Manuscript Number: EES-17-1526R2

Title: Copper-Based Nanomaterials for Environmental Decontamination -An
Overview on Technical and Toxicological Aspects

Article Type: Review article

Section/Category: Environmental Chemistry

Keywords: Copper-based nanomaterials
Environmental clean-up
Toxicology

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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 highly polluted 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.

Subject: Paper to be submitted to **Ecotoxicology and Environmental Safety**

Aveiro, 18 November 2017

Dear Editor,

I am re-submitting here with a manuscript entitled:

“Copper Based NMs for Environmental Decontamination - An Overview on Technical and Toxicological Aspects”

for publication in Ecotoxicology and Environmental Safety.

We would like to appreciate the reviewers for their favorable opinion and their comments which have contributed to more added value to the paper.

We hope now our paper can be fully accepted for publication.

Yours sincerely,
Corresponding author
Mohammadreza Kamali

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Subject: Paper to be submitted to **Ecotoxicology and Environmental Safety**

Aveiro, 18 November 2017

Dear editor

Please find attached the revised version of the paper “Copper-Based Nanomaterials for Environmental Decontamination - An Overview on Technical and Toxicological Aspects”, which we would like to resubmit for publication as a chapter in “*Ecotoxicology and Environmental Safety Journal*”.

We would like to appreciate the reviewers for their favorable opinion and their comments which have contributed to more added value to the paper. In the following we present our point-by-point responses to each of the comments of the reviewers.

We hope now our paper can be fully accepted for publication.

Response to reviewers

Comment	Response	Page	Line
Thanks for your revised manuscript. I think the revised manuscript would be acceptable for the publication of Ecotoxicology and Environmental Saftery. However, the present manuscript looks too long even though the manuscript is regared as review article. Thus, I would like to ask you to shorten the context with concise sentences and limited numbers of figures and tables. Our policy for the numbers of tables and figures is totally 7. I would like to ask to remove some references to save journal space. Therefore, I would like to suggest you to shorten the context, figures, tables and referenes with supporting materials, which could contain detailed information and some relevant figures, tables and refernces.	The comments were accepted and the modifications have been applied as follow:		
	1. Some sentences with less importance have been eliminated, especially in the conclusion.	34 To 36	3 To 20
	2. Some references with less importance have been also eliminated.	3 4 4 4 5 9	23 4 10 19 18-20 21-22
	3. In order to save the journal space, figures 1 and 2 with supporting materials and the respective detailed information have been eliminated.	10 16	

Yours sincerely,

Corresponding author

Mohammadreza Kamali

Highlights

The main properties of CuBNMs affecting their reactivity are addressed.

In vivo and *in vitro* toxicity of CuBNMs are addressed and discussed.

Doped CuBNMs have high reactivity and low toxicity for environmental clean-up.

Copper-Based Nanomaterials for Environmental Decontamination -An Overview on Technical and Toxicological Aspects

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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

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nanomaterial with optimum performance and minimum environmental and health subsequent effects.

Keywords: Water Treatment, Metal Toxicity, Environmental Toxicology.

Nomenclature

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

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18 **1. Introduction**

19 Copper is of high importance material because of its unique chemical, electrical,
20 optical and thermal properties. For instance, CuO and Cu₂O are well-known p-type
21 semi-conductors with a narrow band gap [1]. Such properties for copper-based nano
22 materials (CuBNMs) have made them excellent candidates for a number of
23 applications such as in heterogeneous catalytic reactions [2], [3], energy conversion
24 (for instance due to the direct band gap (2.0 eV) of Cu₂O) [4], bio-sensing [5] in

1 lithium ion electrode systems [2], biological applications [6]. So, various methods
2 have been developed for the preparation of CuBNMs such as chemical reduction [7],
3 thermal decomposition [8], microwave and sonochemical reduction [9], radiation-
4 based methods [10].

5 Environmental application of CuBNMs is an interesting category which has
6 gained particular attention in recent years. So far, various types and modifications of
7 copper-based materials have been applied for the removal of contaminants from the
8 polluted environments such as utilization of nano scale zero-valent copper for in situ
9 removal of nitrate from surface water [11] and hydrogen energy production [11] water
10 refinery of methyl orange (MO) [12] and dichloromethane of the groundwater [13]. It
11 is believed that the catalytic activity of such nanomaterials towards the
12 environmental contaminants is highly related to their properties such as
13 morphology, crystallinity, optical and electrical properties. Hence, manipulation of
14 the synthesis conditions can result in optimization their performances for
15 environmental clean-up purposes. As well, modifications in the nanomaterials
16 properties can affect their toxic effects when they remain in the receiving
17 environment after treatment process or being released to the environment from
18 other sources such as mining activities, from the extractive industry [14], or from
19 marine antifouling paints [15]. It is of high importance topic due to the rising
20 concern of the fate and probable subsequent toxic effects of CuBNMs to the living
21 organisms. However, by reviewing the literature, it is evident that the scientific
22 knowledge for the synthesis of green materials with the properties inducing less
23 toxicity to the receptors is not well developed yet to the lack of enough scientific-
24 based studies on the real toxic effects of these nanomaterials on the terrestrial or
25 aquatic environments [16]. Also, there is an urgent need for a clear conclusion from
26 the recent literature on both technical-economical and toxicological studies have

1 been so far performed. To this end, this paper aims to critically discuss the role of the
2 CuBNMs properties on their reactivity towards environmental contaminants,
3 considering the technical considerations and to explore the effects of the Nano
4 Materials (NMs) characteristics on their toxicity when released to the receiving
5 environments. This can aid to develop a framework for the synthesis and
6 environmental applications of CuBNMs.

7 **2. CuBNMs for environmental clean-up**

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

15 **2.1 CuBNMs; Properties and the reactivity**

16 **2.1.1 Shape, Size and Porosity**

17 Many efforts have been made in the recent years in order to synthesize zero
18 dimensional [17], [18], one dimensional [19], [20], two dimensional [21], [22] or
19 three dimensional [23], [24] nanomaterials (according to Pokropivny & Skorokhod
20 (2007) [25] and Gleiter (2000) [26] classification for NMs) with modified shapes,
21 sizes and porous structures to be applied in a number of applications. The
22 morphology of the NMs can be strongly affected by the synthesis methods applied
23 and the manipulations in the synthesis conditions. Shape, size and porosity can
24 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 & He (2011) [27] 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 hydrogen peroxide (30 wt.%) various degradation rates were observed, regarding their Brunauer Emmett Teller (BET) specific surface areas (Table 1).

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	[27]
		Flower-like	SSA	5.2 m ² /g		96.0	
		Boat-like	SSA	5.1 m ² /g		0 ^a	
		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	[12]
		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	[28]

^a. In the absence of H₂O₂

Liú et al. (2016) [12] indicated the direct positive effects of the smaller size of nano-copper on the elevated degradation rate of MO. They also argued about the roughness of the NMs surface and their reactivity. Under visible irradiation, where no removal of MO was observed by commercially available P25 TiO₂ nanoparticles, nano-copper was a potential visible-light photocatalyst, especially by the smaller sized ones. In addition to the direct effects of shape and size of the CuBNMs on their catalytic activity, it is now evident that such parameters can have a significant impact on their optical and electronical properties. For instance, Sankar et al. (2014) [28] indicated the high photocatalytic activity of the rode-shape CuO nanoparticles (mean particle size of 140 nm) towards commercially used organic dye Coomassie brilliant blue R-250. They concluded that factors such as size and surface area (which also reflects the porosity of the NMs) directly and the optical properties as a function of morphology and shape are the main factors influencing the reactivity of the nanomaterials.

2.1.2 Crystalline structure

According to the classifications of the nanomaterials presented by Gleiter (2000) [26] and modified by Pokropivny & Skorokhod (2007) [25] a set of 36 main classes of NMs covers all the structures of nanomaterials such as particles, fullerenes, nano plates and nanotubes. Based on their definition, nanostructured materials (NSMs) are the materials with submicron or nano-sized building units at least in one direction. Hence, the crystalline structure of the materials is the factor defining whether they are classified in the nanomaterials or in the bulk materials. However, it seems that the ratio between the size of the materials and the crystallite size, the average size of the building blocks can considerably affect the properties of the nanomaterials especially for applications such as environmental clean-up purposes which require the nanomaterials to resist in the harsh environmental conditions. For instance, the defects in the crystalline structure of nanomaterials when face with pHs lower than 4 may cause their catalytic efficiency adversely. Some attempts have been made so far in order to synthesis of CuBNMs with high crystalline structure. For instance, Sreeju, Rufus, & Philip (2016) [29] prepared highly crystalline Cu nano particles (spherical shape, ~15 nm) through a green process including the rapid reduction of CuSO₄ with hydrazine in the presence of *Psidium guajava* leaf extract under microwave irradiation. They stated that the high crystalline structure of the products can enhance their oxidation resistance. It seems that the higher resistance of the materials with higher crystallinity against oxidation can be attributed to the less surface energy of the high crystalline materials which can restrict their tendency for the uptake of oxygen.

The effect of the crystallinity of the nanomaterials on the reactivity of CuBNMs has not been well studied yet. For other types of nanomaterials also there is not an agreement on the effect of the crystallinity on the catalytic activity towards the

recalcitrant pollutants. Wang et al. (2014) [30] stated that the crystallite size and crystallinity of the anatase nanoparticles (TiO_2) has a direct effect on the degradation of phenol. They indicated that an increase in the crystallite size from 6.6 to 26.6 resulted in the improvement in the phenol photocatalytic oxidation. However, there is a need for more information to evaluate the real effects of the improvement of the crystalline structure on the capability of the nanomaterials towards the pollutants. However, it can be stated that the higher degree of crystallinity can reduce the solubility of the nanomaterials, especially when facing with highly acidic environments. It is especially of high importance in terms of economic considerations which can help the recovery and the reuse of the catalyst after being used for the treatment purposes.

2.1.3 Surface charge

The zeta potential (or electrokinetic potential), is known as the potential at the slipping plane of a moving colloid particle under electric field [31]. Immediately after the dispersion of a charged particle, a double layer called electrical double layer (EDL) develops around the particle. Opposite charge to that of the particles is the main characteristic of the inner layer (Stern layer). The outer layer (diffuse layer) consists of both negative and positive charges. The potential difference between EDL and the layer around the moving particle indicates the zeta potential of the particle. This parameter is of high importance for controlling the electrostatic interactions of the particle with the surrounding environment and also to determine the stability of colloidal dispersions [32].

So, the initial pH of the medium has a crucial role in the removal of environmental contaminants under various decontamination processes such as advanced oxidation processes (AOPs) or adsorption [33]. Recent studies have clearly

indicated the importance of the pH of the medium in the adsorption process [34]. Huong, Lee, & Kim (2016) [35] utilized a Cu-nano zeolite (zeta point= ~ 6) for the adsorption of 2-chlorophenol. They observed that the removal efficiency improved by increasing the pH from 2.0 to 6.0 when the medium is acidic with becoming less competitive for 2-chlorophenol and H_3O^+ (by decreasing H_3O^+ availability) and the maximum efficiency was 204.68 mg/g at pH 6. After this point, however a decrease in removal efficiency was observed at pHs from 6.5 to 10 due to the lower tendency of the particles surfaces with a negative charge to adsorb 2-chlorophenol.

The surface charge of the NMs acts also as a highly important factor for the adsorption of special contaminants from the containing environment. Mahdavi & Akhzari (2016) [36] utilized this characteristic of the NMs for the removal of phosphate by CuO nanoparticles (NPs) (22.2 nm). The point of zero charge (PZC) of the materials was calculated 7.9 and so the surface of the particles is assumed to be positively charged in most natural aqueous environments. Such a phenomenon facilitates the electrostatically attachment of the negatively charges (PO_4^-) from the environment. They observed 23.9 $mg_{phosphate}/g_{CuO}$ removal efficiency for the phosphate.

2.1.4 Optical Properties

Optical properties is one of the most important properties of CuBNMs, like other types of catalytic materials, determining their behavior when facing with environments with visible or invisible light irradiation [37], [38]. Due to the narrow band gap of copper, it can show promoted efficiency compared to conventional types of nanomaterials. Promotion of the visible light absorption of CuBNMs has been a subject of the recent studies. Z. Zhang et al. (2016) [39] indicated the promotion in

1 the visible-light absorption and the photo-generated electron migration through
2 loading Cu₂O nanospheres and nano-chitosan into 3DrGO network having highly
3 porous structure leading to effective degradation of rhodamine B (RhB) dye (68.2%).

4 CuBNMs have been also observed as a member of multi-component catalysts in
5 order to improve the optical performances. Graphene which is currently gaining
6 more attention for the purification of water and wastewater contaminated by various
7 pollutants was used by Miao et al. (2016) [40] for such multi-component structure as
8 the supporting material joint with polyaniline cuprous oxide for the removal of congo
9 red dye. The calculated band gap of the component for the Cu₂O and graphene were
10 1.62 and 2.04 eV, respectively. It indicates that by the corporation of Cu₂O, the multi-
11 component material can absorb full Uv-Vis light, expecting to have better
12 photocatalytic activity. They reached 92% of the dye degradation by the multi-
13 component structure only after 20 min of the reaction. A conjunction of the CuBNMs
14 with other types of metal and metal oxide nanomaterials is another possibility to
15 adsorb a wide range of Uv-Vis irradiations. For instance, the most important issue
16 for the application of pure-phase TiO₂ nanomaterials for the degradation of
17 recalcitrant pollutants is the necessity of the ultraviolet (UV) irradiation for the
18 generation of the electrons involving in the advanced oxidation processes. By using a
19 composite of these materials with CuBNMs some advanced applications can be
20 expected for the prepared properties through enhancing the optical properties. Feiet
21 al. (2015) [41] by providing a p-n heterojunction between Cu₂O and TiO₂ NMs
22 prepared an efficient composite for the decolorization of acid red B aqueous solution
23 under visible irradiation of sunlight. A p-n heterojunction is able to improve the
24 separation of the photo-generated electron-hole pairs of Cu₂O and TiO₂. Due to the
25 narrow band gap of Cu₂O, photo electrons are generated under sunlight irradiation
26 and immigrate to the conduction band (CB) of TiO₂, because of the difference

1 between the conduction band and valence band (VB) in Cu_2O and TiO_2 . This process
2 inhibits the recombination of the photo-generated electron–hole pair in Cu_2O . Such
3 photo-generated electrons involve in the production of oxygen peroxide radical
4 (OPR) through their reaction with the existing dissolved oxygens (DO) in the media.
5 This combination significantly enhances the $\text{Cu}_2\text{O}/\text{TiO}_2$ visible light photocatalytic
6 efficiency compared with pure-phase TiO_2 nanomaterials. In another study, Sorolla
7 et al. (2012) [42] used copper as the dopant to shift the photocatalytic activity of TiO_2
8 particles for enhancing the photocatalytic activity of SBA-15 supported TiO_2 from 30
9 to 71% after 8h when 5% of Cu was utilized as dopant agent. There are also more
10 evidence for the positive effects of the Cu doping into the structure of other metal
11 oxides on the promotion of the photocatalytic decomposition of the recalcitrant
12 compounds. Under optimum conditions of initial phenol concentration=158.75 ppm,
13 time=179.50 min, Cu doped TiO_2 dosage=0.52 g/l, Sohrabi & Akhlaghian (2016) [43]
14 achieved phenol degradation of 52% in the presence of H_2O_2 and under the UV
15 irradiation.

16 CuO has been also successfully coupled with other metal oxides for the enhanced
17 removal of complicated organic compounds. Esmaili-Hafshejani & Nezamzadeh-
18 Ejhieh (2016) [44] studied the photocatalytic activity of the coupled ZnO-CuO and
19 ZnS-CuS semiconductors supported onto clinoptilolite nanoparticles (CNP) and
20 micronized one (CMP) for the removal of benzophenone (BP) from the containing
21 solution. They identified a red-shift in the Uv-Vis spectrum of the supported coupled
22 semiconductors compared to the supported monocomponent ones. Hence, the
23 supported coupled system showed better photocatalytic activity than the sulfidic one.
24 They also applied a recovery procedure by re-calcination of the used catalysts at
25 400°C showing that the recovered catalysts maintained 65-75% of their initial
26 photocatalytic activities after 5 re-cycling runs. Cu as a dopant can also improve the

1 photocatalytic activity of the system. As an example, Jamil et al. (2017) [45] indicated
2 that under visible light irradiation a higher total organic carbon (TOC) removal of
3 dibutyl phthalate was achieved for Bi, Cu co-doped SrTiO_3 compared with the Cu
4 undoped ones. They concluded that it can be attributed to a lower band gap energy of
5 Cu doped materials (1.78 eV) compared with band gap energy of undoped materials.

6 Simamora et al. (2012) [46] performed a simultaneous photocatalytic removal of
7 dyes (i.e., methylene blue) and production of solar fuel (H_2) by splitting the water
8 and seawater in the presence of CuO supported nanosized TiO_2 under Uv-visible
9 irradiation. At methylene blue initial concentration of 10 ppm in water, 5h Uv-visible
10 irradiation in the presence of the photocatalyst (2.5%CuO/nano TiO_2) resulted in
11 86% removal of the dye and 5.0 mmol/h g cat H_2 was generated. In the same
12 conditions but in the seawater medium higher efficiency (99 %) while decreasing the
13 H_2 production rate to 3.1 mmol/h g cat was achieved. Decontamination and
14 simultaneously hydrogen production has been also subjected for other recent studies.
15 Lucchetti et al. (2017) [47] investigated the removal of nitrate with hydrogen
16 generation simultaneously using nano zero valent copper (nZVC) modified titania
17 (P25). They also used glycerol as a hole scavenger. Under optimum experimental
18 condition (catalyst load=150 mg/L, initial nitrate concentration=50 mg/L, initial
19 glycerol concentration=0.8 mol/L) they achieved up to 100% nitrate removal and
20 hydrogen generation up to 14 $\mu\text{mol/L}$ of H_2 . The CuBNMs have been also used for
21 the removal of the higher initial concentration of nitrate from the contaminated
22 solutions. Lucchetti et al. (2017) [11] investigated the reduction of nitrate (150 mg/L)
23 to nitrogen and simultaneous hydrogen generation using copper loaded titania (P25)
24 under Uv-vis irradiation. They achieved total nitrogen removal up to 93% and
25 hydrogen production of 14 μM .

2.1.5 Supporting and Encapsulating

Application of low-cost sorbents is another possible way to enhance the absorbance of environmental contaminants. Chitosan is an efficient sorbent used so far to support CuO for the environmental clean-up purposes. The high efficiency of this compound is especially due to the presence of amine groups in their structure [48]. Some recent studies aimed to study the performance of the chitosan encapsulated materials. Elwakeel & Guibal (2015) [49] indicated that the sorption of As (V) by this composite is highly related to the pH of the media which is, in its term, related to the zeta potential of the prepared materials. They found the optimum pH close to 6 for the sorption of arsenic. In this pH, they reached a capacity of 28.1 mg As/g(sorbent) at 20 °C. Kumar et al. (2015) [50] applied 3.025% copper embedded in the chitosan matrix for the degradation rhodamine B dye leading to up to 99% degradation of this pollutants in 60 min. Such a high efficiency can be attributed to some features such as slow rate of electron hole pair recombination as well as of CuO NMs in such a biopolymer matrix. The large specific surface area provided by CuO NMs is another advantage leading to such high degradation efficiency. They also indicated the possibility of recovery of recycling of the composite through a facile hand-picking strategy. Esmaeili & Khoshnevisan (2016) [51] indicated that alginate-coated chitosan nanoparticles (Alg-CS-NPs) can be efficiently used for the removal of heavy metals from industrial wastewaters. Under optimum removal conditions (pH=3, initial nickel concentration of 70 mg/L, biomass dosage of 0.3 g, and contact time of 30 min) they could remove 94.48% of nickel from the effluents. Rajesh et al. (2016) [52] prepared nano copper oxide needle shape materials supported on graphene oxide sheets (BET=266 m²/g) using a sonochemical procedure. They applied this hybrid for the removal (~98%) of coomassie brilliant blue, cogo red and

amidoblack 10B (as organic dyes). They concluded that the synergetic effect between copper oxide nanomaterials and graphene oxide can play a significant role in the overall adsorption of the studied dye species. There are also some other reports in the literature on the synthesis of copper based materials using various supports such as copper oxide species supported on zirconia with various copper loading (3-40%) [53]. However, there is a limited number of reports in the literature for the application of other various types of supports for CuBNMs in order to remove environmental pollutants. In this regard, the application of some other types of clay based materials such as bentonite is highly recommended in this regard.

Activated carbon (AC) has been also used in order to enhance the surface area and porosity of the adsorbents to enhance the total removal efficiency. Nekouei et al. (2015) [54] loaded a copper based composite, CuI-CuO nanoparticles, on activated carbon to enhance the surface area leading to promote the adsorption of contaminants including dyes even under very low dosage of the adsorbent. The adsorption capacity (136.67 mg/g) happened when 0.025 g of the adsorbent introduced to the solution containing 20 and 30 mg/l of malachite green. Also, Nekouei et al. (2014) [55] through applying a surface modification to activated carbon, by the addition of copper oxide nanoparticle (25 nm) to the adsorbent, succeeded 6% improvement in the removal of acid blue 129 from the containing solution compared with the condition of no copper oxide addition condition. In this case, application of CuO caused irregular porosity property, appropriate for the placement of dyes into the developed pores. Through a review of the literature, it is evident that the efficiency of this green and low cost is higher than that of other adsorbents such as almond shell, bentonite-CTAB and raw bentonite [55].

There are some other types of materials which have not been widely used as a support for CuBNMs mainly due to the existing technical limitations. Layered double hydroxides (LDHs) as a class of ionic solids [60] are examples in this regard. These materials are positively charged in the inner surfaces and, so attachment of cations like Cu for the synthesis of copper oxides (e.g., Cu₂O) is very difficult and needs special measures which are not economically and technically beneficial. However, some indirect measures have been recently developed in order to ease such attachments. J. Ma et al. (2015) [61] attached Cu₂O NMs to the surface of LDH by reduction of Cu oxide from MgAlCu-LDH. By providing a relatively higher surface area (76.6 m²/g) for Cu₂O-Mg₇Al₅-LDH compared to Mg₇Cu₉Al₅-LDH (64.1 m²/g), its capacity for Orange II adsorption reached about 126 mg/g higher than that of Mg₇Cu₉Al₅-LDH and Cu₂O (114mg/g and 31mg/g, respectively).

Synthesis of hybrid catalysts using zeolite was also experienced recently in order to carry the CuBNMs. Lin, Wu & Kuo (2014) [62] showed that the Y-zeolite (consisting of silicon dioxide and sodium aluminum with 65 to 35 weight percentage ratio) can support cuprous oxide to effective degradation of gaseous 1,2-Dichloroethane (1,2-DCE) under visible light irradiation. They indicated the efficiency of the hybrid catalyst especially under visible light irradiation following the order of red > UV > blue > green (Table 2).

Table 2

Performance of CuBNMS/Supporting-Encapsulating agents for the removal of environmental contaminants.

NMs/Support	Experimental Conditions					Removal efficiency			Ref.
	pH	Concentration	Time	Other Conditions		Parameter/	Removal	Unit	
		(mg/L)	(min)	Condition	Value	Substance			
Chitosan/CuO	~6			Temperature	20°C	As (V)	28.1	mg/g	[49]

Chitosan/CuO (3.025%)			60				rhodamine B	99	%	[50]
Alginate-coated chitosan/CuO	3	70	30	Biomass dosage	0.3 g		Nickel	94.48	%	[51]
CuI-CuO/ AC							Malachite green	136.67	mg/g	[54]
CuO/ AC							Acid blue 129		mg/g	[55]
Cu ₂ O-Mg ₇ Al ₅ - LDH							Orange II	90	%	[61]
Cu ₂ O							Orange II	70	%	
Cu ₂ O/zeolite		20 ± 5 ppm	120	UV Ir ^d	365 nm		1,2-DCE	22	%	[62]
				Blue Ir	460-465 nm			24.8	%	
				Green Ir	520-525 nm			20.8	%	
				Red Ir	620-625			22.2	%	

^c. amidoblack 10B.

^d. irradiation.

Synthesis of the core-shell structure materials is also an interesting way to support CuBNMs. For instance, Xuekun Luo et al. (2014) [63] indicated that a core-shell structure consisting of the ball of Mg₆₅Cu₂₅Y₁₀ metallic glass as the core and the uniform nanoporous copper layer as a shell constructed on the surface of the core material by dealloying can exhibit higher performance for the degradation of the azo dye of Direct Blue 6 than the pure copper layer. They discussed that the nanoporous structure of the copper layer can significantly increase the specific surface area of the material as well as providing three-dimensional diffusion channels for the ion transport of reaction masses.

2.2 Environmental and operating parameters

2.2.1 Time

Reaction time is one of the main parameters influencing the overall treatment efficiency and cost directly. Various studies have been so far carried out in order to find the optimum duration for the removal of the environmental contaminants using

CuBNMs. So, it is of high importance to find the optimum reaction time for the removal of recalcitrant pollutants using the novel CuBNMs. It seems that the optimum reaction time is more important in the case of adsorptive removal of contaminants. This is due to this fact that after a certain time for a given CuBNM the availability of the free specific surface area for the promotion of the adsorption decreases. For instance, Huong, Lee & Kim (2016) [35] indicated that the adsorption of 2-chlorophenols using Cu-nano zeolite is very slow after 120 min of the reaction due to the less available surface area for the adsorption of the pollutant after the mentioned reaction time. The effective reaction time however is highly dependent on the type of the nanomaterial and the contaminant being removed from the carrying environment. As an example, this period was 20 min for the removal of malachite green (MG) at initial concentrations of 20 and 30 mg/L using CuO-CuI-NC-AC with the optimum dosage of 0.5 g/L [54]. The similar trend was also observed by Nekouei et al. (2015) [55] for the adsorption of AB 129 dye by CuO-NP-AC particles. They found that the adsorption process is optimized after 25 min at 400 rpm for the initial concentrations of 0.9 g/L and 20 mg/L for NMs and the dye, respectively.

The reaction time can directly affect the cost of treatment, especially when the CuBNMs are desired to be used in real applications. For instance, the reaction time can considerably affect the design parameters of the reactors, e.g., size and type. Development of CuBNMs with enhanced visible light activity [64] or the application of advanced techniques to obtain nanomaterials with enhanced surface area [65] can be considered as a solution to decrease the reaction time. In addition, this operating variable can be highly influenced by the surface charge of the particles. In this regard, the manipulation of the nanomaterials properties to overcome the repulsion force between the nanomaterials and the contaminants would be a practical option to promote the reactions faster and more efficient.

2.2.2 pH

As previously mentioned, two main mechanisms including adsorption and AOPs are involved in the removal of environmental pollutants including organic and inorganic materials using NMs. Adsorption is the main mechanism for the removal of heavy metals while organic compounds are mostly degraded via the AOP mechanism [33], [66]. For the former mechanism pH plays an important role where the efficiency of the adsorption process is directly related to the surface charge of the nanomaterials. It is evident that for the adsorption of the heavy metal cations, the negative charge of the NMs surface is a key factor. Ahmadi, Sadjadi, & Hosseinpour (2012) [67] indicated that CuO NPs (18.74 m²/g) prepared under batchwise supercritical hydrothermal method immobilized into the porous matrix of sodium alginate can adsorb Pb⁺² very efficiently at high pHs. In fact, the lower pH restricts the adsorption of Pb due to the positive characteristics of the catalyst surface.

This phenomenon is also of high importance for the degradation of the organic compounds. Yehia et al. (2014) [68] indicated that the degradation of phenol using nano zero valent copper is highly dependent on the working pH. Due to this fact that the initial step for the degradation of phenol is the attachment of the compound to the surface of the nanomaterials, the removal process can be facilitated when the surface of the nanomaterials is positively charged in order to adsorb the negatively surface charged 2-chlorophenols. Due to this fact that zero point charge of the zero valent copper is around 8.5, the pHs higher than this point can potentially improve the removal of the chlorophenol. Huong, Lee & Kim (2016) [35] determined the optimum operational pH for 2-chlorophenol adsorption at 6.0 by Cu-nano zeolite. At pHs from 6 to 10, they observed less adsorption of the 2-chlorophenol to the nanomaterials due to the repulsion between the negatively surface charged of the

1 nanomaterials and 2-chlorophenols at basic pHs. They also stated that when the pH
2 increases from 2 to 6, the competition between 2-chlorophenol and H_3O^+ decreases
3 leading to increase the adsorption of the organic compound. However, in some cases
4 the positive surface charge of the pollutants can restrict their attachment to the
5 surface of the catalyst with positive surface charge due to the electrostatic repulsion
6 between two surfaces. Nekouei et al. (2015) [54] synthesized cuprous iodide-cupric
7 oxide festooned activated carbon (CuI-CuO-NC-AC) for the adsorption of MG. They
8 stated that at pH=7 the optimum uptake and removal of MG can be achieved. At the
9 pHs higher than this value, the removal of MG was considerably dropped due to the
10 repulsion force between the both negatively charged catalysts and dye molecules.
11 They followed their work on the removal of dyes by the application of CuO-NP-AC for
12 the adsorption of AB 129 dye [55]. They concluded that the pH is the most important
13 working parameter resulting in the maximum dye removal at pH=2 (100%).

14 Although key references reviewed in this manuscript have shown that the acidic
15 pH may promote the removal of the pollutants, in some cases such as removal of
16 organic dyes with CuBNMs [69] neutral pH would be more preferred. Hence,
17 controlling the operating pH is a main factor determining the type of the
18 environmental contaminants to be removed or degraded. However, under real
19 conditions adjustment of pH to desired values may bring some technical and
20 economic issues. In these conditions, manipulation of the nanomaterials for instance
21 through surface modifications leading to desired surface charge can be considered as
22 an applicable option to deal with the specific types of environmental contaminants.

23 It must be also taken into consideration that the removal system may include
24 some specific reagents with the crucial effect on the optimum operational pH. For
25 instance, Raut, Kamble & Kulkarni (2016) [70] applied a system including Cu^0 (2.5
26 g/L) and NaBH_4 (1g/L) as the reductant agent producing H_2 for the removal of mono

chloroaromatic. They stated that in this system, pH=10 for 12 h can result in the highest removal percentage (90%) higher than that of pH=4 (60%). They explained that under lower pHs, H^+ reacts with $NaBH_4$ and deactivates it.

2.2.3 Temperature

The operating temperature is considered a significant parameter that can potentially affect the efficiency of persistent pollutants removal. The increase in the temperature can play some roles such as reduction of the solvent-solid surface interaction leading to enhance in the active sites on the surface of nanomaterials [54], reduction of the solubility of the materials especially in the case of using oxidation agents such as ozone, etc. [71]. In addition, the increase in the temperature can lead to better diffusion of the molecules in the media and also change the equilibrium capacity of the adsorbents for a certain adsorbate [55]. However, due to economic consideration, finding the optimum operational temperature would be of high importance. While Gupta, Chandra, Tyagi, & Verma (2016) [72] indicated that the removal of hexavalent chromium ions with CuO nanoparticles increased from 83 to 94% when the temperature increased from 20 to 45 °C, in some cases, there are no significant differences between the removal efficiencies under elevated temperatures. For instance, Hu et al. (2016)[71] applied different temperatures from 30 °C to 60 °C for the removal of RB-5 dye by a carbon aerogel supported copper oxide. They mentioned that by increasing the temperature from 30 °C to 60 °C, the difference of color removal rate was not significant, proposing that degradation of RB-5 at high temperature is not necessary when the economic considerations are of high importance.

Although elevated temperatures can be expected for the wastewaters from industrial activities, in most environmental conditions working under elevated

temperature is not economically feasible. Hence, optimization of the CuBNMs performance for the removal of recalcitrant pollutants requires more studies which can help to determine the effects of the temperatures and relative importance of this factor compared with other influencing factors.

2.2.4 Humidity

Humidity is another influencing parameter for the removal of gaseous pollutants from the containing environments. Lin, Wu, & Kuo (2014) [62] indicated the indirect effects of the humidity on the removal of 1,2-DCE in the gaseous state. While under relatively high humidity (65%) only 23% of the pollutant was removed using a hybrid NMs (zeolite-Cu₂O) due to the competition between the pollutants and the free radicals to be adsorbed on the surface of the hybrid materials. Providing low humidity of 15% resulted in the 40% higher adsorption of 1,2-DCE on the surface of the catalyst to be decomposed after irradiation of the light.

2.2.5 Additional measures

Some recent studies have emphasized the effects of additional measures to enhance the efficiency of the CuBNMs when used for the removal of recalcitrant pollutants from the polluted environments. Ultrasonic irradiation is among the environmentally friendly and low-cost methods with high efficiency for such applications. Yehia et al. (2014)[68] utilized ultrasonic irradiation in the presence of nano-sized zero-valent copper and nickel to degrade phenol. They accomplished alternative tests to show that neither sonolysis nor catalyst solely can degrade the phenol considerably. Ultimately, they achieved 65 and 60% removal of this contaminate using nZVC and nano zero valent nickel (nZVN), respectively (1 g/L) and H₂O₂ (20 mM) after 60 min of sonication. They also stated that the higher removal efficiency under such a described system can be attributed to the presence of

a heterogeneous catalysis and also the effects of the ultrasonic irradiation resulting in the release of the higher amount of hydroxyl radicals. Elshafei et al. (2014) [73] also emphasized the role of the sonication (20 kHz) on the promotion of the removal of nitrobenzene (NB) (10 mg/L) in the presence of nano-sized oxides of α -Fe₂O₃ and CuO at 25 °C. They achieved complete degradation of NB at pH 7 in presence of 10 mM H₂O₂ after 10 min of sonication in presence of α -Fe₂O₃ (1.0 g/ L) and after 25 min in case of CuO. It is assumed that the intensity of the ultrasonic irradiation can also lead to higher hydroxyl radical generation. Chand et al. (2009) [74] studied the phenol degradation using zero valent copper under three frequencies (20, 300 and 520 kHz) of ultrasound. They identified that ultrasonic irradiation of 300 kHz results in optimum phenol degradation and TOC removal.

In recent years, increasing attention has been paid on the co-application of NMs with other oxidative agents especially hydrogen peroxide (H₂O₂) for promoting the systems of depletion such as AOPs [75]. In the presence of UV irradiation, H₂O₂ is dissociated to hydroxyl radicals ($\text{H}_2\text{O}_2 + h\nu(\text{UV}) \rightarrow 2\text{OH}^\bullet$) [76]. Hydroxyl radical as a strong oxidant may react with the organic pollutants to destroy them or to react with another H₂O₂ molecule to provide more hydroxyl radicals. However, the effectiveness of hydrogen peroxide is highly dependent on the catalyst used in the degradation process. For instance, Srivastava, Anu Prathap, & Kore (2011) [77] indicated that when H₂O₂ was used as the reductant in the absence of catalyst (CuO micro/nanostructured materials) very slow degradation of the pollutant (methylene blue) (13%) was observed in the 10h of the reaction. When the catalyst was included in the experiments, complete removal of this pollutant was observed after 4 h of the reaction. Ozone is another source of hydroxyl group generation which has been extensively used for the degradation of the recalcitrant compounds [78], [79]. Hu et al. (2016) [71] indicated the efficiency of the ozonation of simulated dyeing

wastewater for Reactive Black 5 (RB-5) dye degradation in the presence carbon aerogel supported copper oxide (CuO-Cu₂O/MCA). To highlight the effect of the ozone concentration the changed the concentration of ozone flow to the wastewater from 2 to 8 mg/L resulting in the increase in the chemical oxygen demand (COD) removal from 35% to 57% after 60 min of ozonation. The generation of higher amounts of hydroxyl radicals is the possible explanation for such higher COD removal efficiency. However, in some case, ozone is not able to degrade some complicated organic compounds such as oxalate. The efficiency of ozonation for the removal of this compound when combined ceria supported copper oxide was studied by Zhang, Li, & Croué (2012)[80]. They found a significant improvement of the oxalate removal using such a combination. They also found the increase of the degradation with the increase of the ozone dose.

3. Toxicological studies

Toxicological studies of the CuBNMs are of high importance due to this fact that there is always a possibility of the release of the nanomaterials after being used as for the removal of environmental contaminants. In this regard, it would be essential to pay enough attention to both *in vitro* and *in vivo* studies on the toxic effects created or induced by CuBNMs to have a precise estimation of the probable toxic effect of these nanoparticles [33].

3.1 *In vitro* studies

In Vitro studies have been performed mostly on the specific cells as the models for human or mammalian cells such as human alveolar epithelial cells, N-hTERT keratinocytes, and SZ95 sebocytes and on reconstructed human epidermi, *Xenopus laevis* (A6), PC12 and A549.

A schematic of the CuO NPs (34.38 ± 0.76 nm and surface area $29 \text{ [m}^2\text{/g]}$) cytotoxicity on human alveolar epithelial cells is shown in the Fig.1. According to this Fig. the uptake of CuO NPs can happen through the vesicle-mediated endocytosis and an un-characterized internalization mechanism. It is of high importance to note that the toxicity of CuO NPs is not only attributed to the dissolved copper ions in the medium but also to the nature of the NPs and their contraction with the surrounding environment [81]. In a recent study, the promotion in the reactive oxygen species (ROS) generation was found to be the dominant mechanism for the toxicity effects induced by CuO NPs (12 nm, rod shape, 5-50 $\mu\text{g/ml}$) on N-hTERT keratinocytes and SZ95 sebocytes and also on the reconstructed human epidermis [82]. Further, a study [83] on the mechanism and the toxic effects of Cu NPs (15-30 nm) with various concentrations (0, 1, 10, 30, and 100 $\mu\text{g/mL}$) on PC12 cells revealed that the increase in the Cu NPs concentration can cause a reduction in the cell viability (time and concentration dependent pattern) and significant apoptosis in PC12 cells. The ROS generation was also found to be the main mechanism of Cu NPs toxicity. In another recent study, the untargeted metabolomics approach adopted for study the CuO NPs (28.2 nm, 0-40 $\mu\text{g/ml}$) toxic effect on the metabolic in A549 cells showed that the induced CuO toxicity is related to pro-inflammatory conditions, oxidative stress, and programmed cell death and the concentration of released Cu^{2+} ions cannot induce the Cu NPs toxicity [84]. Thit, Selck, & Bjerregaard (2013) [85] indicated that continuous exposures of three different forms of copper (Cu ions, CuO NPs and poly-dispersed CuO NPs) at concentrations of 143-200 μM to *Xenopus laevis* (A6) led to both an increase in the cell death and the change in the cell cycle progression. Although the cell state (dividing or differentiated) were found to be very important in response to copper exposure, but poly-CuO NPs represented more cell death, via apoptosis, only within 48 h of exposure.

1 In addition, the physico-chemical properties of nanoparticles (i.e., surface
2 oxidation, hydrophobicity, etc.) can determine their interactions with medium and
3 the living cells. For instance, Minocha & Mumper (2012) [86] indicated carbon-
4 coated (C-Cu NPs) and non-coated Cu NPs can cause different toxicity effects to the
5 plasma and damage to the mitochondria of A549 (alveolar epithelial cells).

6 **3.2 *In vivo* studies**

7 **3.2.1 Terrestrial ecosystems**

8 The nature and ionic state of the CuBNMs can considerably determine their toxic
9 effects to the terrestrial living organisms. Rousk et al. (2012) [87] found that the CuO
10 bulk particles are not toxic to the bacterial growth while Cu²⁺ could highly inhibit
11 bacterial growth in the soil considerably higher than CuO NPs (40-80 nm). They
12 concluded that the toxicity of CuO NPs can be related to the ion releasing from CuO
13 NPs and it is not attributed to the nanometric size of CuO [87]. However, Mortimer,
14 Kasemets, & Kahru (2010) [88] found showed a size-dependent toxicity for the
15 copper oxide towards *Tetrahymena thermophile* where nano CuO was 10-20 times
16 more toxic than that of bulk particles. In spite of these findings, Zhao et al. (2011)
17 [89] observed no significant difference between the toxic effects of CuO
18 nanoparticles (20-40 nm) and its counterpart bulk particles (10, 50, 100, 200, 300,
19 500 and 1000 mg/L) towards juvenile carp (*Cyprinus carpio*). However, by
20 increasing the exposure time from 96 h to 30 days, CuO NPs (100 mg/L) significantly
21 inhibited the carp growth compared with the control, CuO bulk particles and Cu²⁺
22 groups.

Fig.1

Transmission electron microscopy (TEM) micrograph of A549 cells exposed to CuO nanoparticles (10 $\mu\text{g/ml}$) for 3 h (A-F) and for 24 h (G-I). Few number of nanoparticles are internalized in a small cytoplasmic vesicles (arrowhead) (A), nanoparticles are adhering to the cell membrane and are scattered throughout the cytoplasm (B), nanoparticles are agglomerated in the nucleus (C), high magnification of the same nanoparticles agglomerate (C*), an abnormal mitochondria, and endoplasmic reticulum (D), degrading phagolysosomes (E), lyses of the cell membrane (F), massive ultrastructure loss reflecting cell necrosis (G-H), a large autophagosome with abundant nanoparticles (I). (M: Mitochondria, N: nuclei), used with permission from Moschini et al. (2013) [81].

CuBNMs can also result in the inhibition of the plant growth in the terrestrial ecosystems. Hong et al. (2015) [90] through the toxicity study on the lettuce (*Lactuca sativa*) and alfalfa (*Medicago sativa*) suggested that Cu NPs and CuO (10-100nm) NPs are able not only to reduce the size (49% decrease in the root length) of the plants but also they can change the nutrient content and enzyme activity in both studied plant species higher than that of Cu and CuO bulk particles [90]. In addition, less abundant on root hairs and lower shoot biomass of Ipt-cotton were found when

the plants faced with 10, 200, and 1000 mg/L of CuO NPs (30 ± 10 nm) after 10 days [91]. The plant height and the root length of Ipt-transgenic cotton decreased when exposed to the highest concentration of CuO 26.91% and 42.80%, respectively. Also, it was observed [92] that the roots of *Allium cepa* grew slowly after 24 h of exposure to CuO NPs (40 nm, 10, 20, 40, 80 mg/L) and the surface of the root cap and meristematic zone were clearly decayed. As well, an increase of CuO NPs concentration caused the increase in the Cu concentration in the roots remarkably. The toxic effects of CuO nanomaterials on the plant roots were also studied by Nair & Chung (2014) [93]. They observed that the exposure of soybean (*Glycinemax* L.) seedlings to CuO NPs (50 nm, 100, 200, 400, and 500mg/L) during 14 days significantly increased the lignification of root cells and, consequently, altered the root development in the plant. It is also worthy to note that the reduction of the root length and fresh weights of plant occurred in high and low concentrations of CuO NMs (500 and 50 mg/L, respectively). The hydrogen peroxide level and peroxidase (POD) enzyme activity of soybean also boosted remarkably in exposure to CuO NPs (100, 200, 400, and 500mg/L). Zhenyu Wang et al. (2016) [94] indicated that the growth inhibition and Cu uptake of *Arabidopsis thaliana*, in exposure to CuO NPs were higher compared with that of Cu^{2+} ions or CuO bulk particles. Moreover, the seeds contained Cu mostly in the form of CuO NPs (88.8%). But, about 6.0% of Cu_2O was found in the seeds. Transformation of CuO NPs may occur during uptake or transport of NPs in the plant. The surface areas of CuO NPs (20-40 nm) and bulk particles were 13.3 and 0.52 m^2/g , respectively. In addition to the mentioned adverse effects, Tang et al. (2016) [95] detected the toxicogenomic impacts of 10 and 20 mg/L of CuO NPs on *Arabidopsis thaliana*. CuO NPs contributed much stronger up-regulation of oxidative stress-related genes than the corresponding Cu ions.

1 However, it has been discussed in the literature that the toxicity of CuBNMs can
2 be altered in terrestrial ecosystems by changing the content of the medium or any
3 possible modification in NPs composition. Perreault, Popovic, & Dewez (2014) [96]
4 by studying the phytotoxicity of both nano and bulk particles of Cu on wheat
5 (*Triticum aestivum L.*) showed that the behavior and related toxicity of Cu bulk and
6 Cu NPs particles can be highly affected in the presence of humic acid (50 mg/L).
7 They identified that the ion content of the bulk Cu solution was dropped to 42% in
8 the presence of humic acid (50 mg/L) while the Cu²⁺ content of NP solutions
9 increased up to 2.9 times [97]. However, Zhenyu Wang et al. (2011) [98] claimed that
10 Suwannee river fulvic acid (SRFA), is able to significantly increase the toxicity of CuO
11 nanoparticles to prokaryotic alga *Microcystis aeruginosa*. In order to explain why
12 the interaction of CuO and benzoic acid (BA) can enhance the toxic effects of copper
13 oxide to green alga *Scenedesmus obliquus*, they explained that the presence of BA
14 can increase the dissolved Cu released from the copper oxide nanomaterials as a dose
15 dependent manner.

16 The surface modifications applied to the CuBNMs may potentially alter their
17 toxic effects towards living organisms. However, the type and the intensity of such
18 adverse effects have not been well clarified yet. Perreault et al. (2014) [96] showed
19 that the toxicity induced by CuO NPs with a polymer shell (polystyrene-co-butyl
20 acrylate) to *Lemna gibba* is 10 times higher than (50% decrease of growth rate) that
21 of induced by CuO NPs (30-40 nm) without a shell. Worthington et al. (2013) [99]
22 compared the toxicity of Cu NPs in both presence and absence of chitosan coating *in*
23 *vitro* and *in vivo* on mice lung. The results indicated that *in vitro* treatments,
24 chitosan coating can remarkably reduce the toxicity of Cu NPs while in the case of *in*
25 *vivo* treatments presence of Cu NPs with chitosan coating raise the inflammatory
26 response of lung in mice. Cu NPs induced a toxic effect in different parts of

mammalian body organism such as rats. The repeated oral dose (0, 100, 200, and 400 mg/kg/day) of Cu NPs (32.7 ± 10.45 nm) and Cu bulk particles on rats during 28 days, caused damages to the red blood cells, thymus, spleen, liver, and kidney at ≥ 200 mg/kg/days. While in the case of Cu bulk particles, no effects were found even at the highest dose applied. In this regard, the non-observed adverse effect of Cu was reported to be 100 and ≥ 400 mg/kg/days for Cu NPs and Cu bulk particles, respectively [100].

3.2.2 Aquatic ecosystems

In addition to the exposure of the CuBNMs with the terrestrial organisms, they can be released to the aquatic environments from various sources such as from wastewater treatment systems [101]. Subsequently, they can induce toxic effects to the aquatic living communities directly or indirectly. Such effects can be highly influenced by the properties of the nanomaterials and also by the environmental characteristics. Study of the copper oxide nano rod toxicity (length= 57.69 ± 19.64 nm and breadth= 7.76 ± 1.47 nm) on *Hydra magnipapillata*, a simple invertebrate organism, revealed that CuO nano rods can induce toxic effects on Hydra morphology, feeding, growth and regeneration [102]. Also, some other *in vivo* lethal effects at the cellular level were identified including the induction of oxidative stress, S-phase cell cycle arrest and toxicological implications at cellular and molecular levels. The toxicity of CuO nano rods in *Hydra* followed a concentration and time-dependent manner on regeneration and induction of genotoxicity. Xiao et al. (2016) [103] found that any changes in the medium condition can alter the CuNPs (50 nm, specific surface area of $6-8\text{ m}^2/\text{g}$) toxicity (36 to 216 $\mu\text{g}/\text{L}$ CuNPs) to *Daphnia magna*. Altering the exposure conditions such as aging only after 7 days clearly reduced the LC_{50} values of CuNPs exposure by 30%. In this condition, the toxicity can be mainly

1 attributed to the particles exist in the suspension (around 70%). In addition, the
2 presence of dissolved organic carbon (DOC) (0 to 10 mg/L) or altering the pH (from
3 6.5 to 8.5) increased the LC₅₀ values 12-fold and 3-fold, respectively [103].

4 To study the mechanisms involving in the toxicity of CuO on *D. magna*, Adam et
5 al. (2015) [104] observed that CuO (≤ 50 nm) nanoparticles (0.18-19.97 mg Cu/L) can
6 reduce the glycogen, lipid and protein concentrations in the exposed *Daphnis*
7 compared with unexposed ones. Additionally, no significant different transcribed
8 genes were identified between the *Daphnis* exposed to the nanoparticle and Cu²⁺
9 *Daphnis*. So, it can suggest that the CuO nanoparticles toxicity to *D. magna* may
10 cause by releasing the metal ions from the nanoparticles to the medium. Such an
11 observation was also supported by other recent studies. Adam et al. (2015) [105]
12 indicated that the toxicity of CuO nanoparticles (< 50 nm nanoparticles, 0.037, 0.092,
13 0.230, 0.575, 1.438 mg Cu/L) to *D. magna* is caused by the release of the copper ions
14 during the dissolution of the nanoparticles in the medium. They also indicated that
15 the chronic (21-day) effects of CuO nanoparticles to *Daphnia* are lower than copper
16 salt CuCl₂·2H₂O (0.004, 0.007, 0.015, 0.030, 0.060 mg Cu/L) effects. Saif et al.
17 (2016) [106] stated that the 48-h acute toxic effects from the plant-synthesized CuO
18 nanoparticles (*Pterospermum acerifolium* leaves) are higher than that of engineered
19 CuO nanoparticles on *Daphnia* due to higher Cu ion released from the plant-
20 synthesized nanoparticles to the medium. In addition to the release of the ion from
21 the nanomaterials it seems that the properties of the nanomaterials can determine
22 the amount of the ion release from the NMs. The higher adverse effect of the Cu ions
23 compared with CuO nanomaterials was emphasized by Hoseini et al. (2016) [107].
24 They studied the toxicological effects of dissolved copper (0.25 mg/L copper sulfate)
25 and copper nanoparticles (40 nm, 0.25 mg/L and 25 mg/L) on common carp,
26 *Cyprinus carpio*. Both forms of copper damaged the fish liver and kidney. However,

1 they observed that the damages from copper sulfate were more severe compared with
2 nanoparticle copper. Pradhan et al. (2012) [108] by determining a very high 96 h
3 LC₅₀ of CuO (< 50 nm) to *Ilogamus ligonifer* (569 mg/L) stated that leached Cu ions
4 released in the medium from CuO play a key role in the toxicity of the nanomaterials.
5 Kennedy et al. (2013) [109] indicated that the nano sphere CuO particles (particle
6 size <50 nm, surface area=29 m²/g) are more stable than copper oxide
7 nanorods(diameter: 8-12 nm and length: 100-120 nm, surface area=100-120 m²/g).
8 Higher surface area of the nanorods is considered the main reason for the higher
9 release of the Cu ions to the medium. In order to reduce the toxic effects of CuBNMs
10 some measured have been so far adopted. Mantecca et al. (2015) [110] indicated by
11 doping of Zn to the CuO nanomaterials (Zn-CuO, 2-4 nm) the toxicity of the
12 nanomaterials on the Frog Embyo compared to CuO nanoparticles (5-100 nm). In
13 fact, no lethal effects were observed after nZn-CuO exposure. Two main reasons
14 seem to play the key roles for the lower toxic effects of the Zn doped CuO
15 nanomaterials including the lower intensity of ROS generated in the medium and
16 less Cu ions released to the receiving environment.

17 However, the extent of the toxic effects raised from CuBNMs is also related to the
18 susceptibility of a specific tissue to the toxic effects. For instance, Gomes et al. (2012)
19 [111] exposed *Mytilus galloprovincialis* to 10 µg Cu/L as CuO (<50nm) nanoparticles
20 and copper ions for 15 days. It was observed that both forms of copper induced
21 oxidative stress and the digestive gland was the most sensitive tissue to the toxic
22 effects of copper nanomaterials. For a goldfish species (*Carassius auratus*) the most
23 sensitive tissue for the bioaccumulation of CuO nanoparticles (40 nm) was intestine
24 and gills indicated by Ates et al. (2014) [112].

25 In addition to the nature and characteristics of the nanomaterials, the
26 environmental parameters such as pH, temperature, dissolved oxygen, etc. and their

interactions can considerably determine the extent of the toxic effects towards the living organisms. As an example, Rispoli et al. (2010) [113] indicated that the maximum toxic effects from zero valent copper (ZVCN, 25nm, 312.5 - 1250ppm) towards *Escherichia coli* (*E. coli*) can be expected under acidic conditions, higher temperatures, high aeration and the high concentrations of nanoparticles and bacteria. According to the Li et al. (2013) [114], such adverse effects of nano zero valent copper to *E. coli* can be detected only in 30 min after the exposure. They observed various toxic effects i.e. oxidative stress, protein damage, DNA damage and the damage to the membrane of the bacteria when exposed to spherical shape CuNPs (90 nm) (Fig. 2).

Fig. 2

TEM micrograph of the *E. coli* cells exposure to 80 mg/L CuNPs after 30 min adopted from Li et al. (2013) [114].

In the case of the toxicity of the CuBNMs to the bacterial species, it seems that physical interaction of the nanomaterials with the cells is a main factor for the subsequent toxic effects. For instance, Baek & An (2011) [115] studied the toxicity of the copper oxide nanomaterials (20-30 nm, 25, 50, 75, 100, 125 mg/L) on the three bacterial species *Escherichia coli*, *Bacillus subtilis*, and *Streptococcus aureus*. They concluded that the Cu ions released to the medium had negligible toxic effects on the

bacteria. The particle toxicity of the CuO nanomaterials to tested bacterial strains was identified in their study as the main involving toxicity mechanism.

4. Conclusion and future outlook

Although CuBNMs have shown a promising efficiency for the removal of a variety of environmental contaminants, it is vital to have a clear perspective of the economic considerations involving in the life time cycle (i.e., synthesis, application and disposal) of the nanomaterials. In our best knowledge, there is no report in the literature for the comparison of various methods applied for the synthesis of the CuBNMs in terms of properties of the nanomaterials, synthesis costs and the potential for recovery and reuse. In this regard, it is of high importance to consider both the production cost and the efficiency of synthesized materials. Precursors, equipment used, energy consumption for the synthesis of the nanomaterials and the manipulations performed are the main elements for such investigations. The main barrier for such techno-economical evaluations is the lack of the enough information related to the synthesis conditions in the literature which can restrict the proposals for the most economical methods for the synthesis of CuBNMs. Among the various methods for the synthesis of CuBNMs, the chemical reduction which leads to precipitate the synthesized nanomaterials is one the most applied techniques due to its relative simplicity and being cost-effective and efficient facilitating the control and manipulation of the synthesis conditions to achieve the optimum properties for the CuBNMs [116]. Hence, this pathway would be particularly suitable for the pilot-scale or large-scale synthesis of Cu and Cu₂O nanoparticles. Although precise controlling the characteristics of the nanomaterials can be performed using other methods such as solvothermal synthesis or hydrothermal route, the economic considerations arising from the energy input necessity can potentially restrict the wider application

of such methods for large-scale productions. The recent publications reviewed in this paper can considerably emphasize the role of the CuBNMs properties on their catalytic activities for the removal of recalcitrant compounds from the polluted environments. Morphology and crystalline structure of the nanomaterials are among the main measures which can determine the reactivity of the nanomaterials. By manipulation of the synthesis conditions resulting in the lower size nanoparticles, a higher surface area can be provided for the nanomaterials to facilitate the removal of the contaminants. However, according to the literature, crystalline structure and size might have a diverse relationship. In many cases, the conditions leading to a good growth of the nascent particles can often result in high crystalline nature. It is evident that in this condition, a low surface area for the nanomaterials can be expected. This can potentially limit their reactivity towards the targeted pollutants [117], [118]. Hence, adoption of the measures for the future studies with the aim of maintaining the surface area of the particles while improving the crystalline structure would be of high importance [119].

Although some measures have been so far adopted to increase the visible light activity of the CuBNMs (such as synthesis of multi components including Cu_2O), it seems that there is a need for more economical and technical viable methods to improve the band gap energy of the nanomaterials for adsorbing full Uv-Vis lights. Doping an inorganic element to the structure of the oxide nanomaterials has been indicated in the literature a potential way to improve the optical properties of the nanomaterials. Due to the narrow band gap of CuBNMs, such measures seem to be able to aid maximizing their reactivity towards the targeted contaminants [120], [121].

Environmental and operating parameters can also potentially promote or restrict the yield of the treatment process using CuBNMs. Although some parameters such as

time, pH, temperature, etc. are very effective in the overall performance of the removal using CuBNMs, it seems that the relative importance of the mentioned factors has not been well studied yet. It is of high importance, especially due to the economic considerations, to set the optimum operating conditions with a minimum number of experiments and minimum energy and material input. Application of the economic and precise statistical techniques such as Taguchi [122]–[124] approach can be highly recommended in this regard.

The *in vitro* and *in vivo* studies have been performed so far are mainly in agreement that the CuBNMs can cause a size dependent toxic effect on the terrestrial and aquatic organisms. However, it seems that the real fate of the nanomaterials in the environment after being used is under the toxic levels estimated in the published papers. It is evident that by improving some properties of nanomaterials such as crystallinity, their stability will increase and hence less copper ions can be released to the medium. In contrary, when the shape of the nanomaterials changes from spheres to the nano rods, the higher specific surface area is provided for the release of higher Cu ions to the environment. Another possibility to control the release of the Cu ions to the medium is doping of another metallic compound to the structure of the CuBNMs. This way is highly recommended due to this fact that several studies have indicated that such combinations can significantly enhance the reactivity of the nanomaterials toward the environmental pollutants [125]–[127].

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6

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

Table 1
Effects of size and morphology on the catalytic activity 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	[38]
		Flower-like	SSA	5.2 m ² /g		96.0	
		Boat-like	SSA	5.1 m ² /g		0 ^a	
		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	[18]
		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	[39]

^a. In the absence of H₂O₂

Table 2
Performance of CuBNMS/Supporting-Encapsulating agents for the removal of environmental contaminants.

NMs/Support	Experimental Conditions					Removal efficiency			Ref.
	pH	Concentration (mg/L)	Time (min)	Other Conditions		Parameter/ Substance	Removal	Unit	
				Condition	Value				
Chitosan/CuO	~6		60	Temperature 20°C		As (V)	28.1	mg/g	[61]
Chitosan/CuO (3.025%)						rhodamine B	99	%	[62]

Alginate-coated chitosan/CuO	3	70	30	Biomass dosage	0.3 g	Nickel	94.48	%	[63]
CuI-CuO/ AC						Malachite green	136.67	mg/g	[66]
CuO/ AC						Acid blue 129		mg/g	[67]
Cu ₂ O-Mg ₇ Al ₅ -LDH						Orange II	90	%	[73]
Cu ₂ O						Orange II	70	%	
Cu ₂ O/zeolite		20 ± 5 ppm	120	UV Ir ^d	365 nm	1,2-DCE	22	%	[74]
				Blue Ir	460-465 nm		24.8	%	
				Green Ir	520-525 nm		20.8	%	
				Red Ir	620-625		22.2	%	

^{c.} amidoblack 10B.

^{d.} irradiation.

Figure1

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Figure2
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