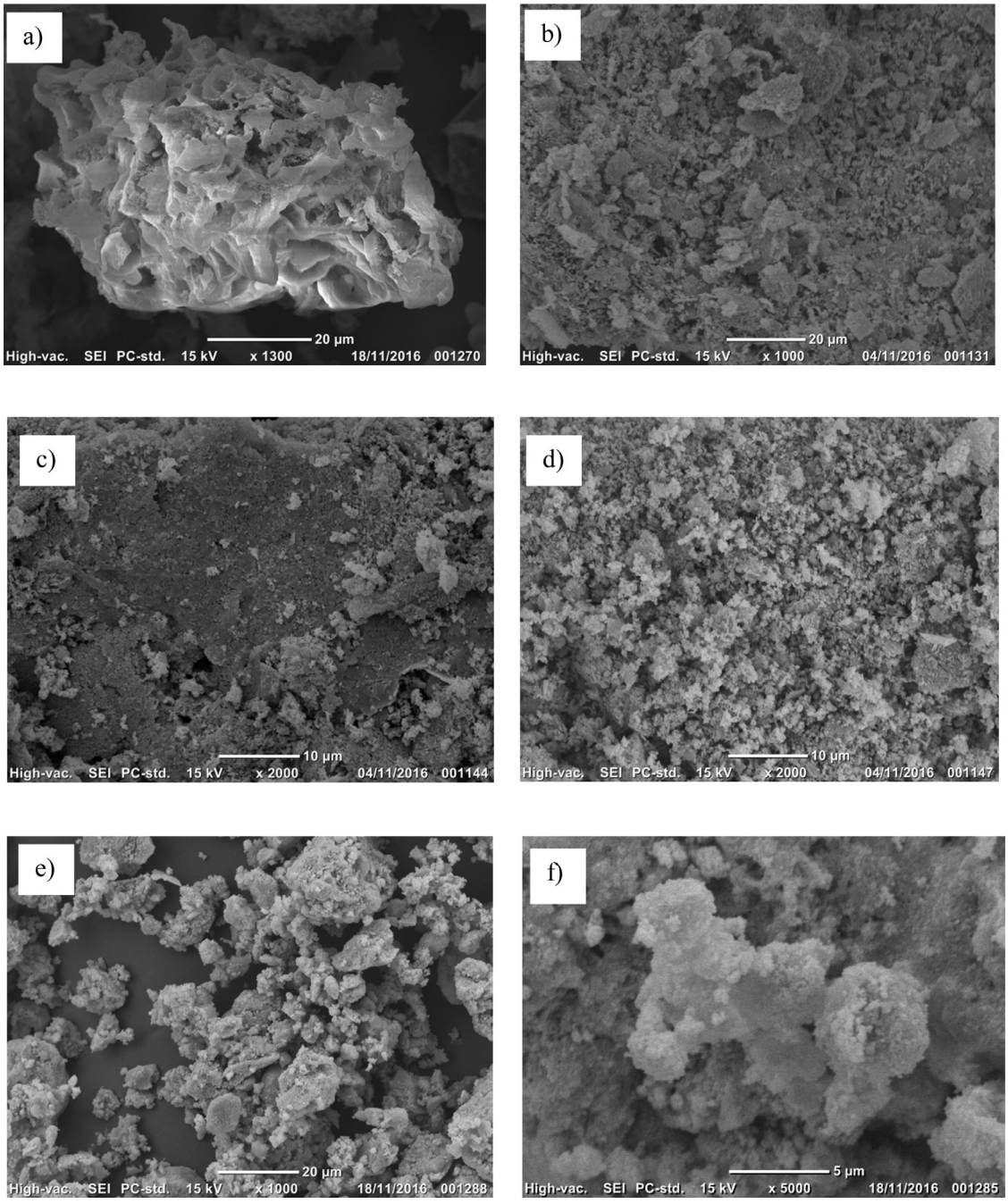


Fig. 1. SEM images of HC (a), HC@ZnO (b), HC@ZnO–ClPTES (c), HC@ZnO–Si–$N(OH)_2$ (d) and Cu-MIOCS (e and f).

providing clear evidence of ClPTES grafting but accompanied by an unavoidable self-condensation of the triethethoxysilane groups [35,44,45]. The appearance of the 3440–3700 and 1674 cm^{-1} bands assigned to the N–H stretching vibration and NH_2 bending vibration, respectively was attributed to amine grafting [46,47]. The marked depletion of the 3400 cm^{-1} after APTES grafting indicates the occurrence of HC–O–Si-propyl bridges.

The total disappearance of the 2919 cm^{-1} band related to the asymmetric stretching vibration of CH_2 and C–H aliphatic groups after Cu^0 incorporation must be due to the occurrence of strong Cu: OH– and Cu:N– interactions that induce a compaction of the organic entanglement around CuNPs, in agreement with our previous statements [35,36]. Incorporation of CuNPs also induced a marked shift of the 1065 cm^{-1} band towards lower wavenumber (Fig. 4), suggesting a N–C bond weakening by the appearance of strong Cu^0:N-propyl interaction. Terminal OH groups should also contribute to this compaction of the organic entanglement via Cu^0: OH- Lewis-acid-base interactions with a possible synergy between the N and O atoms in CuNP stabilization, as supported by the slight intensity decrease of the 3300–3600 cm^{-1} bands [36,37].

Deeper insights through XPS analysis showed a shift of the O-1s signal from 529.98 eV to 530.53 peak after ClPTES grafting (Table 2). This can be explained in terms of a bond strengthening on the oxygen atom, most likely due to the genesis of Zn–O–Si and/or C–O–Si bridges. The O-1s binding energy values were in good agreement with those reported for ZnO [48]. Diethanolamine grafting induced a slight decrease of this binding energy from 530.53 eV to 530.42 eV, most likely due to the presence of high

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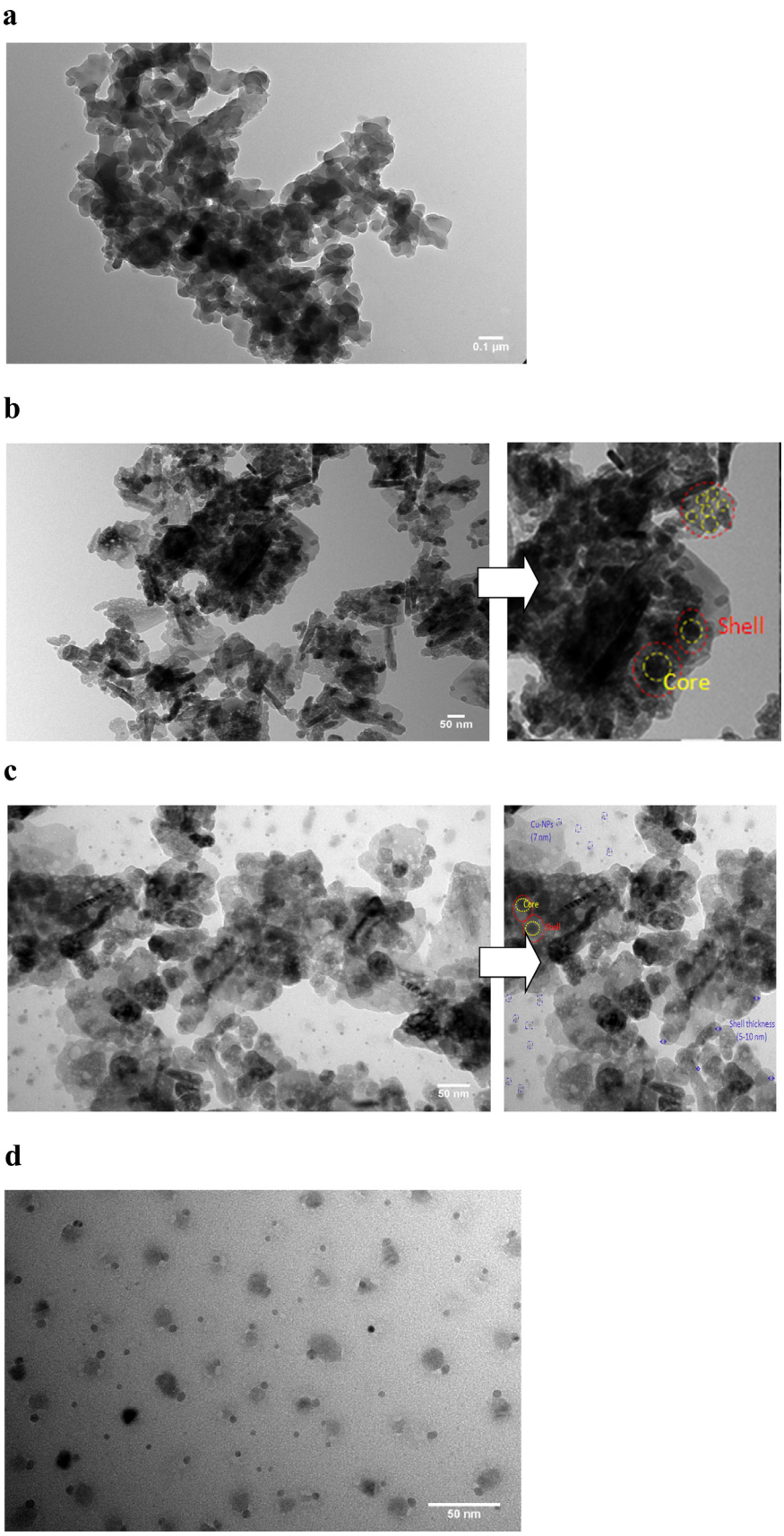


Fig. 2. TEM images of HC (a), HC@ZnO (b), Cu-MIOCS (c) and close-up on clear areas (d).

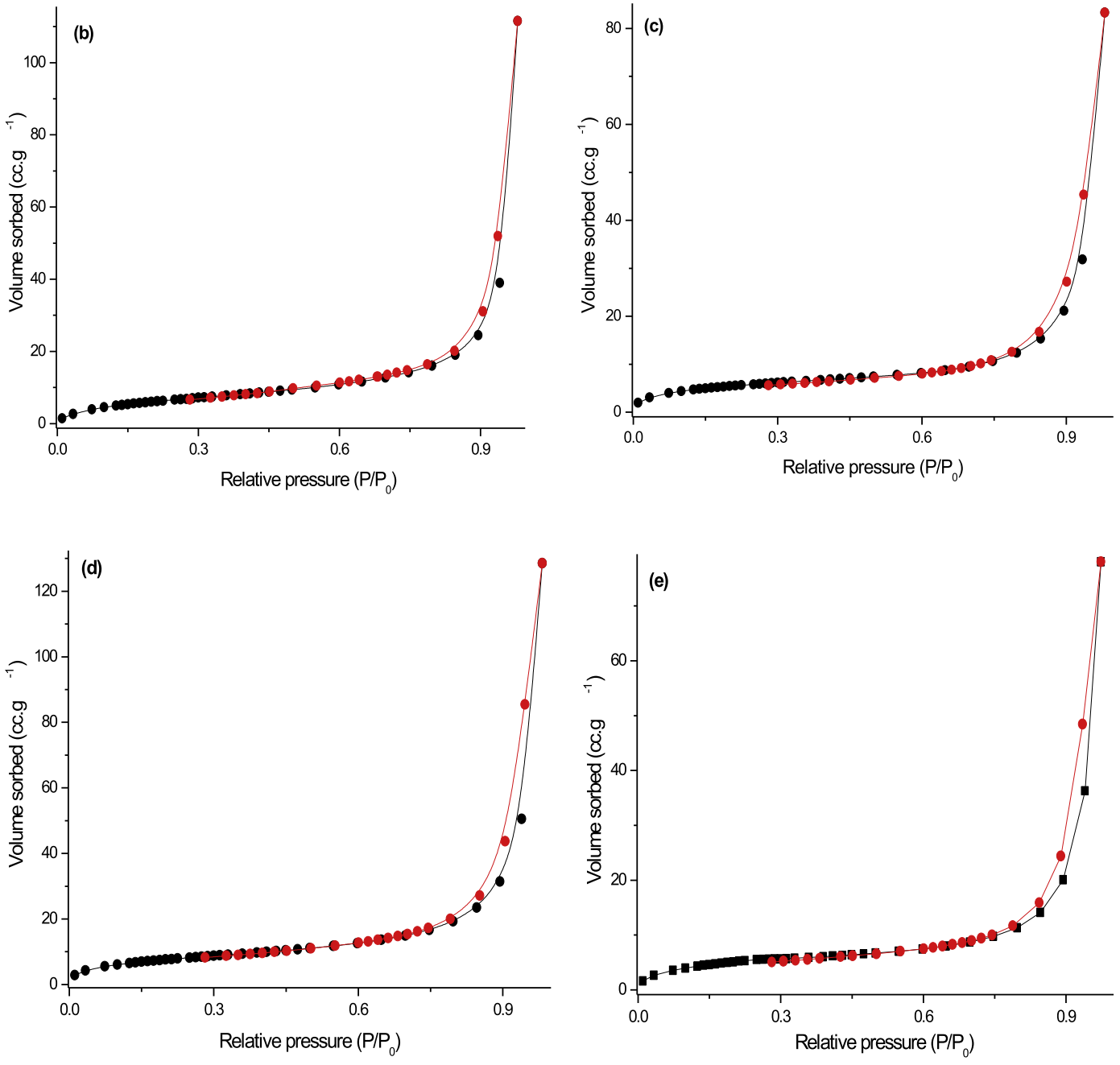


Fig. 3. Nitrogen adsorption–desorption of HC@ZnO (a), HC@ZnO–ClPTES (b), HC@ZnO–Si–N(OH)$_2$ (c) and Cu-MIOCS (d).

electron density due to next-neighboring N atoms. The involvement of the N and O atoms in CuNP stabilization was well supported by noticeable shifts of the binding energy of N-1s electrons from 399.71 to 400.33 eV and of O-1s electron from 530.42 eV to 530.91 eV, respectively, in agreement with previous data. [36] Cu incorporation was also supported by an additional Cu-2p signal at 935.70 eV (Table S1), with agrees with the literature [49].

HC encapsulation by ZnO was confirmed by the appearance of the Zn-2p$_{3/2}$ and Zn-2p$_{1/2}$ doublet at 1021.25 and 1044.34 eV, respectively [50]. The shift of both values up to 1022.24 and 1045.34 eV after ClPTES grafting accounts for a binding strengthening of the corresponding electrons, due to the formation of –Zn–O–Si–R bridges. These shifts indicate preponderant grafting of ClPTES on ZnO on HC [51]. The slight consecutive decrease of these values down to 1022.10 and 1045.30 eV must be due to the grafting of an electronegative atom (N). This was supported by the shift of the N-1s electron binding energy from 400.7 to 399.5 eV.

The C-1s XPS signal of HC@ZnO slightly shifted from 285.01 to 284.94, presumably as a result of an increase in electron density on ZnO by ClPTES grafting, which seems to act as "electron pump" due to the electronegativity of the chlorine atom. Chlorine substitution by diethanolamine grafting appears to revive the binding energy of the C-1s electrons, due to the higher electron density on the N atom. The fact that the binding energy of the C-1s electrons remained constant at 285.02 eV after Cu^0 incorporation indicates unequivocally that the organic chain grafted does not contribute to metal stabilization.

Metal stabilization was confirmed through additional Zeta potential measurements (Fig. 5), which revealed noticeable increases in the Zeta potential (ZP) and surface charge density (SPC) upon

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Table 2
Binding energies of the core level spectra for the different samples.

Adsorbent	Binding energy (eV)					
	C-1s	O-1s	N-1s	Zn-2p$_{1/2}$	Zn-2p$_{3/2}$	Cu-2p
HC@ZnO	285.01	529.98	–	1044.34	1021.25	–
HC@ZnO–ClPTES	284.94	530.53	400.07	1045.34	1022.24	–
HC@ZnO–Si–N(OH)$_2$	285.02	530.42	399.71	1045.30	1022.10	–
Cu-MIOCS	285.02	530.91	400.33	1046.35	1023.19	934.70

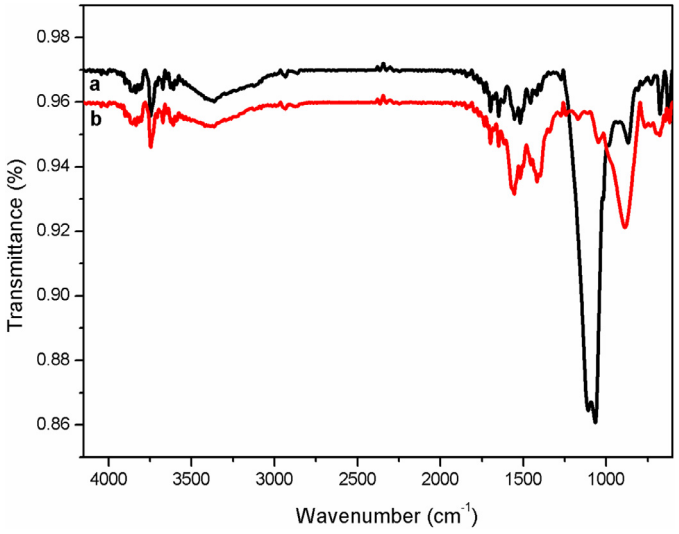


Fig. 4. FTIR spectra of HC@ZnO–Si–N(OH)$_2$ (a) and Cu-MIOCS (b).

ZnO incorporation. This must be due to the polarity of Zn–O bonds and terminal Zn–O–H groups [52]. Their consumption upon silylation by ClPTES induced a significant decrease of both the Zeta potential and surface charge density. Further functionalization by diethanolamine induced a slight SPC decrease but a marked ZP depletion.

Pronounced ZP depletion was registered after Cu^0 insertion, most likely due to the appearance of metal-matrice LAB interactions that favor the stability of the colloid suspension [53,54]. The fact that the zeta potential was reversed from positive to low negative value after Cu^0 incorporation must arise from an increase in electron density around CuNPs as a result of strong Cu^0: OH- and Cu^0–N- interactions.

3.3. Thermal behavior

DSC measurements (Fig. 6) showed thermal stability for HC up to 130–140 °C (*a*). Two exothermal processes were noticed around 250 °C and 450 °C due to the decomposition of cellulose and lignin, which are the main components of cocoa shell [55]. ZnO incorporation induced a stability improvement up to *ca.* 300 °C (*b*), as supported by the flattened bump around 350 °C. This can be explained by the formation of a more thermally stable inorganic ZnO shell.

HC@ZnO–Si–N(OH)$_2$ (*c*) displayed slightly lower thermal stability of up to 250 °C (*c*) due to the degradability of the grafted organic moiety. The latter appears to be enhanced by Cu^0 incorporation (*d*), presumably due to the appearance of copper-catalyzed decomposition processes.

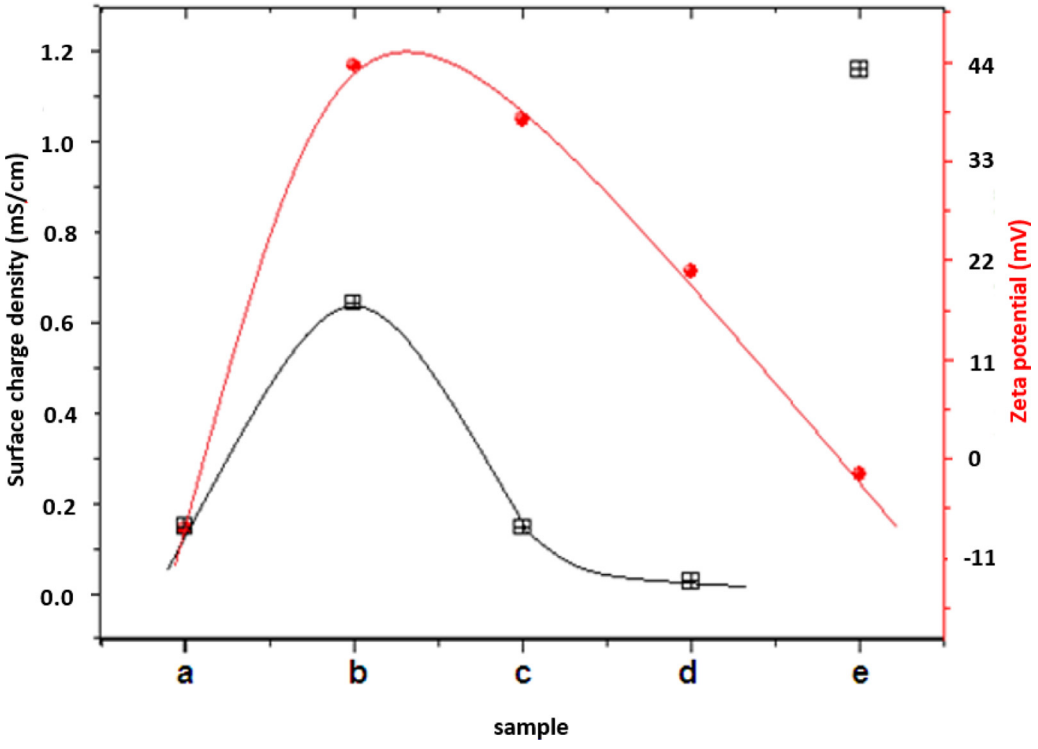


Fig. 5. Zeta potential (circle) and surface charge density (cross) for HC (a), HC@ZnO (b), HC@ZnO–ClPTES (c), HC@ZnO–Si–N(OH)$_2$ (d), and Cu-MIOCS (e).

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Table 3
Kinetics parameters for the intraparticle diffusion model.

Sample	k_{ID} [a] g/(mmol min$^{1/2}$)	C_I [a] mmol/g	[c] R^2	Standard deviation for k_{ID} g/(mmol min$^{1/2}$)
HC	0.43472	0.01087	0.934	0.05060
HC@ZnO	1.13768	−0.00982	0.951	0.07745
HC@ZnO–ClPTES	1.34847	−0.01047	0.977	0.06499
HC@ZnO–Si–N(OH)$_2$	1.23477	−0.06636	0.980	0.05337
HC@ZnO–Si–N(OH)$_2$–Cu	1.82982	0.26887	0.954	0.12614

[a] k_{ID} is the constant for the intraparticle diffusion model.
[b] C_I is assessed as the *Y*-axis intercept.
[c] R^2 is the correlation coefficient.

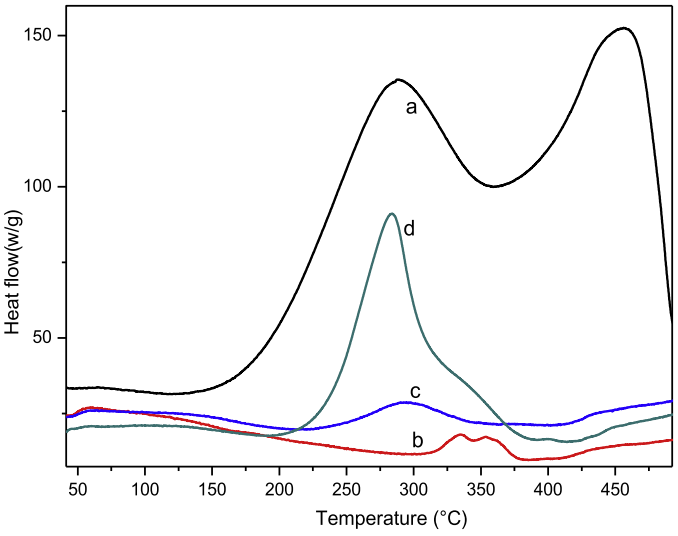


Fig. 6. DSC patterns of HC (a), HC@ZnO (b), HC@ZnO–Si–N(OH)$_2$ (c) and Cu-MIOCS (d).

3.4. Affinity towards CO_2 and adsorption kinetics

CO_2 adsorption tests under normal pressure and ambient temperature showed an increase in time of the amount of adsorbed CO_2 (Fig. 7). The latter reached a maximum and constant level after *ca.* 2 min for HC (*a*) and approximately 9–10 min for its modified counterparts (*b–d*).

It is worth mentioning that each material presents a reversible adsorption upon slight heating up 40 °C or under forced convection upon strong air stream of 15 mL/min with a maximum capacity for the first experiment. It results that, under these tests conditions, CO_2 adsorption must involve only weak interaction with the solid surface. This maximum level accounts for the real value of the CO_2 retention capacity (CRC) under these specific conditions. The highest CO_2 uptake was registered for Cu-MIOCS under normal pressure (5.423 mmol/g). This value is considerably higher than those registered under similar conditions for numerous other materials such as mesoporous silica [56], clays [12], zeolites [57], metal oxides [58], and others [56,59,60]. This improvement of the affinity towards CO_2 suggests simultaneous contributions of all incorporated species through specific interactions with a possible synergy that remains to be elucidated [61–65]. The slow evolution in time of the CO_2 uptake for the modified samples suggests the occurrence of diffusion hindrance. The two bump-shaped evolution curves suggest the occurrence of successive kinetic-determining steps, namely inter and intraparticle diffusion processes that differ from a sample to another according to the particle morphology and textural features [66].

Attempts to apply the pseudo 1st and 2nd order models [30,67] showed that CO_2 capture on HC obeys a pseudo-first order kinetics (Fig. 7). Here, physical adsorption through interactions between the oxygen atoms of carbon dioxide and terminal OH groups of HC seems to prevail in agreement with previous data [68–71] Nonetheless, neither models can apply to the other HC derivatives, the pseudo 1st order appearing as the most closest to the experimental curves. The most plausible explanation is that CO_2 adsorption on HC derivatives involves predominant kinetics-controlling diffusion processes and weak contributions of additional interaction involving both the amino and hydroxyl groups of the incorporated organic moiety [72] even in the presence of Cu^0 nanoparticles [16].

Deeper insights in CO_2 adsorption kinetics were achieved by applying the intraparticle diffusion (ID) model (Eq. (1)) that correlates the kinetics constant (k_{ID}) to the intraparticle diffusion constant (CI) [30]:

$$Q_t = k_{ID}.t^{1/2} + C_I \quad (1)$$

As expected, plotting Q_t (instant CO_2 amount adsorbed) as a function of $t_{1/2}$ resulted in sufficiently linear correlations for almost all the synthesized samples, excluding HC (Fig. 8), thereby confirming the occurrence of intraparticle diffusion on HC derivatives.

The wide dispersion of the of the measured data gave estimated values of the correlation factor (R^2) ranging from 0.93 to 0.98 according to the sample texture, the closest to unity being those obtained for HC@ZnO–Si–N(OH)$_2$ (Table 3). In this adsorbent, the intraparticle diffusion appears to prevail more than in Cu-MIOCS, where other processes such as physical adsorption and multilayer CO_2 condensation should also take place at a more or lesser extent. The occurrence of different slopes accounts for that of different intraparticle diffusion constants within a same particle of a same adsorbent, in agreement with our previous statements and other works [73].

As expected, the values of k_{ID} were found to vary in a reverse proportionality with the textural properties. Indeed, k_{ID} increased from 1.13768 g/(mmol min$^{1/2}$) (HC@ZnO) to 1.34847 g/(mmol min$^{1/2}$) (HC@ZnO–ClPTES) and from 1.23477 g/(mmol min$^{1/2}$) (HC@ZnO–Si–N(OH)$_2$) to 1.82982 g/(mmol min$^{1/2}$) (Cu-MIOCS), when the total pore volume decreases from 0.17 to 0.13 cc/g and from 0.20 to 0.12 cc/g, respectively (Table 1). In the meantime the specific surface area decreases from 25 to 21 and from 29 to 20 m^2/g, respectively. This provides additional evidence of the enhancement of the diffusion contribution to the overall CO_2 retention process with the structure compaction. The mere fact that CO_2 desorbs only upon heating or forced convection clearly demonstrates the occurrence of effective physical CO_2 retention. The latter should probably occur in the form of multilayer condensation, more or less pronounced according to the pore size and surface affinity towards CO_2. Investigations are still in progress in this direction.

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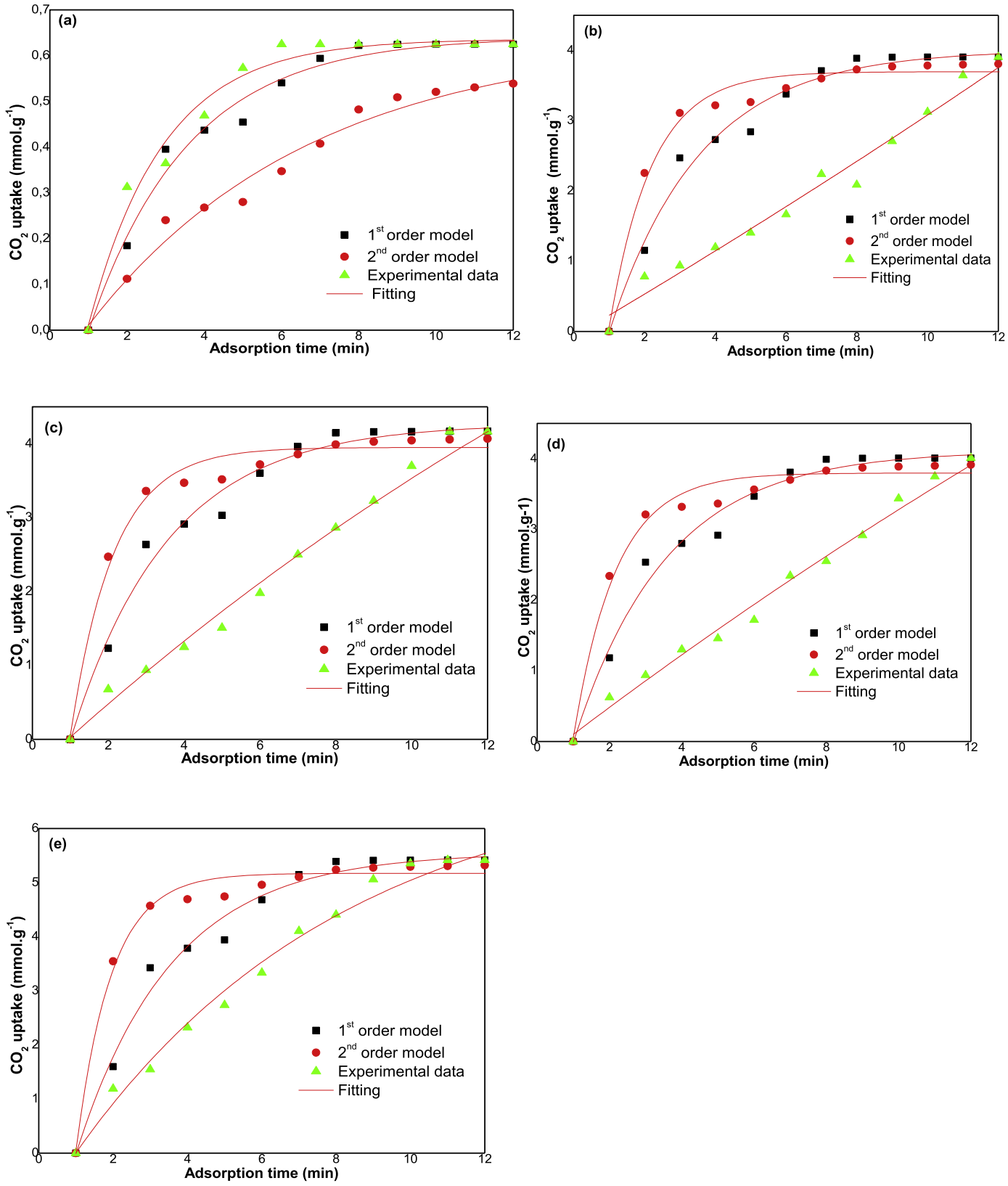


Fig. 7. Evolution in time of CO_2 uptake on hydrochar and modified derivatives as compared to adsorption kinetical models. (a) HC; (b) HC@ZnO; (c) HC@ZnO–ClPTES; (d) HC@ZnO–Si–$N(OH)_2$ and (e) Cu-MIOCS. These experiments were conducted by contacting, at room temperature and normal pressure, 10 mg of adsorbent previously dried overnight at room temperature with 3 mL of pure dry CO_2.

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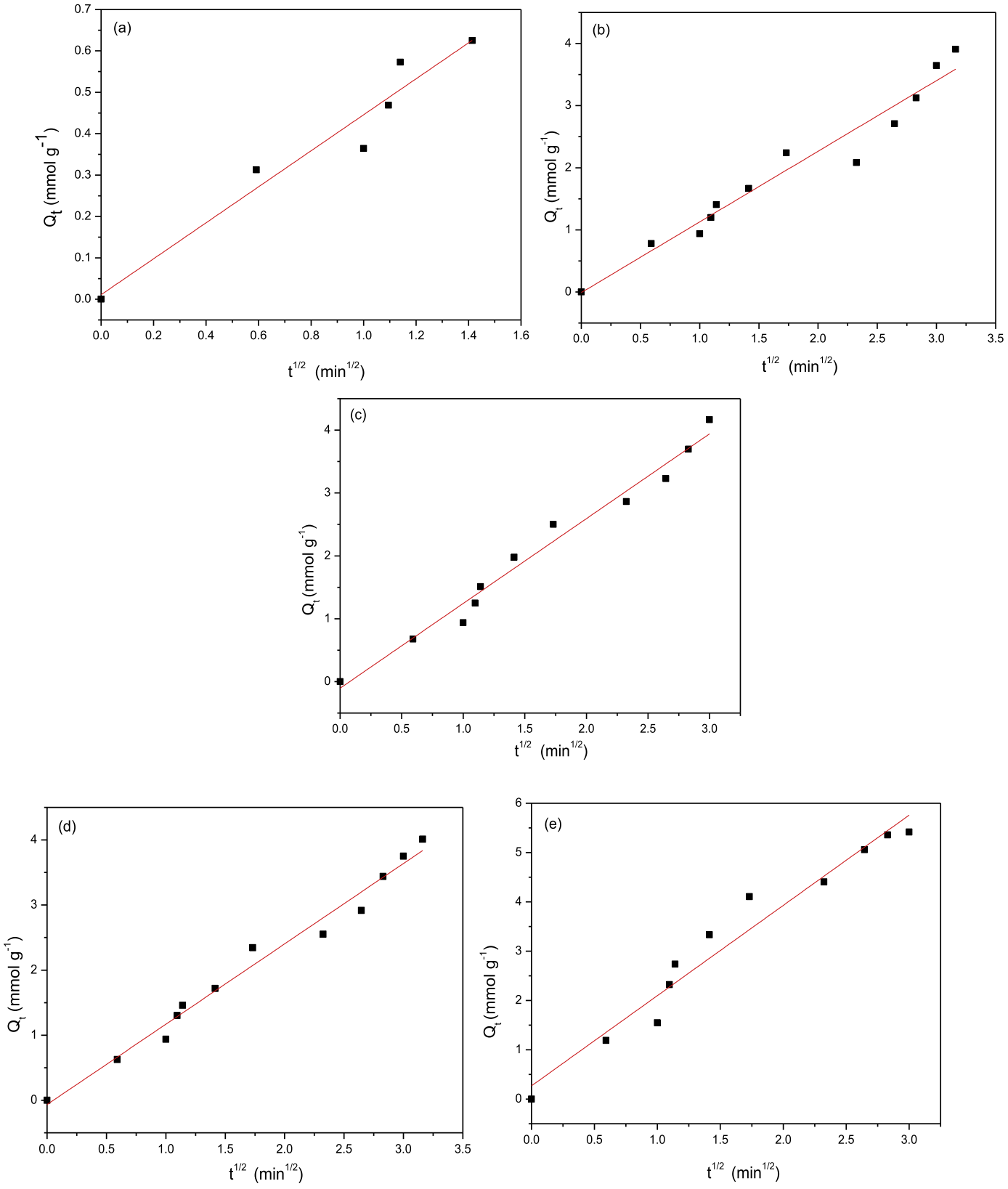


Fig. 8. Intraparticle diffusion model for CO_2 adsorption at ambient temperature and pressure of HC (a), HC@ZnO (b), HC@ZnO–ClPTES (c), HC@ZnO–Si–$N(OH)_2$ (d) and Cu-MIOCS (e).

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4. Conclusion

The present study provides the proof-of-concept that vegetal-deriving composites can display high affinity towards CO_2 at ambient temperature after judicious modification. Hydrochar encapsulation into HC@ZnO, functionalization with diethanolamino groups and copper incorporation produced an effective adsorbent for CO_2, affording an appreciable CO_2 uptake of 5.423 mmol/g. The latter was found to adsorb reversibly at ambient conditions, being easily released upon weak heating or forced convection. This was explained in terms of an attenuation of the Lewis basicity of the N atoms involved in Cu^0 stabilization and structure compaction. The appearance of –N:Metal and -O:Metal Lewis-Acid-Base (LAB) interactions are responsible of a structure compaction that promotes preponderantly physical interactions of CO_2 around entrapped CuNPs surrounded by O and N atoms belonging to the incorporated organic moiety. The easy CO_2 release only upon heating or forced convection must originate from effective physical adsorption of CO_2 in the form of multilayer condensation. This finding opens new prospects for the manufacture of highly added-value vegetal-deriving matrices for a reversible CO_2 capture. Significant affinity improvement towards CO_2 can be envisaged through judiciously tailored material texture and surface interaction. Investigations are still in progress in this direction.

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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Supplementary materials

The TEM image of the distribution of Cu nanoparticles; XPS analysis and chemical composition for the different samples; CO_2 adsorption measurements; IR analysis of CO_2-saturated materials; Kinetic parameters of pseudo 1st and 2nd order models.

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtice.2018.08.020.

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