Ecotoxicology and Environmental Safety 148 (2018) 813–824

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Review

Copper-based nanomaterials for environmental decontamination – An overview on technical and toxicological aspects

Mohammadreza Khalaj[a], Mohammadreza Kamali[b,*], Zahra Khodaparast[c], Akram Jahanshahi[d]

[a] Department of Environment and Planning, University of Aveiro, 3810-193 Aveiro, Portugal
[b] Department of Environment and Planning, Center for Environmental and Marine Studies, CESAM, Aveiro Institute of Materials, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
[c] Department of Biology, Center for Environmental and Marine Studies, CESAM, University of Aveiro, 3810-193 Aveiro, Portugal
[d] Department of Economics, Management, Industrial Engineering and Tourism, Department of Mechanical Engineering, University of Aveiro, 3810-193 Aveiro, Portugal

ARTICLE INFO

Keywords:
Water treatment
Metal toxicity
Environmental toxicology

ABSTRACT

Synthesis of the various types of engineered nanomaterials has gained a huge attention in recent years for various applications. Copper based nanomaterials are a branch of this category seem to be able to provide an efficient and cost-effective way for the treatment of the persistent effluents. The present work aimed to study the various parameters may involve in the overall performance of the copper based nanomaterials for environmental clean-up purposes. To this end, the related characteristics of copper based nanomaterials and their effects on the nanomaterials reactivity and the environmental and operating parameters have been critically reviewed. Toxicological study of the copper based nanomaterials has been also considered as a factor with high importance for the selection of a typical nanomaterial with optimum performance and minimum environmental and health subsequent effects.

1. Introduction

Copper is of high importance material because of its unique chemical, electrical, optical and thermal properties. For instance, CuO and Cu_2O are well-known p-type semi-conductors with a narrow band gap (Isherwood, 2017). Such properties for copper-based nano materials (CuBNMs) have made them excellent candidates for a number of applications such as in heterogeneous catalytic reactions (Ke et al., 2014; Zhang et al., 2015), energy conversion (for instance due to the direct band gap (2.0 eV) of Cu_2O) (Park et al., 2017), bio-sensing (Etefagh et al., 2013) in lithium ion electrode systems (Ke et al., 2014), biological applications (Razeeb et al., 2014). So, various methods have been developed for the preparation of CuBNMs such as chemical reduction (Ahmad et al., 2016), thermal decomposition (Hao et al., 2015), microwave and sonochemical reduction (Li et al., 2016), radiation-based methods (Jushi and Mahumuni, 1999).

Environmental application of CuBNMs is an interesting category which has gained particular attention in recent years. So far, various types and modifications of copper-based materials have been applied for the removal of contaminants from the polluted environments such as utilization of nano scale zero-valent copper for in situ removal of nitrate from surface water (Lucchetti et al., 2017a) and hydrogen energy production (Lucchetti et al., 2017a) water refinery of methyl orange (MO) (Liú et al., 2016) and dichloromethane of the groundwater (Huang et al., 2012). It is believed that the catalytic activity of such nanomaterials towards the environmental contaminants is highly related to their properties such as morphology, crystallinity, optical and electrical properties. Hence, manipulation of the synthesis conditions can result in optimization their performances for environmental clean-up purposes. As well, modifications in the nanomaterials properties can affect their toxic effects when they remain in the receiving environment after treatment process or being released to the environment from other sources such as mining activities, from the extractive industry (Ermolin et al., 2016), or from marine antifouling paints (Conway et al., 2015). It is of high importance topic due to the rising concern of the fate and probable subsequent toxic effects of CuBNMs to the living organisms. However, by reviewing the literature, it is evident that the scientific knowledge for the synthesis of green materials with the properties inducing less toxicity to the receptors is not well developed yet to the lack of enough scientific-based studies on the real toxic effects of these nanomaterials on the terrestrial or aquatic environments (Ivask et al., 2013). Also, there is an urgent need for a clear conclusion from the recent literature on both technical-economical and toxicological studies have been so far performed. To this end, this paper aims to critically discuss the role of the CuBNMs properties on their reactivity towards environmental contaminants, considering the technical considerations

* Corresponding author.
E-mail address: Kamali@ua.pt (M. Kamali).

https://doi.org/10.1016/j.ecoenv.2017.11.060
Received 16 August 2017; Received in revised form 18 November 2017; Accepted 22 November 2017

Nomenclature

AC	Activated Carbon
AOPs	Advanced Oxidation Processes
BA	Benzoic Acid
BET	Brunauer Emmett Teller
BP	Benzophenone
CB	Conduction Band
COD	Chemical Oxygen Demand
CMP	Clinoptilolite Micronized Particles
CNP	Clinoptilolite Nanoparticles
CuBNMs	Copper-Based Nanomaterials
CTAB	Cetyltrimethylammonium Bromide
DEC	Dichloroethane
DO	Dissolved Oxygens
DOC	Dissolved Organic Carbon
EDL	Electrical Double Layer
LDHs	Layered Double Hydroxides
MB	Methylene Blue
MG	Malachite Green
MO	Methyl Orange
NB	Nitrobenzene
NCS	Nano-Chitosan
NMs	Nano Materials
NPs	Nanoparticles
NSMs	Nanostructured Materials
nZVC	Nano Zero Valent Copper
nZVN	Nano Zero Valent Nickel
OPR	Oxygen Peroxide Radical
POD	Peroxidase
PZC	Point Of Zero Charge
RB-5	Reactive Black 5
RhB	Rhodamine B
ROS	Reactive Oxygen Species
SSA	Specific Surface Area
TEM	Transmission Electron Microscopy
TOC	Total Organic Carbon
UI	Ultrasonic Irradiation
UV	Ultraviolet
VB	Valence Band

and to explore the effects of the Nano Materials (NMs) characteristics on their toxicity when released to the receiving environments. This can aid to develop a framework for the synthesis and environmental applications of CuBNMs.

2. CuBNMs for environmental clean-up

In order to optimize the performance of CuBNMs, it is vital to study and control those properties of nanomaterials which can affect their reactivity towards environmental contaminants, directly or indirectly. To this end, this section is aimed to study and discuss: a) the properties of the copper based nanomaterials affecting their reactivity (Section 2.1), and b) the environmental and operating parameters with the potential to influence the degradation and removal efficiency using CuBNMs (Section 2.2).

2.1. CuBNMs; properties and the reactivity

2.1.1. Shape, size and porosity

Many efforts have been made in the recent years in order to synthesize zero dimensional (Gao et al., 2016; Azarafza et al., 2016), one dimensional (Joulazadeh and Navarchian, 2015; Iodice et al., 2016), two dimensional (Feng and Wang, 2016; Al Lafi and Abdullah, 2015) or three dimensional (Xie et al., 2015; Song et al., 2015) nanomaterials (according to Pokropivny and Skorokhod, 2007; Gleiter, 2000 classification for NMs) with modified shapes, sizes and porous structures to be applied in a number of applications. The morphology of the NMs can be strongly affected by the synthesis methods applied and the manipulations in the synthesis conditions. Shape, size and porosity can potentially affect the total removal yield of the environmental contaminants by CuBNMs and as a result, the economic consideration and commercialization of the novel materials for environmental applications.

Shape of the CuBNMs is an important structural property to enhance their efficiency. This is due to reasons such as the direct relationship between the shape and the size (and as a result surface area) of the NMs and also the effects of the shape on the inherent properties of nanomaterials like band gap energy. Yang and He (2011) indicated that the modulation of reaction conditions i.e. reactants, reaction temperature and reaction duration under a simple precipitation method can result in the formation of various shapes including a three-dimensional (flower-like) and three types (boat-like, plate-like and ellipsoid-like) of two-dimensional CuO nanomaterials. In addition to the effects of the morphology on the band gap of the prepared materials, the specific surface area (SSA) of the particles showed differences by changing the particle shapes. When they were used (20 mg of as-prepared CuO) for the degradation of methylene blue (MB) (10 mg/L) in presence of 20 ml of

Table 1
Effects of size and morphology on the reactivity of CuBNMs.

NMs	Highlighted specifications/ Experimental conditions				Removal efficiency		Ref.
	Main Specification	Value/ state	Other specifications	Value/ state	Parameter/ Substance	Removal (%)	
CuO	Shape	Flower-like	SSA	5.2 m^2/g	Methylene blue (MB)	0[a]	(Yang and He, 2011)
		Flower-like	SSA	5.2 m^2/g		96.0	
		Boat-like	SSA	5.1 m^2/g		0	
		Boat-like	SSA	5.1 m^2/g		96.1	
		Plate-like	SSA	9.3 m^2/g		0[a]	
		Plate-like	SSA	9.3 m^2/g		97.2	
		Ellipsoid-like	SSA	1.9 m^2/g		0[a]	
		Ellipsoid-like	SSA	1.9 m^2/g		89.7	
nano-copper	Morphology	Smooth	The ratio of SSA	12	Methyl orange	6.6	(Liú et al., 2016)
		Rough	The ratio of SSA	80 + x		35	
		Smooth	The ratio of SSA	80		24	
		Smooth	The ratio of SSA	7		6.2	
CuO		rode-shape	particle size	140 nm	organic dye blue R – 250	34	(Sankar et al., 2014)

[a] In the absence of H_2O_2.