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Evaluating catalytic and antibacterial properties of composite hydrogel based on biomimetically synthesized CeO_2 nanoparticles anchored onto microcrystalline cellulose/reduced graphene oxide

Saima Sohni [a,*], Abdullah [a], Esraa M. Bakhsh [b], Faryal Mazhar [a], Waqas Ahmad [a], Junidah Lamaming [c], Arshad Iqbal [d], Hafiz Nidaullah [e], Murtaza Sayed [f], Sher Bahadar Khan [b,*]

[a] Institute of Chemical Sciences, University of Peshawar, Peshawar 25120, Pakistan
[b] Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia
[c] Chemistry Programme, Faculty of Resource Science and Technology, Universiti Malaysia Sarawak (UNIMAS), 94300 Kota Samarahan, Sarawak, Malaysia
[d] Department of Botany, Islamia College University, Peshawar, Pakistan
[e] College of Veterinary Sciences, University of Agriculture, Peshawar 25130, Pakistan
[f] Radiation and Environmental Chemistry Lab., National Centre of Excellence in Physical Chemistry, University of Peshawar, 25120 Peshawar, Pakistan

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A B S T R A C T

The present study suggests a scalable approach to fabricate a composite hydrogel based on cerium dioxide (CeO_2) nanoparticles anchored onto microcrystalline cellulose (MCC) in a three-dimensional reduced graphene oxide (rGO) hydrogel with bifunctional performances in water reclamation. Herein, CeO_2 nanoparticles were biosynthesized using Banana pseudo-stem extract as a stabilizer and reducing agent. Afterwards, a series of hierarchical scaffolds of 3D hydrogels were fabricated employing different contents of CeO_2, MCC and rGO via. self-assembly process. Analytical techniques provided useful insights regarding chemical structure and morphology of the fabricated hydrogel. Results showed that the proportion of CeO_2, MCC and rGO controlled performance characteristics of the resulting composite hydrogels. Under optimal conditions, 95 % of the catalytic reduction of methylene blue dye solution (50 ppm) was achieved rapidly in the presence of catalyst (20 mg) using $NaBH_4$ solution (0.25 M) at ambient temperature. Recyclability tests demonstrated long term stability of composite hydrogel all through four successive cycles without any significant loss of its effectiveness. Moreover, as-prepared hydrogels demonstrated appreciable antibacterial potential against Gram-positive and Gram-negative bacteria. It is evident that using MCC and rGO as supporting substrates with CeO_2 accorded more functions to the resulting composite hydrogel due to synergistic effects that resulted in a high performance, easily retrieving and steady material for wastewater purification.

1. Introduction

Environmental sustainability has taken precedence in gathering a great deal of attention from the scientific community in this century, also referred to as “Century of Environment” [1]. Its relevance stems from the profound alterations introduced by the overpopulation and industrialization that has severely impacted humans, animals, plants, soil, and the overall environment [2]. The contamination of water resources with organic chemicals and pathogens is a critical challenge that needs to be addressed. In this scenario, designing novel filter materials with scavenging ability for organic and bacterial pollution is crucial and thereby deserves scientific attention. Besides, upsurge in the demand for green and sustainable chemistry has shifted interest towards abundantly available and cheaper bio-based materials for high-end uses.

Metal oxides and zero-valent metal nanoparticles (NPs) have been widely used in many technological applications particularly in the field of environmental remediation [3]. Among them, CeO_2 NPs offer remarkable potential as a sustainable platform for environmental protection due to their catalytic and antimicrobial attributes. It is essentially a non-toxic, durable and highly stable material possessing interesting electrochemical properties such as quick transformation between two oxidation states, i.e. Ce^{3+} and Ce^{4+}, which enhances its catalytic and antioxidant properties [4]. Despite aforesaid promising attributes, their deployment is not without challenges particularly irreversible

* Corresponding authors.
E-mail addresses: saima.sohni@gmail.com (S. Sohni), dr.khanchemist@gmail.com (S.B. Khan).

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Table 1
Synthesis of composite materials.

Sr. no.	Material	CeO_2 NPs (g)	MCC (g)	GO (g)
1	H-1	0.2	2	0.5
2	H-2	0.2	2	1
3	H-3	0.2	2	1.5
4	H-4	0.2	2	2
5	CeO_2@MCC	0.2	2	–
6	rGO@MCC		2	1
7	CeO_2@GH	0.2	–	1

aggregation in the reaction mixture which leads to their poor performance [5].

A review of literature showed that various support materials such as zeolites [6], β-Cyclodextrin [7,8], graphene [9,10], chitosan [11] and metal organic frameworks [12] etc. offered better degree of dispersion and more superficial active sites than the pristine CeO_2 NPs. Nevertheless, much still remains to be done in order to enhance the performance characteristics and reusability of these materials. Microcrystalline cellulose (MCC) is a cellulose derivative which possesses unique structure and properties such as a highly ordered structure, great mechanical strength and high surface area [13]. MCC is an ideal candidate for composites fabrication because it is biodegradable, stable and multifunctional [14]. Moreover, it can serve as an eco-friendly support material for CeO_2 NPs immobilization due to plenty of –OH and –COOH groups which can effectively facilitate their dispersion. Additionally, MCC can provide supplementary contribution to the adsorption sites on its surface [15]. On the other hand, graphene is a unique carbon material having extraordinary attributes in terms of surface area, stability, electrical conductivity and mechanical strength [16]. In addition to these properties, graphene can efficiently anchor different NPs due to strong interfacial interactions besides being an efficient non-metal co-catalyst, both factors contributing towards excellent performance in wastewater clean-up.

Few studies in literature have reported the synthesis of CeO_2/graphene nanocomposites for usage in high performance supercapacitor [17], neuroregenerative cell therapies [18] and sensor technology [19]. In the field of catalysis, Jiang et al. designed a facile strategy for synthesizing CeO_2/graphene catalyst by a simple hydrothermal method for uric acid oxidation [10]. In another study, Peng et al. reported excellent electrocatalytic ability of CeO_2/rGO nanocomposites for oxygen reduction [20]. Verma and Sanjoy K. Samdarshi successfully prepared CeO_2/rGO in one-step hydrothermal reaction for dye degradation under visible light [21]. On the other hand, combination of graphene with cellulose has recently emerged as a new class of green materials for advanced applications due to synergistic effects. Numerous graphene/cellulose reinforced composites for instance 3D RGO/cellulose [22], graphene nanoplatelets/cellulose [23], cellulose nanocrystals-rGO [24], cellulose/GO [25] and MCC/GO [26] [27] are been fabricated and characterized.

An important derivative of graphene is reduced graphene oxide (rGO) hydrogel which refers to macroscopic porous materials formed as a result of self-assembly of graphene sheets. By this way, nano-scale interactions are transformed into macroscopic level which enables practical applicability of graphene while retaining inherent properties [28]. Thus, coupling of CeO_2 NPs with graphene in a three dimensional (3D) scaffold will be an ideal strategy for improved performance due to synergistic effects. Up until now, main focus has remained on adsorptive technology based on GO/MCC [29,30], GO/cellulose/Fe_3O_4 [31] and rGO/CNC-based hybrid aerogels [32] with few studies on catalysis employing 3D graphene materials [33–36]. Despite promising attributes of rGO hydrogels, their 3D scaffolds are prone to physical damage which restricts their practical utility. We propose that the inclusion of MCC will confer structural stability besides serving to enhance adsorption efficiency of these hydrogels. To the best of our knowledge, studies on 3D CeO_2 NPs/MCC/rGO hydrogel as bifunctional filter material for scavenging organic and bacterial pollution have not been investigated yet. In the light of aforesaid perspective, objectives of this work are; facile preparation of CeO_2 NPs and MCC, and their incorporation into 3D rGO matrix to fabricate a composite hydrogel, henceforth called CeO_2@MCC-GH for wastewater clean-up. The application of composite hydrogel scaffold as bifunctional water filtration material is evaluated by performing catalytic degradation of model pollutant as well as antimicrobial studies. We hypothesize that anchoring CeO_2 NPs onto durable and chemically stable MCC and fabricating unique scaffold employing large 3D surface of rGO sheets can endow composite hydrogel with enhanced performance characteristics.

2. Materials and methods

2.1. Materials

Analytical grade chemicals and solvents were used in this study. Ethanol (96 %), toluene (99.5 %), acetic acid glacial, sodium hydroxide, 98 % sulfuric acid (Merck), sodium nitrate (Merck), potassium permanganate, hydrogen peroxide (30 % *w*/w), ascorbic acid (Sigma-Aldrich), cerium (IV) sulfate hexahydrate (Sigma-Aldrich), sodium borohydride (Sigma-Aldrich) were used. The commercially available methylene blue (MB) dye was used as model pollutant. rGO hydrogel was synthesized using graphite powder (50 mesh, Mol. Wt. 12.01 g/mol) acquired from AVONCHEM, UK. Nutrient agar media (HiMedia Laboratories Pvt. Ltd.) was used for the culturing and growth and nutrient broth was used for incubation and standardization of different bacterial strains.

2.2. Sampling and preliminary processing

Banana pseudo-stem is a major residue of Banana which is among the highly cultivated and utilized fruit. Interestingly, high cellulose content of pseudo-stem allows its use for the production of MCC. For present study, pseudo-stem has been exploited in two ways, i.e. i) aqueous extract for biofabrication of CeO_2 and ii) MCC as catalyst support, for the first time under biorefinery concept. The chunks of Banana pseudo-stem samples were collected and then cut with the help of laboratory knife. The pieces of plant samples were sun dried to reduce moisture content followed by grinding for its conversion to powder form using grinder. For the synthesis of CeO_2 NPs and MCC, aqueous extract and fibre, respectively of Banana pseudo-stem were used. In order to prepare extract, Soxhlet extraction was continued for 6–8 h using 10 g of dried fibers with 100 mL of water at 100 °C.

2.3. Isolation of MCC

Extractive free Banana pseudo-stem fibre was subjected to chemical treatment for the extraction of cellulose. This was followed by conversion of isolated cellulose to MCC using acid hydrolysis according to a reported method [37]. In a typical procedure, 1 g of cellulose was hydrolyzed with 2.5 M HCl at a fraction of (1/20 *w*/*v*) at 100 °C for 30 min under reflux. After that, hydrolyzed fibre was washed with distilled water several times until neutral pH was obtained. As-prepared MCC was oven dried at 70 °C for 48 h. Finally, a pure white powder of MCC was obtained.

2.4. Biomimetic synthesis of CeO_2 nanoparticles

In present work, biosynthesis route was used for the preparation of CeO_2 NPs using plant extract. This approach is eco-friendly, economical and less energy intensive, offering promising solution for sustainable water remediation. In a typical procedure, 0.5 M solution of cerium salt precursor was prepared and was mixed with 50 mL of banana pseudo-stem extract. Afterwards, stirring was continued using a magnetic stirrer for 2 h at 80 °C until the colloidal solution changed its color from