

Research Article

Nanodeserts: A Conjecture in Nanotechnology to Enhance Quasi-Photosynthetic CO₂ Absorption

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This paper advances “nanodeserts” as a conjecture on the possibility of developing the hierarchical structured polymeric nanomaterials for enhancing abiotic CO₂ fixation in the soil-groundwater system beneath deserts (termed as quasi-photosynthetic CO₂ absorption). Arid and semiarid deserts ecosystems approximately characterize one-third of the Earth’s land surface but play an unsung role in the carbon cycling, considering the huge potentials of such CO₂ absorption to expand insights to the long-sought missing CO₂ sink and the naturally unneglectable turbulence in temperature sensitivities of soil respiration it produced. “Nanodeserts” as a reconciled concept not only indicate a conjecture in nanotechnology to enhance quasi-photosynthetic CO₂ absorption, but also aim to present to the desert researchers a better understanding of the footprints of abiotic CO₂ transport, conversion, and assignment in the soil-groundwater system beneath deserts. Meanwhile, nanodeserts allow a stable temperature sensitivity of soil respiration in deserts by largely reducing the CO₂ release above the deserts surface and highlighting the abiotic CO₂ fixation beneath deserts. This may be no longer a novelty in the future.

1. Introduction

Attempts to account for the global atmospheric CO₂ fluxes by quantifying CO₂ sources and sinks have provided evidence of an unneglectable missing CO₂ sink [1–3]. There are numerous studies that claimed to find the “missing sink,” but none of those claims has been widely accepted [4, 5]. Recently, the reports of carbon uptake by arid and semiarid desert ecosystems revealed rates of carbon uptake in many forests (i.e., the CO₂ absorption rate is up to the photosynthetic absorption level) and focused research attention on arid and

semiarid deserts ecosystems as the location of the long-sought “missing CO₂ sink” [6–13], which was termed as quasi-photosynthetic CO₂ absorption [6]. There is strong evidence suggesting that absorbed CO₂ significantly contributes to the total soil CO₂ flux [7–10]. Arid and semiarid deserts ecosystems approximately characterize one-third of the Earth’s land surface and play unsung role in the carbon cycling [9]. But where the absorbed CO₂ has gone remains undetermined [11, 12]. A latest publication claimed that such absorption can be attributed to geochemical CO₂ dissolution in saline aquifers beneath deserts [9], but the intensity of

CO₂ dissolution and absorption and the extent to which it modulates the global C balance are still a matter of controversy [9, 13, 14].

Differential, difference, and dynamic equations are used for quantitative analysis in the engineering and natural sciences [15–18]. This suggests us trying to develop some differential equations to describe the dynamics of CO₂ dissolution and absorption beneath deserts. Since absorbed CO₂ is largely dissolved in saline aquifers [9, 10], the dynamic equations for groundwater dissolved in CO₂ (DIC) are representative for both dissolution and absorption. Before this modeling work, the possible difficulties and uncertainties must be theoretically analyzed. Particularly, the quasi-photosynthetic CO₂ absorption as a component of soil respiration in deserts is abound to produce turbulence in temperature sensitivities of soil respiration. The first estimate of the absorption intensity is very promising [12], but a subsequent challenge is how to reduce the CO₂ release above the deserts surface and enhance the abiotic CO₂ fixation beneath deserts. Otherwise, the abiotic CO₂ fixation cannot be utilized [19–22]. Hierarchical structured polymeric materials, benefitting from nanotechnology enhancement, exhibited superior adsorption selectivity, high adsorption capacity, water tolerance, and low energy consumption with respect to physisorption, holding great promise for CO₂ capture, and the capture can consequently, maybe, employed in the future utilization and enhancement of quasi-photosynthetic CO₂ absorption beneath deserts. Considering the rapid development of nanotechnology and the wide applications hierarchical structured polymeric materials [23, 24], it can be conjectured that there are opportunities for the innovative design of self-assembling polymeric materials for the separation of aboveground CO₂ release and underground CO₂ fixation.

This paper hypothesizes that in the future it is possible to develop some hierarchical structured polymeric materials to enhance quasi-photosynthetic CO₂ absorption in deserts and advance “nanodeserts” as a conjecture in nanotechnology for modulating abiotic CO₂ fixation in the soil-groundwater system. To illustrate the necessity for introducing this concept, the influences of quasi-photosynthetic CO₂ absorption on temperature sensitivities of soil respiration are explicitly analyzed. A perspective Riccati Equation for the quasi-photosynthetic CO₂ absorption in the soil-groundwater system is established, providing that the hierarchical structured polymeric materials physically reduce the soil surface CO₂ release and enhance the abiotic CO₂ fixation beneath nanodeserts and allow a stable temperature sensitivity of soil respiration in deserts and a reliable quantification of CO₂ absorption intensity on regional and global nanodeserts.

2. Materials and Methods

2.1. Data Sources. “Nanodeserts” are a conjecture on the possibility of developing hierarchical structured polymeric materials to enhance abiotic CO₂ fixation in the soil-groundwater system, where nanoporous materials are supposed to be able to largely reduce the CO₂ release from the surface of the soil-groundwater system and enhance the quasi-photosynthetic CO₂ absorption beneath nanodeserts.

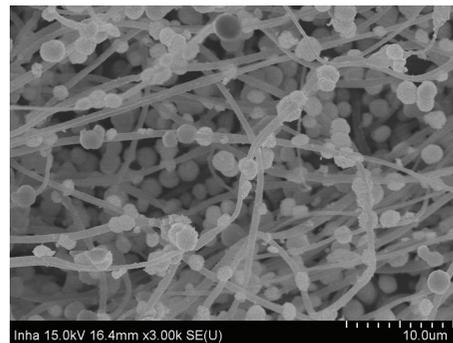


FIGURE 1: SEM image of polyethylenimine (PEI) nanofibers, loading with BiOCl nanoparticles.

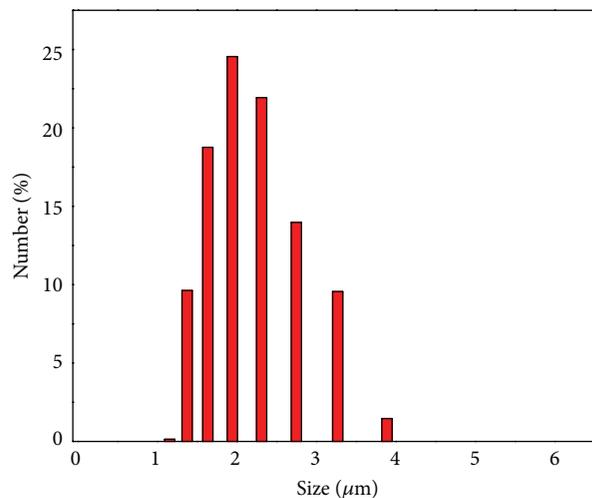


FIGURE 2: SEM image of polyethylenimine (PEI) nanofibers, loading with BiOCl nanoparticles.

As a particular example, the higher-resolution SEM images of polyethylenimine nanofibers (Figures 1, 2, and 3; loading with BiOCl nanoparticles) were collected. The morphology was evaluated via scanning electron microscopy (SEM, Model SU8010, Hitachi Co., Ltd.).

To highlight the necessity for this conjecture, the potential influences of the quasi-photosynthetic CO₂ absorption on the temperature sensitivities (Q_{10}) of soil respiration (R_s) are basically analyzed. This work is based on the R_s values (both positive and negative values) and the corresponding θ_s , T_a , and T_s values collected from some previous publications, with the analysis of Q_{10} of R_s to soil temperature at 5 cm depths (T_s) and air temperatures at 10 cm above the soil surface (T_a) at typical ecosystems along a gradient of soil alkalinity at 5 cm depths within the Manas River Basin [6, 12, 25].

The Manas River Basin is located at the southern periphery of the Gurbantunggut Desert and in the hinterland of the Eurasian continent. Soils in this inland river basin bear typical physical and chemical characteristics, which are resulting from the soil water and soil salt transport during regional hydrological processes [26]. Almost 10×10^6 km² of the hinterland of the Eurasian continent is arid and

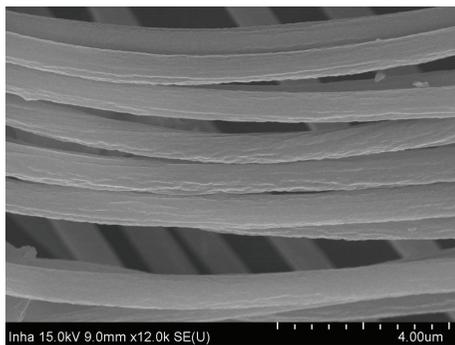


FIGURE 3: The SEM image of polyethylenimine (PEI) nanofibers.

semiarid deserts ecosystems. The inland rivers carried large quantities of salt into the Eurasian continent, resulting in strong, complicated ecological responses and forming the world largest desert-oasis compound system, which allows us to carry experiments at typical saline desert sites and typical cropped farmland sites, respectively.

2.2. Calculation and Modeling. The size of the nanoparticles was statistically analyzed utilizing the DLS measurement (Figure 2). Q_{10} values used in the analysis were calculated using the following formula (for consistence, the negative values of R_s were not included in calculations of Q_{10}), using the simple model of R_s (the derivative of the exponential chemical reaction-temperature equation originally developed by Van't Hoff) [27]:

$$\frac{R_{sT}}{R_{sT_0}} = Q_{10}^{(T-T_0)/10}, \quad (1)$$

where R_{sT} and R_{sT_0} are the R_s rates ($\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$) at T and T_0 , respectively.

Developing hierarchical structured polymeric materials to enhance quasi-photosynthetic CO_2 absorption beneath nanodeserts is very urgent and might draw much attention in the future. Hypothesizing that such nanoporous carbon materials were finally synthesized, the performance of CO_2 absorption, conversion, and assignment beneath nanodeserts would be further studied. Therefore, it is also necessary to present a preliminary discussion of the coming modeling work when this interesting and innovative conjecture was demonstrated [28]. Riccati Equation is traditionally serving for the theory of transonic gas-dynamic flows and is hence employed in the present study to illustrate how to model CO_2 footprints beneath nanodeserts.

3. The Major Results

3.1. Necessity to Introduce "Nanodeserts". The necessity to introduce "nanodeserts" depends on whether wide utilization of quasi-photosynthetic CO_2 absorption is feasible and reliable quantification of its overall importance is possible. Since it has been demonstrated that the current soil-groundwater system in arid and semiarid deserts ecosystems contributes

both positive and negative CO_2 fluxes and the magnitudes of these two fluxes components are almost the same [9–13], wide utilization of quasi-photosynthetic CO_2 absorption is infeasible unless nanodeserts are introduced. Considering the rapid development of nanotechnology and its applications in CO_2 capture and storage technology [29–36], nanodeserts as an emerging technology may be no longer a novelty in the future since deserts are attracting more and more interest in the increasingly urbanized world [37–40]. Because the wide range of nanomaterials and the particle sizes provides optional sizes of nanoparticles in the fabrication of nanomaterials (Figure 1), we can conjecture that there is an optimal size of nanoparticles to largely reduce CO_2 release and meanwhile enhance the abiotic CO_2 dissolution and fixation beneath nanodeserts.

The turbulence in Q_{10} values is evident. Quasi-photosynthetic CO_2 absorption was demonstrated to have significant influences on temperature sensitivities (Q_{10}) of soil respiration (R_s), which highlight the necessity to introduce "nanodeserts." Using positive R_s values, Q_{10} was calculated by the relative change in R_s with each 10°C increase of T_s in the saline desert and cropped farmland largely fell into [1, 2] and [1, 3], respectively, while calculated Q_{10} by the relative change in R_s with 10°C increases of T_a largely fell into [3, 13] and [2, 4], respectively. The mean Q_{10} value of R_s to T_a ($Q_{10} = 4.88$) was almost three times the mean Q_{10} value of R_s to T_s ($Q_{10} = 1.66$), implying that R_s in the alkaline land was much more sensitive to T_a than to T_s . The mean Q_{10} value of R_s to T_a in the desert ($Q_{10} = 6.83$) was more than the mean Q_{10} value of R_s to T_a in the farmland ($Q_{10} = 2.95$), implying that R_s in the desert was more sensitive to T_a than R_s in the farmland. However, R_s in the desert was less sensitive to T_s (with the mean $Q_{10} = 1.33$) than R_s in the farmland (with the mean $Q_{10} = 1.98$). Although those negative R_s were excluded and only the positive values were used in the calculations of Q_{10} , their significant influences on the response of R_s to T_s still existed. Additionally, the calculated Q_{10} uniformly decreased with temperature ($T = T_s$ or T_a) at both sites. This indicated that the variations of Q_{10} with temperature in alkaline lands were not different from that in other terrestrial ecosystems (Figure 4).

Such turbulence in Q_{10} values majorly resulted from the alternatively appearing positive and negative R_s . It is therefore essentially necessary to introduce "nanodeserts" as a conjecture on the possibility of developing hierarchical structured polymeric materials to largely reduce the CO_2 release from the surface of the soil-groundwater system and enhance the quasi-photosynthetic CO_2 absorption beneath nanodeserts by nanoporous modulation of the abiotic CO_2 fixation in the soil-groundwater system. A series of polymers are suitable for nanodeserts working in the future and the chemical structure of polymer specially used for illustration here. The chemisorption of CO_2 via amine-based materials is an efficient approach to reduce the greenhouse gas emission. In particular, polyethylenimine (PEI) impregnated materials exhibit superior adsorption selectivity, high adsorption capacity, water tolerance, and low energy consumption with respect to physisorption, holding great promise for CO_2 capture (Figure 5).

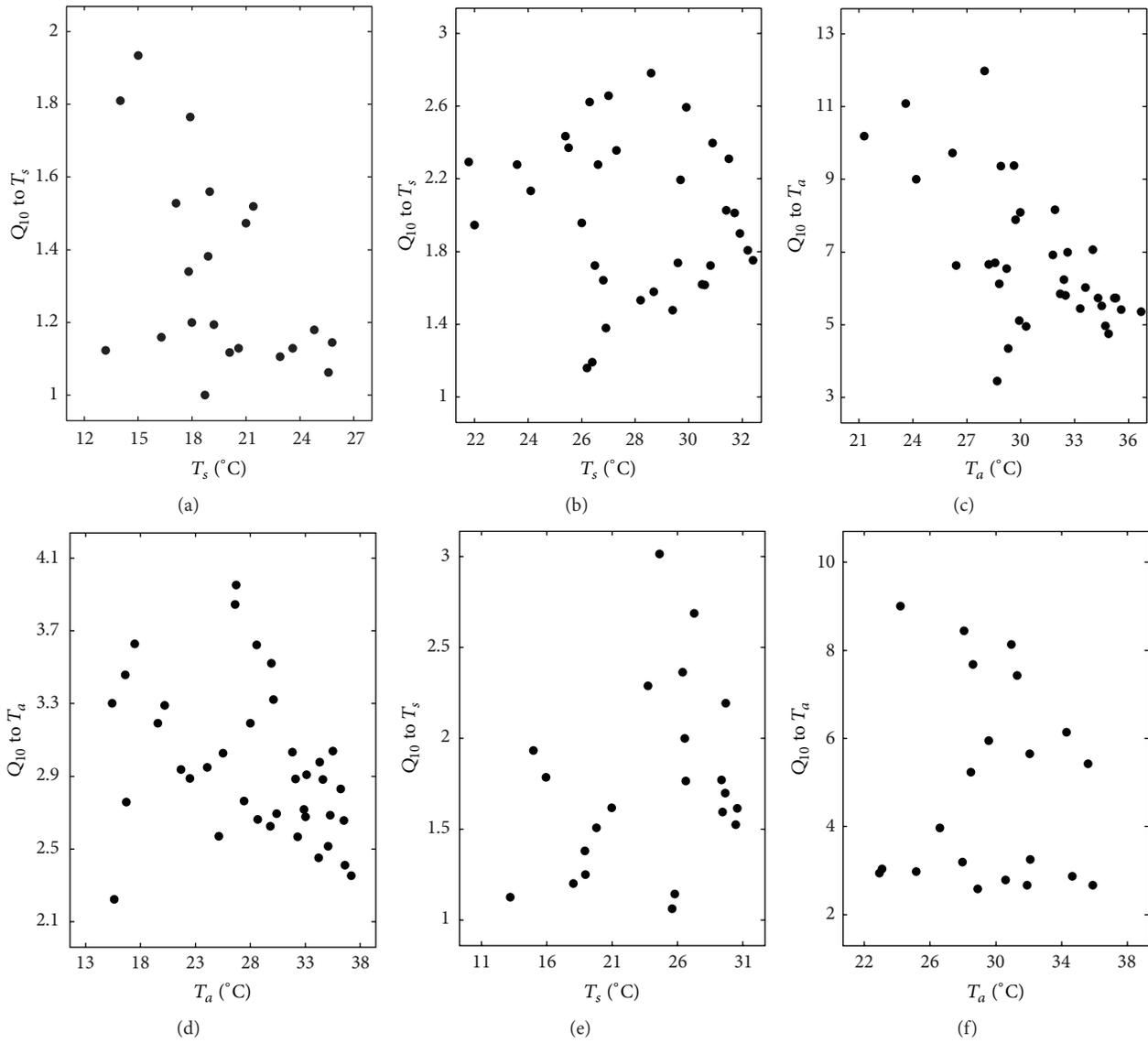


FIGURE 4: Responses of the temperature sensitivity (Q_{10}) to soil temperature at 5 cm depth (T_s) and air temperature 10 cm above the soil surface (T_a) in saline desert (a, c) and cropped farmland (b, d) and the responses of Q_{10} to T_s and T_a when taking the saline desert and cropped farmland data together (e, f).

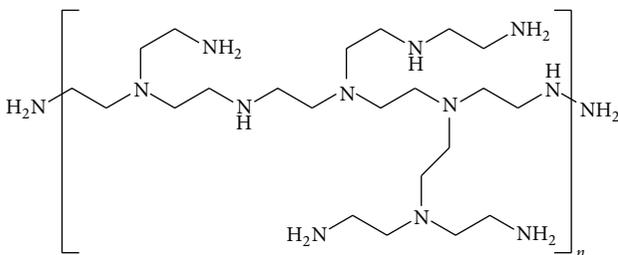


FIGURE 5: The chemical structure of polyethylenimine (PEI).

3.2. *CO₂ Footprints beneath Nanodeserts.* Nanodeserts equipped with hierarchical structured polymeric materials can largely reduce the CO₂ release from the surface of

the soil-groundwater system and enhance the quasi-photosynthetic CO₂ absorption beneath nanodeserts by nanoporous modulation of the abiotic CO₂ fixation in the soil-groundwater system, which not only allows a stable temperature sensitivity (Q_{10}) beneath CO₂ absorption and dissolution in the soil-groundwater system, but also makes it easy for deserts researchers to predict the CO₂ footprints beneath nanodeserts. Despite the wide applications of hierarchical structured polymers [41–46], they are slightly associated to modulate the carbon cycle in deserts and so it is difficult to provide the quantification data of polymer used for CO₂ absorption and the efficiency of CO₂ fixation beneath deserts. This is really a challenge. At current stage, we can only present a first approach to quantification data of polymer used for CO₂ absorption and the efficiency of CO₂ fixation beneath deserts based on the parameter of CO₂

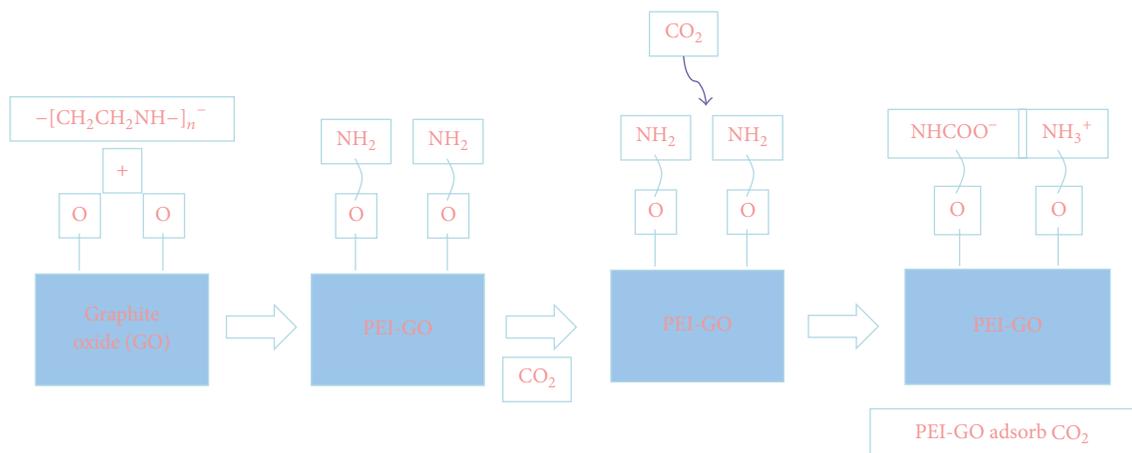


FIGURE 6: Effect of CO₂ capture of impregnated-graphite oxide by polyethylenimine.

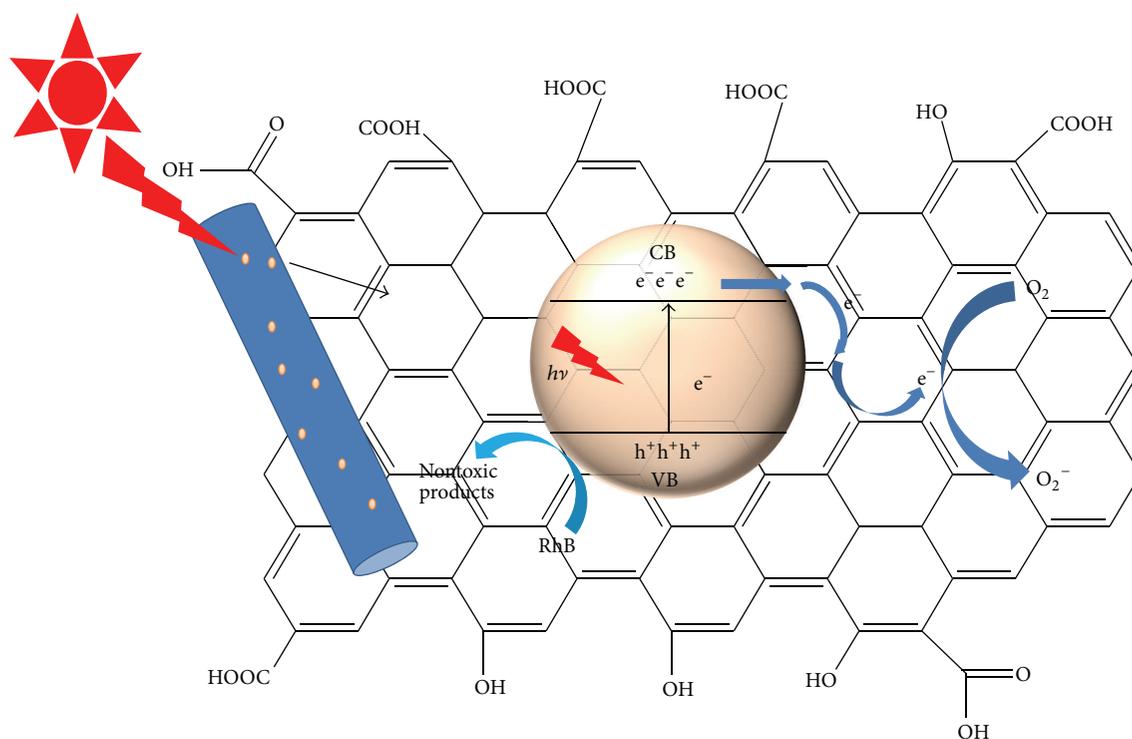


FIGURE 7: A conceptual mechanism about the graphene oxide/BiOCl heterostructured nanofibers (the specified example in this study) for visible-light photocatalytic enhancements of CO₂ fixation.

content, power of visible-light for photocatalysis they used for calculation and modeling. Here is a specific example to explain how to carry out and evaluate the CO₂ capture on polyethylenimine in future investigations. As an illustrating example, the CO₂ adsorption-desorption isotherms were measured at 298 K and 308 K at low pressure (1 bar) using a Model Belsorp Max instrument (BEL Japan, Inc.). A volumetric measurement method was used to obtain the CO₂ adsorption capacity. Before measurement, the samples were degassed for 10 h at 200°C until the residual pressure

fell below 0.01 kPa and then cooled to room temperature. Photocatalytic activities of the as-prepared samples were estimated by the degradation rate of RhB under a Solar Simulator (Sun 2000, ABET) with a 440 nm cutoff filter (Figures 6 and 7).

To predict CO₂ footprints beneath “nanodeserts,” first we establish a mathematical equation to describe the dynamics of CO₂ in the groundwater-soil system beneath hypothetically built “nanodeserts.” Suppose that CO₂ absorption per square-meter alkaline soils was finally dissolved in the groundwater

of volume V . Let D_0 be the initial amount of DIC at t_0 and the growth rate of DIC is r . Ignoring groundwater flows and the restricting effect of current DIC, it is straight that

$$\frac{dD_1(t)}{dt} = D_0 \cdot r(t - t_0), \quad (2)$$

where $D_1(t)$ represents the one-dimension groundwater DIC dynamics.

Noting that $D_1(0) = D_0$, the analytic solution of (2) is $D_1(t) = D_0 \cdot e^{r(t-t_0)}$.

Now take into account groundwater flows. It is natural to provide that outflow = inflow, with volume Q . Because such flows are very slow, assume that groundwater flows out after the inflow is uniformly mixed with the groundwater unit V . The quality conversation law implies

$$D_2(t + \Delta t) - D_2(t) = Qp\Delta t + \int_t^{t+\Delta t} rD_2(t) - Q\frac{D_2(t)}{V+Q}dt, \quad (3)$$

where p is DIC proportion in the inflows (hypothesized as a constant).

Simplifying and taking the limit $\Delta t \rightarrow 0$, it implies

$$\frac{dD_2(t)}{dt} = Qp - \left(\frac{Q}{V+Q} - r\right)D_2(t). \quad (4)$$

Noting that $D_2(0) = D_0$, the analytic solution of (2) is

$$D_2(t) = \frac{Qp(V+Q)}{Q-r(V+Q)} - \left(D_0 - \frac{Qp(V+Q)}{Q-r(V+Q)}\right)e^{(r-Q/(V+Q))t}, \quad (5)$$

where $D_2(t)$ represents the two-dimension groundwater DIC dynamics.

Finally take into account both the groundwater flows and the restricting effect of current DIC. The quality conversation law implies

$$D_3(t + \Delta t) - D_3(t) = Qp\Delta t + \int_t^{t+\Delta t} r(R - \lambda D_3(t))D_3(t) - Q\frac{D_3(t)}{V+Q}dt, \quad (6)$$

where $R - \lambda D_3(t)$ determines the restricting effect of current DIC on r .

Simplifying and taking the limit $\Delta t \rightarrow 0$, it implies

$$\frac{dD_3(t)}{dt} = Qp + \frac{rR(V+Q) - Q}{V+Q}D_3(t) - \lambda rD_3(t)^2, \quad (7)$$

where $D_3(t)$ represents the three-dimension groundwater DIC dynamics.

Equation (7) is the famous Riccati Equation, where the parameters p , Q , r , R , and V are allowed to be changing with t [15–18]. Equations (2) and (4) are both simple forms

of (7) and hence are also special forms of the famous Riccati Equation. Generally the Riccati Equation has no analytic solutions unless some assumptions are imposed. And it is better to provide a specific example to prove analytic solutions in certain conditions, which help to understand the full story of CO₂ footprint and make chances for the subsequent quantitative analysis of quasi-photosynthetic CO₂ absorption and fixation beneath nanodeserts (Figure 8).

Suppose its analytic solutions by discussing that root of

$$Qp + \frac{rR(V+Q) - Q}{V+Q}D_3(t) - \lambda rD_3(t)^2 = 0 \quad (8)$$

is zero; that is, $4\lambda rpQ^2 + (4\lambda rpV + rR - 1)Q + rRV$ is zero; then (8) has two same real roots, say d , and (7) is simplified as

$$\frac{dD_3(t)}{(D_3(t) - d)^2} = \lambda rdt, \quad (9)$$

where the analytic solution can be obtained by $D_3(0) = D_0$ and

$$D_3(t) = d - \frac{\lambda r}{t+c}, \quad c \text{ is arbitrary constant.} \quad (10)$$

CO₂ footprints beneath nanodeserts can be therefore theoretically characterized. First, to note the auxiliary role of soil-groundwater metal ions in the CO₂ footprints beneath nanodeserts is significant, which prepare chemical condition for the quasi-photosynthetic CO₂ absorption beneath deserts (Figure 8). This is a key point of the whole story. Those metal ions come from the dissolution of soil salt during the discharge and recharge of groundwater. The percentages of those metal ions beneath deserts can be very different in different sites and the local extremes amount to 80 mg/L [47–56]. Second, the CO₂ movements in the soil-groundwater system beneath nanodeserts are usually accompanied by the movements and sequestration of these metal ions. Finally, such accompanied movements present advantageous conditions for geochemical processes and therefore reconstruct CO₂ footprints beneath nanodeserts. The above assumption and analytic solution (10) indicate that the quasi-photosynthetic CO₂ absorption beneath deserts significantly contributed to the dynamic of the soil-groundwater CO₂ concentration beneath deserts. In other words, the subterranean C pool and CO₂ footprints would be reconstructed in next centuries when/if the quasi-photosynthetic CO₂ absorption becoming the predominant processes was beneath “nanodeserts.”

4. Discussion

In subsequent studies, the diverse kinds of hierarchical structured nanoporous materials should be synthesized as a set of microporous nanomaterials with small pore size and their CO₂ sorption performance should be mechanically analyzed. The performance of CO₂ absorption by the hierarchical structured polymeric nanomaterials needs to be systematically investigated to find the critical pore size to enhance the CO₂ uptake according to the arithmetic method

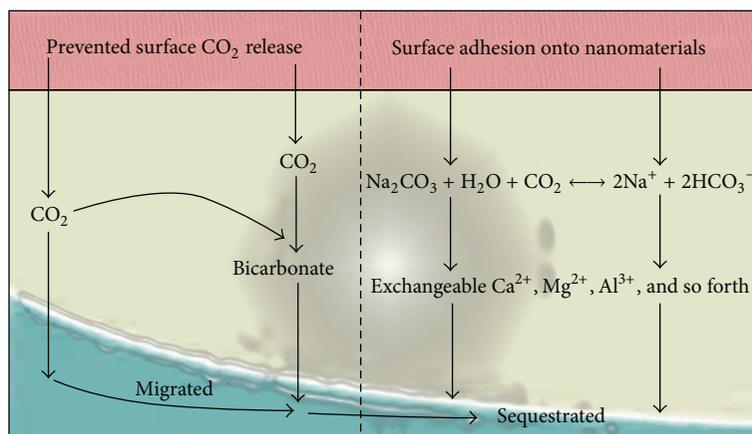


FIGURE 8: Hypothetical CO₂ footprints beneath nanodeserts and the C sink kinetics in CO₂ explosion.

proposed in subsequent studies. Moreover, the exact mechanisms about the heterostructured nanofibers for visible-light photocatalytic enhancements and full utilization of the solar thermal sources above nanodeserts are also worthy of further investigations [57–60].

In the present study it is indicated that it is the micropores with pore size smaller than a necessary pore size for soil CO₂ release that play a crucial role in such abiotic CO₂ adsorption. Such efforts are practical considering the wide applications of the hierarchical structured polymers and the nanomaterials. The pore structure and surface chemical properties of these prepared nanomaterials should be symmetrically studied by using different kinds of testing methods. Additionally, the DLS was used to measure the size of the nanoparticles in the present study since the size of the nanoparticles had been decorated on the PEI fibers. Considering the size of the particles is important for photocatalytic performance [61], it is very important to employ the DLS to measure the size distribution of the nanoparticles. Nevertheless, when measuring the diameter or the length of the PEI nanofiber, other suitable methods must be additionally employed since it is not appropriate to use DLS to measure such size of the fiber.

At the current stage it is impossible to obtain a reliable quantification of the CO₂ adsorption capacity, but a preliminary approach can be concluded from Figures 6 and 7. One can get detailed information from Figures 6 and 7, respectively. In Figure 6, it is highlighted that chemisorption of CO₂ via amine-based solid adsorbents is another efficient approach to reduce the greenhouse gas emission [62]. In particular, polyethylenimine (PEI) impregnated materials exhibit superior adsorption selectivity, high adsorption capacity, water tolerance, and low energy consumption with respect to physisorption, holding great promise for CO₂ capture [63]. Nevertheless, the low thermal conductivity of PEI coupled with high adsorption heat (ΔH) of chemisorption commonly generates overheating of these adsorbents during the CO₂ capture. This unavoidably leads to partial degradation of PEI, poor cycle stability, and even safety problems. Therefore, the development of a suitable material

with high CO₂ adsorption capacity, superior adsorption selectivity, and excellent cycle performance remains a major challenge. In Figure 6, the GO sheets can serve as an efficient carrier support for PEI via a nanocasting technology. Such features are favorable for the efficient diffusion and adsorption of CO₂ as well as the rapid thermal transfer. As for Figure 7, PEI nanofibers were prepared by electrospinning so that the graphene oxide/BiOCl heterostructured PEI nanofibers can be synthesized through in situ method. As well known, harmful chemical compounds have become the main cause of water pollution. For instance, organic dyes are often discharged with wastewater into the local environment without adequate treatment. Although the preparation of graphene-based composite hydrogels for photocatalyst has been previously reported [64, 65], recovering the photocatalyst after waste water purification has been a challenging issue. Thus, polymer-based photocatalyst nanocomposites have been attracting more interest due to their advantages for photocatalyst recovery. Exactly, the formation of graphene oxide/BiOCl heterostructured PEI nanofibers using an in situ reduction approach has been stated in the present study. Interestingly, this composite hydrogel matrix can be further utilized as highly efficient catalyst for wastewater treatment.

Furthermore, the Riccati Equation presented in the present studies demands further investigations by the mathematicians who are interested in this conjecture and are able to make contributions. Therefore, the analysis of qualitative properties of solutions to Riccati Equation is crucial for understanding the CO₂ absorption, offering some cautionary notes for interpretations based on first principles for CO₂ capture at ecosystem level and large-scale applications, which is also a future research priority.

5. Conclusion

“Nanodeserts” as a reconciled concept not only indicate a conjecture in nanotechnology to enhance quasi-photosynthetic CO₂ absorption, but also aim to present to desert researchers a better understanding of the footprints of abiotic CO₂ transport, conversion, and assignment in

the soil-groundwater system beneath deserts. Meanwhile, nanodeserts allow a stable temperature sensitivity of soil respiration in deserts by largely reducing the CO₂ release above the deserts surface and highlight the abiotic CO₂ fixation beneath deserts. When/if the dream is realized, it is not difficult then to widely utilize the quasi-photosynthetic CO₂ absorption in the soil-groundwater system and present further explicit modeling results towards a reliable quantification of the quasi-photosynthetic CO₂ absorption beneath nanodeserts. This may be no longer a novelty in the future since deserts are attracting more and more interest in the increasingly urbanized world.

Competing Interests

The authors declared that there are no competing interests.

Acknowledgments

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