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Contents

Fluorescence detection of Zinc oxide nanoparticles in water contamination analysis based on surface reactivity with porphyrin

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ABSTRACT

A simple rapid analytical method for determining the concentration of ZnO nanoparticles in aqueous dispersion has been developed by adding porphyrin (TCPP) as a fluorophore into the water sample for fluorescence analysis. Quenching of the emission intensity at 650 nm provides a Stern-Volmer plot with adequate sensitivity for the detection of ZnO nanoparticles from 0.15 mg/mL up to 1.5 mg/mL. A new emission peak at 605 nm can be attributed to the formation of a unique ZnO-TCPP complex. This unique emission peak is good for both identification and quantitation of ZnO nanoparticles at low concentrations down to 0.0015 mg/mL. The new method affords a linear dynamic range up to 1.2 mg/mL.

Keywords: *fluorescence; nanoparticles; porphyrin; quenching; Stern-Volmer; water contamination analysis; zinc oxide*

1. Introduction

Nanomaterials exhibit novel physicochemical properties that determine their application in various industrial manufacturing processes. Three metal oxide nanoparticles namely titania (TiO2), zinc oxide (ZnO), and ceria are produced in high tonnages for use as additives in nanomaterials. ZnO nanoparticles are a widely used ingredient of cosmetics. They have a wide range of antibacterial activities toward various Gram-positive and -negative microorganisms [1] and could be developed as antibacterial agents to control and prevent the spreading of persistent bacterial infections. Unfortunately, ZnO nanoparticles can induce toxicity in biological cells leading to the generation of reactive oxygen species, oxidant injury,excitation of inflammation, and cell death [2]. Their induction of cell death and carcinogenesis depends on the endogenous genetic, transcriptomic and proteomic landscape of the target cells [3]. Oral exposure to ZnO nanoparticles in mice leads to an accumulation of nanoparticles in the liver causing oxidative stress mediated DNA damage and apoptosis [4]. The nanoparticles also possess a genotoxic potential in human epidermal cells even at low concentrations [5].

Fluorescent nanoparticles are widely used for the purpose of bioimaging cells and tissues. Compared to molecular fluorophores, fluorescent nanoparticles offer many meritorious features [6]. Two fluorescence maxima were observed for ZnO particles—the bandgap fluorescence at 365 nm and the visible luminescence at 520 nm—with a low overall fluorescence quantum yield of 0.03 [7]. Intrinsically fluorescent ZnO nanowires (NWs) were adopted for molecularly targeted imaging of cancer cells, after they were functionalized to render water solubility, biocompatibility, and low cellular toxicity [8]. ZnO nanoparticles were conjugated with a hydroxysuccinimide ester of Cy5.5 to investigate their accumulation in rats using optical imaging after oral exposure [9]. Combining ZnO nanoparticles and ammonia gas increased the photoluminescent intensity of the ZnO nanoparticles, thereby showing their tremendous applicability in optical sensors for the detection of ammonia gas [10]. Quenching of the visible emission of

ZnO colloid particles was reported for ferricyanide, ferrocyanide and chloroplatinate anions in the presence of polybrene [11]. The fluorescence of bovine serum albumin conjugated ZnO nanoparticles could be quenched selectively by Cu^{2+} ions in physiological buffer solution. The quenching was static with a rate constant of 7×10^{12} L mol^{-1} s^{-1} [12]. ZnO nanorods have a bimodal photoluminescence spectrum that consists of an ultraviolet excitonic peak and a visible surface-defect-related peak. The intensities of both UV and visible peaks were decreased due to quenching by covalently linked gold nanoparticles [13].

Surface catalytic reactivity of nanoparticles could be applied to detect the type and concentration of nanoparticles with limit of detection down to part per million [14]. ZnO nanoparticles could be detected by capillary electrophoresis (CE) coupled with UV detection after adsorption of dithiothreitol (DTT) or cysteine (Cys) [15]. However, in this work, a quantitative fluorescence method is developed for the analysis of ZnO nanoparticles in water. Porphyrins are a group of heterocyclic compounds that occur in nature with several important biochemical properties. Each porphyrin molecule is composed of four pyrrole rings connected by methylene bridges to α-carbon atoms, forming an aromatic macrocycle structure [16]. Free base porphyrins are recognized to have stable interactions with a wide range of metal cations to produce intense absorption bands in the UV to visible spectral region [17]. This also provides a good opportunity of fluorescence detection by specific adsorption of porphyrin onto ZnO nanoparticles to afford a low detection limit towards 1 μg/mL in water contamination analysis.

2. Method and materials

2.1. Materials

Methanol was purchased from VWR (Mississauga, ON, Canada). Meso-tetra(4-carboxyphenyl)porphyrin (H_2TCPP) and all metal oxide nanopowders Al_2O_3 (<50 nm particles size), CuO (<50 nm particles size), CeO_2 (<50 nm particles size), TiO_2 (21 nm particles) and ZnO (<50 nm particles size) were obtained from Sigma-Aldrich (Oakville, ON, Canada). Zinc acetate was purchased from Fisher Scientific Company (USA).

2 mg of H_2TCPP was dissolved in 20 mL of methanol. The stock solution of ZnO nanoparticles (1.5 mg/mL) was prepared by dispersing 15 mg of ZnO in 10 mL of methanol using an ultrasonic processor (WQY 064). Serial concentrations of ZnO nanoparticles were prepared in methanol from 0.0 to 1.5 mg/mL (see Table 1) for testing them as a quencher of the fluorescence emission from H_2TCPP. To determine the time-dependent quenching effect, the same batch of samples were stored on standing at 298 K for different days before analyzing. The interference effect of TiO_2 nanoparticles was prepared by dispersing serial concentrations of TiO_2 nanoparticles from 0.0 to 0.5 mg/mL (Table 2) in constant concentration of ZnO nanoparticles.

Table 1. Concentration of ZnO nanoparticles for porphyrin (TCPP) quenching.

Sample ID	0	1	2	3	4	5	6	7	8	9	10	11
Concentration (mg/mL)	0	0.15	0.225	0.3	0.45	0.6	0.75	0.9	1.05	1.2	1.35	1.5
ZnO stock (mL)	0	0.1	0.15	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
Methanol (mL)	1	0.9	0.85	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
H_2TCPP (μL)	400	400	400	400	400	400	400	400	400	400	400	400

Table 2. Concentration of ZnO nanoparticles and TiO2 nanoparticles for TiO2 interference analysis.

Sample ID	0	1	2	3	4	5
Concentration of ZnO (mg/mL)	0.5	0.5	0.5	0.5	0.5	0.5
Concentration of TiO_2 (mg/mL)	0	0.1	0.2	0.3	0.4	0.5
H_2TCPP (μL)	400	400	400	400	400	400

2.3. UV-visible spectroscopy

Zn-TCPP was prepared by adding 400 μL of porphyrin stock solution to 1 mL of 0.01M Zinc Acetate as a comparison. Absorption spectra were measured on a Thermo Scientific GENESYS 10S UV-vis spectrophotometer with a slit width of 1.0 nm.

2.4. Spectrofluorometry

Metal oxide dispersion (0.75 mg/mL, 1 mL) was mixed with 400 μL of H2TCPP solution (1 mg/mL). Metal oxide-porphyrin (200 μL) and 2 mL of methanol were added into a 1-cm quartz cuvette. The fluorescence intensity was recorded while the emission wavelength was scanned from 550 nm to 750 nm with fixed excitation of 420 nm using a FluoroMax-4 spectrofluorometer (Horiba Scientific).

3. Results and discussion

3.1. UV-visible spectroscopy

In Figure 1, the UV-vis absorption spectrum of free base porphyrin (TCPP) shows a Soret band at 414 nm and four Q bands at 514 nm, 548 nm, 590 nm, and 646 nm. The UV-vis absorption of ZnO nanoparticles in methanol exhibited a peak at 360 nm. Porphyrin-coated ZnO nanoparticles showed a combination of ZnO absorption peak at 357 nm and a red-shifted porphyrin Soret band at 421 nm (Figure 1a). Porphyrin can react with zinc acetate to form the Zn-TCPP complex (or conjugate) where a zinc ion binds to the center of porphyrin. The UV-vis spectrum of Zn-porphyrin exhibits a Soret band that overlaps with the 421 nm band of porphyrin-coated ZnO nanoparticles [18], which indicated a chemical interaction of the porphyrin coating with the ZnO nanoparticles. In Figure 1b, the magnification of wavelength from 450 to 700 nm also indicates a red-shift of 2–4 nm on all four Q bands of Zn-TCPP [19].

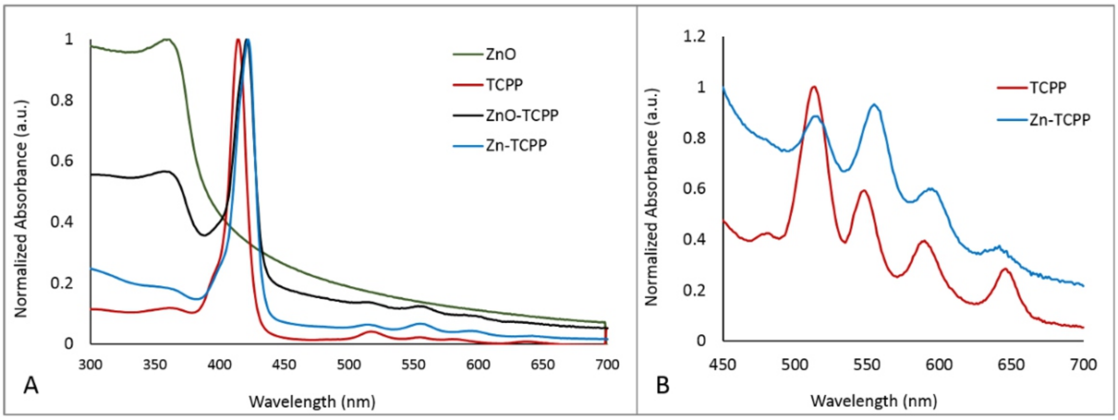

Figure 1. (A) Normalized UV-visible absorption spectrum of ZnO nanoparticles, porphyrin, porphyrin-coated ZnO and Zn-porphyrin in methanol; (B) Magnification of Q-bands of porphyrin and Zn-porphyrin from 450 nm to 700 nm.

3.2. Fluorescence spectroscopy

Among five metal oxide nanoparticles (Al2O3, CeO2, CuO, TiO2 and ZnO) tested for porphyrin quenching, ZnO has the highest quenching efficiencies to both peaks at ~650 nm and ~710 nm (Figure 2a). From the data in Figure 2a, it appears that divalent metal oxides (ZnO and CuO) are better quenchers than trivalent metal oxide (Al2O3) and tetravalent metal oxides (TiO2 and CeO2). In addition, the interaction between ZnO nanoparticles and porphyrin raises a new peak at 605 nm, which gives zinc oxide a unique fluorescence emission compared to other metal oxide nanoparticles. To identify the source of emission peak at 605 nm from porphyrin-coated ZnO nanoparticles, the fluorescence emission of Zn-TCPP also showed a peak with nearly identical wavelength at ~607 nm. Thus, this peak at 605 nm is unique for Zinc ion and ZnO nanoparticles due to the electron transfer between metal and the porphyrin π-system [20]. Moreover, the fluorescence emission of Zn-TCPP had a significant red shift from 647 nm to 654 nm compared with that of porphyrin [21]. Upon adding ZnO nanoparticles, the intense pink color of porphyrin faded and became pale yellow (Figure 2c). With excess of Zn2+ and ZnO adding to H2TCPP, the emission spectra showed an overlap of the peaks at ~607 nm after normalization (Figure 2b).

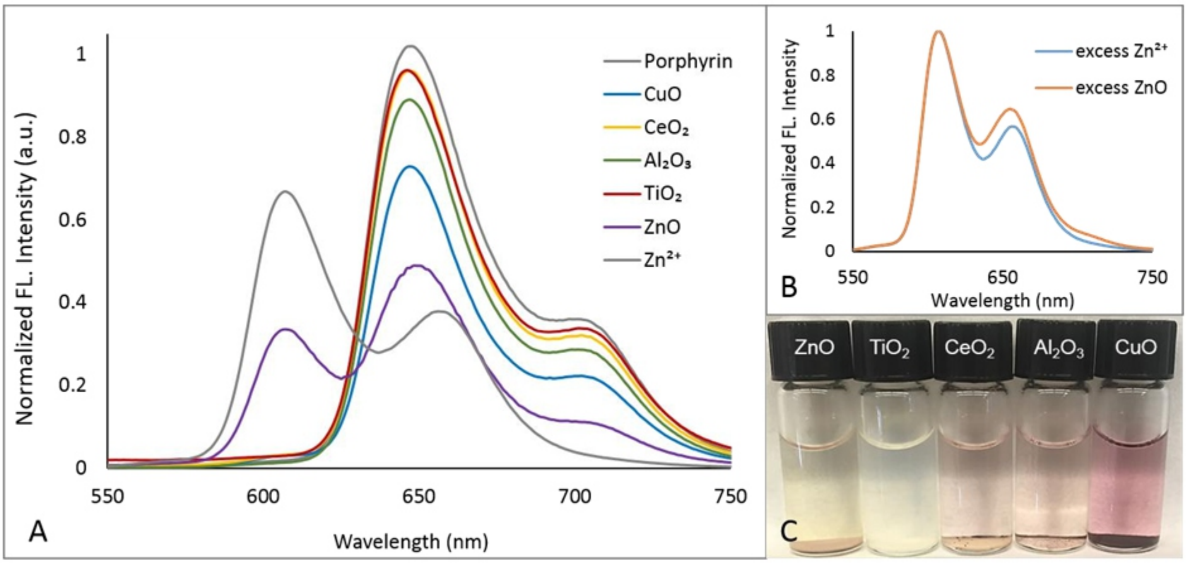

Figure 2. Fluorescence emission spectra using an excitation wavelength of 420 nm: (A) porphyrin and its quenching by Zn^{2+} and different metal oxide nanoparticles (CuO, CeO_2, Al_2O_3, TiO_2 and ZnO) at the same mass concentration of 1.5 mg/mL, and (B) porphyrin with excess Zn acetate and ZnO nanoparticles in PBS buffer. (C) Colour change of porphyrin in presence of different metal oxide nanoparticles.

3.3. Detection of ZnO by quenching effect

The fluorescence intensity of porphyrin decreased at a wavelength of ~650 nm (green arrow in Figure 3) as the concentration of ZnO quencher increased from 0.15 mg/mL to 1.5 mg/mL. The fluorescence intensity of porphyrin also decreased at ~710 nm (blue arrow) and finally diminished when the concentration of ZnO reached 1.35 mg/mL [19]. Meanwhile, the fluorescence intensity originating from the interaction between ZnO and porphyrin continued to increase the fluorescence intensity of a new peak at 605 nm (red arrow). Similar quenching of TCPP fluorescence and a slightly increasing peak at 605 nm had previously been reported by Jones et al. for Zn2+ produced from photoetching ZnO nanopowder solution under UV irradiation [22]. Most importantly, it is evident that the 605 nm peak increased its intensity faster than the fluorescence quenching of both the 650 and 710 nm peaks to offer enhanced detection sensitivity.

3.4. Calibration curve of Stern-Volmer plot

The calibration curve of fluorescence intensity and quencher concentration can be best expressed by the Stern-Volmer equation which usually gives a linear relationship [23]:

$$I_0/I = 1 + K_{sv}[Q] \tag{1}$$

where I_0 is the maximum fluorescence intensity in the absence of quencher, I is the maximum intensity when quencher is present, K_{sv} is the Stern-Volmer constant, and $[Q]$ is the concentration of quencher. The linear range of the Stern-Volmer plot is from 0.05–1.2 mg/mL with a K_{sv} value of 0.66 mL/mg. However, the Stern-Volmer plot of low concentration ZnO nanoparticles quenching porphyrin exhibits a high overall quenching effect trend, as the incubation time has significant influence to quenching effects, which will be explained in detail in next section (Figure 4).

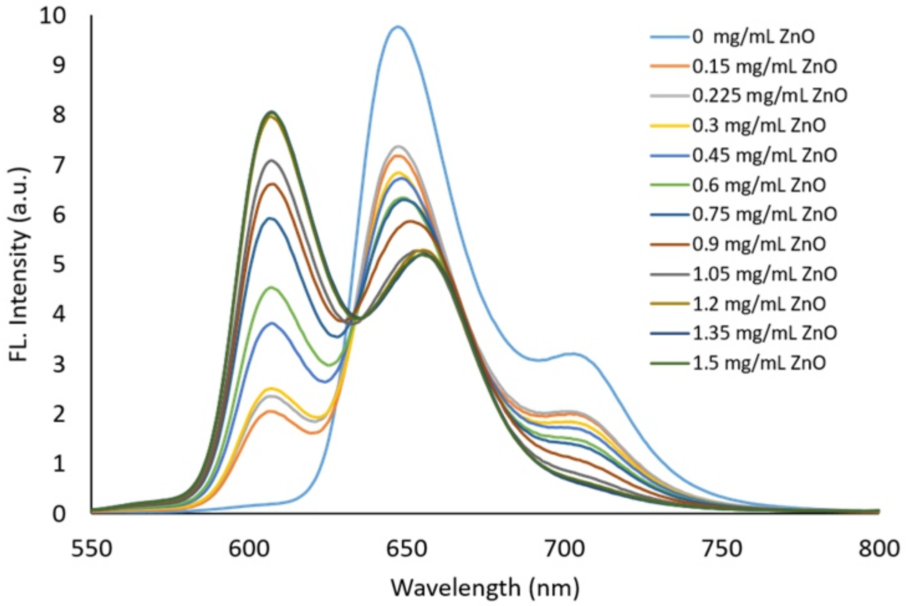

Figure 3. Fluorescence emission spectra of porphyrin (TCPP) with different concentrations of ZnO nanoparticles, using an excitation wavelength of 420 nm.

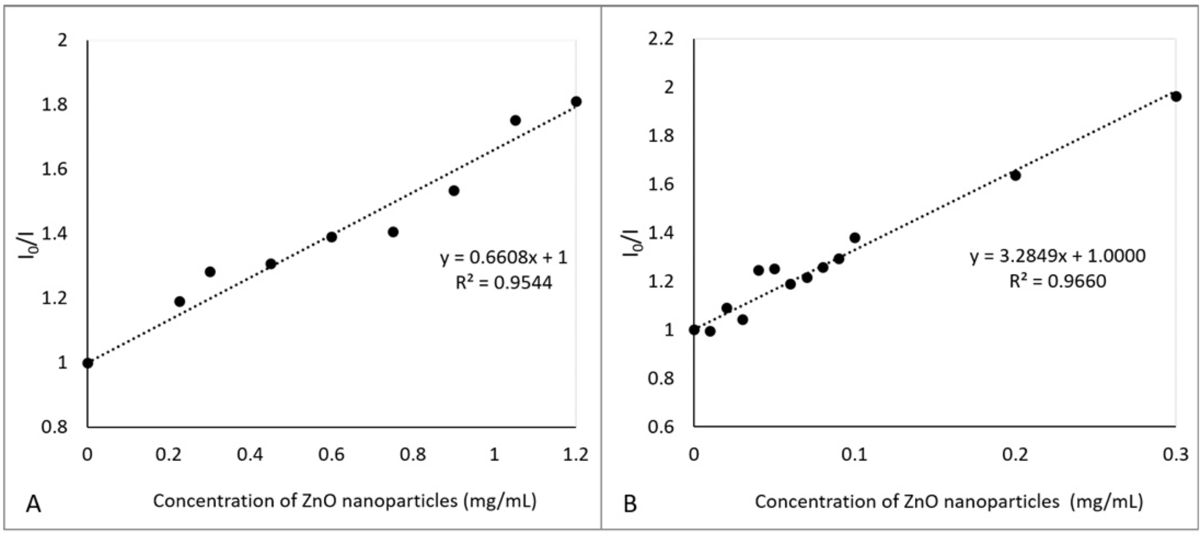

Figure 4. Stern-Volmer plot for porphyrin (TCPP) at (a) medium concentrations and (b) low concentration of ZnO nanoparticles, using excitation wavelength of 420 nm and maximum emission wavelength.

3.5. Time-dependent quenching

The kinetic rate of complex formation between TCPP and ZnO nanoparticles is relatively slow especially for low concentrations. Overnight reaction affords only a modest I0/I result after 1 day. However, the fluorescence intensity of TCPP decreases continuously with increasing reaction time especially at ZnO nanoparticle concentrations lower than 0.1 mg/mL, which results in an increase of the corresponding I0/I value (Figure 5). Therefore, the Stern-Volmer constant (Ksv) experiences a significant increase with reaction time and can be modelled in a second-order polynomial function with an R2 value greater than 0.99 (Figure 5b). A similar second-order polynomial relationship between Ksv and reaction time was reported in a previous work [24]. Although greater Ksv can provide a more sensitive calibration curve, the shortened linear dynamic range from 0.7 mg/mL to 0.1 mg/mL will not provide an accurate determination (Figure 5a) unless the unknown sample is diluted to repeat the fluorescence intensity measurement. The macrocycle strain effect of porphyrin structures on the complex formation rate with zinc was previously studied by Simonova et al. They optimized the molecular structure of porphyrin by the PM3 quantum-chemical method in order to obtain the best complex formation rate [25].

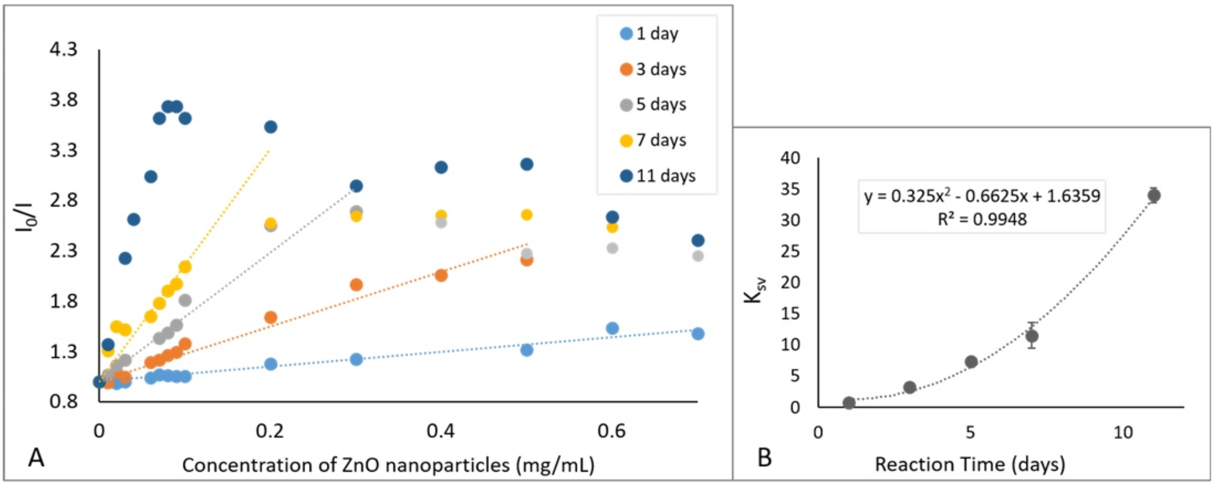

Figure 5. (a) Stern-Volmer plots on different days after mixing porphyrin (1 mg/mL) with different concentrations of ZnO nanoparticles (0.0 to 0.7 mg/mL); (b) Stern-Volmer constant (obtained from figure 5a) versus reaction time, using excitation wavelength of 420 nm and maximum emission wavelength.

3.6. Direct fluorescence emission from ZnO-TCPP

The unique peak at 605 nm from ZnO-TCPP complex was utilized for the quantitative analysis of ZnO nanoparticles by direct fluorescence emission (rather than quenching). A plot of maximum intensities at 605 nm versus different concentrations of ZnO nanoparticles displayed a linear regression fit (Figure 6). For 1 mg/mL porphyrin, the linear dynamic range is up to 1.2 mg/mL ZnO nanoparticles; the detection limit is 0.0015 mg/mL, where the unique peak at 605 nm is not distinguishable from the broad shoulder (based on the average blank signal + 3*standard deviation).

The limit of detection is at the scale of former reported detection method to ZnO nanoparticles and will be efficient to 1000-fold pre-concentrated environmental surface water, regarding that the reported hypothetical concentration is approximately 1 × 10−5 mg/mL [15,26]. This direct fluorescence measurement is more useful in unknown water analysis, as the appearance of a peak at 605 nm has very high selectivity and sensitivity in detection of ZnO nanoparticles.

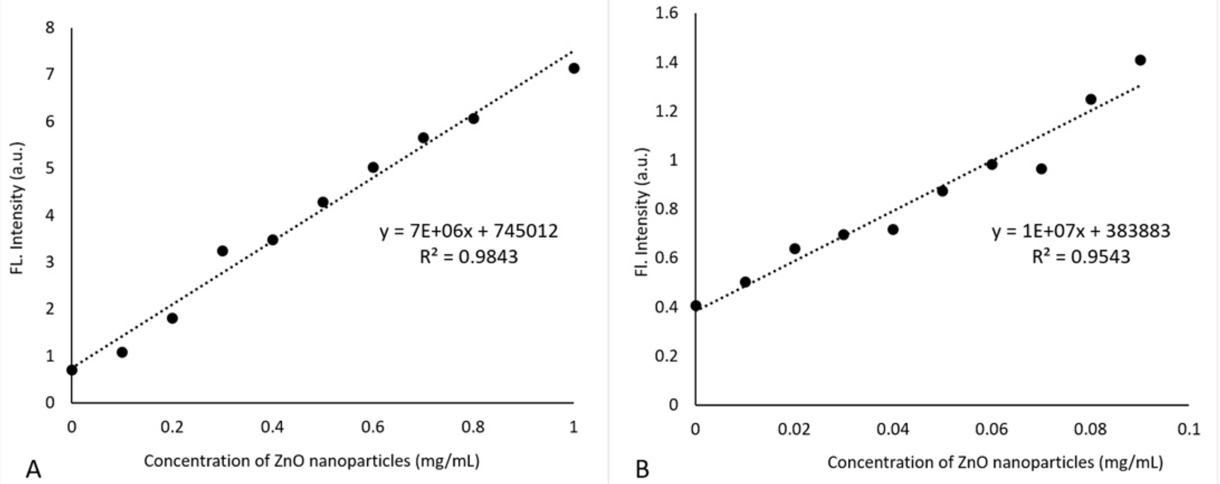

Figure 6. Fluorescence intensity of ZnO-TCPP complex at (a) medium concentrations and (b) low concentrations of ZnO nanoparticles, using excitation wavelength of 420 nm and maximum emission wavelength of 605 nm.

3.7. ZnO in mixture with TiO2 nanoparticles

To determine the interference of other metal oxide nanoparticles with porphyrin quenching by ZnO nanoparticles, two mixtures were prepared with and without ZnO nanoparticles. The color of porphyrin becomes pale yellow with the presence of ZnO in the mixture of metal oxide nanoparticles (Figure 7a), which indicates the presence of ZnO nanoparticles because ZnO is the only one can diminish porphyrin color among five metal oxides. The fluorescence emission spectra shows an obvious peak at 605 nm in ZnO sample comparing to that of no ZnO added sample which has a flat shoulder in the correspond area (Figure 7a). The interference test with serial concentration of TiO2, one of common used nanoparticles with relatively high affinity to porphyrin, shows no trend in neither the Stern-Volmer quenching plot nor the direct fluorescence method (Figure 7b). Overall, even in the presence of TiO2 nanoparticles, the unique emission peak at 605 nm can selectively determine the presence and concentration of ZnO nanoparticles.

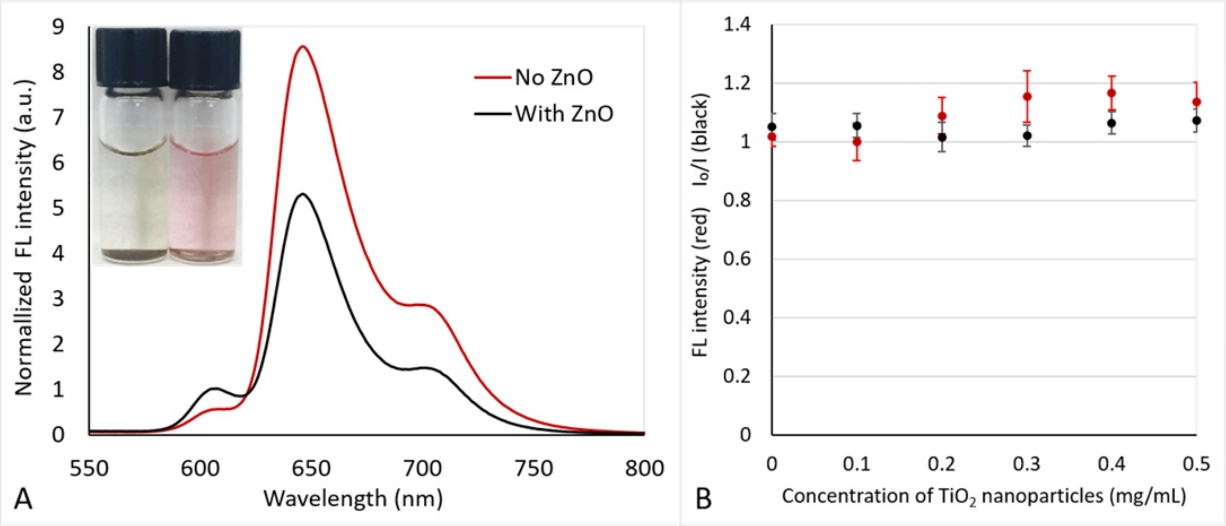

Figure 7. (a) Fluorescence emission spectra of porphyrin with a mixture of metal oxides in the presence and absence of ZnO nanoparticles. (b) Fluorescence intensity at 605 nm (red) and Stern-Volmer plot (black) of interference test with serial concentrations of TiO2 nanoparticles.

3.8. Effect of pH on direct fluorescence emission from ZnO-TCPP

In the case of ZnO nanoparticles, the predominant effect of pH is for dissolution and aggregation level of nano-structure. The dispersion of ZnO nanoparticles in water normally results pH 7.7, which is considered at a stable pH for ZnO with not much Zn2+ leaking from nanoparticles. Their solubility limit is close to pH ~8.2 but nearly complete dissolution occurs at pH 4.8–6.5 [27]. This pH dependency of ZnO nanoparticles dissolution can be utilized to differentiate them from Zn2+ in an unknown water sample. If the direct fluorescence emission intensity of ZnO-TCPP is first measured and then the sample pH is adjusted to 4.8 using acetic acid/sodium acetate buffer, the dissolution of ZnO nanoparticles will produce significant concentration of Zn2+ to enhance the emission intensity significantly at 605 nm. This intensity enhancement is directly proportional to the concentration, but inversely correlated with the size, of ZnO nanoparticles. Alternatively, centrifugation of the water sample can remove dissolved Zn2+ first. Then the pellet can be re-dissolved in the acetate buffer to produce Zn2+ which is useful to rapid quantification with TCPP.

4. Conclusion

We have developed an analytical method for determining the contamination of water by ZnO nanoparticles. The method is initially based on the quenching of fluorescence emission from porphyrin (TCPP) that acts as a fluorophore. ZnO nanoparticles have high quenching efficiency to generate a Stern-Volmer plot that provides sensitive detection at low concentrations (0.1 mg/mL). Interestingly, the quenching efficiency increases with time and temperature which can be optimized to further improve the detection limit in water contamination analysis. Unlike other metal oxide nanoparticles, ZnO nanoparticles produce a unique emission peak at 605 nm that is attributed to the formation of a ZnO-TCPP complex. This unique emission peak can be used for both identification and quantitation of

ZnO nanoparticles, without any significant interference by TiO2 nanoparticles. Other divalent metal oxide (CaO, MgO and SnO) nanoparticles can be studied in the future to evaluate their potential interference with the unique ZnO peak produced by the complexation of ZnO with TCPP.

Acknowledgment

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Conflict of interest

The authors declare there is no conflict of interest.

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Mineral resource active regions: The need for systems thinking in management

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ABSTRACT

Energy and mineral resource extraction has fuelled economic development in the modern world but has caused unprecedented environmental destruction. Economically viable to extract resources are not evenly distributed but found in a few regions of the world due to unique geologic characteristics. Inequity in distribution of resource benefits and environmental costs predispose regions to resource conflict and war. Traditional resource management has failed to address their complexity, with most models utilised lacking multi-disciplinary perspective. Understanding the complexity of these regions is a key prerequisite for their management to be effective and sustainable. Here, we investigate the potential of re-assessing mineral resource active regions from a systems perspective. Findings demonstrate that the application of systems thinking in resource management has the potential to deliver benefits to all stakeholders while maintaining ecological integrity. System tools offer an alternative to the reductionist end-of-pipe thinking of traditional resource management and policies. Rather than simply relying on competition, focusing on the interdependencies between the various players and sectors in these regions can deliver system improvements that should be further investigated because of their potential to deliver integrated and holistic solutions that could benefit all involved.

Keywords: *mineral active region; environment; complexity; traditional management; systems thinking*

1. Introduction

The natural environment is an emporium of resources; renewable and non-renewable [1]. Natural mineral resources are the lifeblood of modern civilization: the indisputable driver of unprecedented development and prosperity the world has experienced over the past century [2]. Their extraction has fuelled economic development, industrialisation, urbanisation and modern society as a whole [3]. Natural resources are broadly described as natural capital [4,5]; a term that captures those resources known to be repositories of goods and services (geodiversity and biodiversity) provided by nature. They function to preserve and stabilise natural environmental conditions, whilst provisioning resources and economic gains [6–8]. Profits from the exploitation of mineral resources by extracting companies are viewed as physical materials from a capitalist perspective [9]. Despite the inalienable right of all States freely to dispose of their natural wealth and resources in accordance with their national interests1, resource extraction has provided a rather difficult path to development for countries with abundant natural resources. Historically, these countries have struggled to maximize benefits to their economies. Economic exploitation of minerals and energy resources has been coupled to environmental and social consequences, that have not allowed the sustainable wealth and prosperity of the regions where the resources are extracted from. Studies have further attributed this to corruption, democratic failures, conflicts and resource wars [10–12], with natural resource rent-seeking associated to corruption, political instability and ultimately a slowing down of economic growth [13].

Stocks of mineral resources exist in reserves unevenly distributed in space and usually concentrated in localised geographical areas [14], with some regions more minerally active than others because of geological, spatial and temporal configuration. The variance in the geological distribution of resources, from regions of abundance to regions of scarcity, drives demand and supply relationships and constitutes the basis of international mineral and energy resource trade. These mineral resources are spatially complex [15] and could be ―point-source‖, ―fugacious‖ and/or ―diffuse‖. They cannot be fully described based on geographical location since they are associated with human systems of demand and control, channels, and networks. Point source resources such as oil, gas and solid minerals attract aggressive entrepreneurship [16]. The economic viability of their extraction depends on many factors including ore grade and type, mineral quality, as well as the engineering resources available for their extraction [17,18].

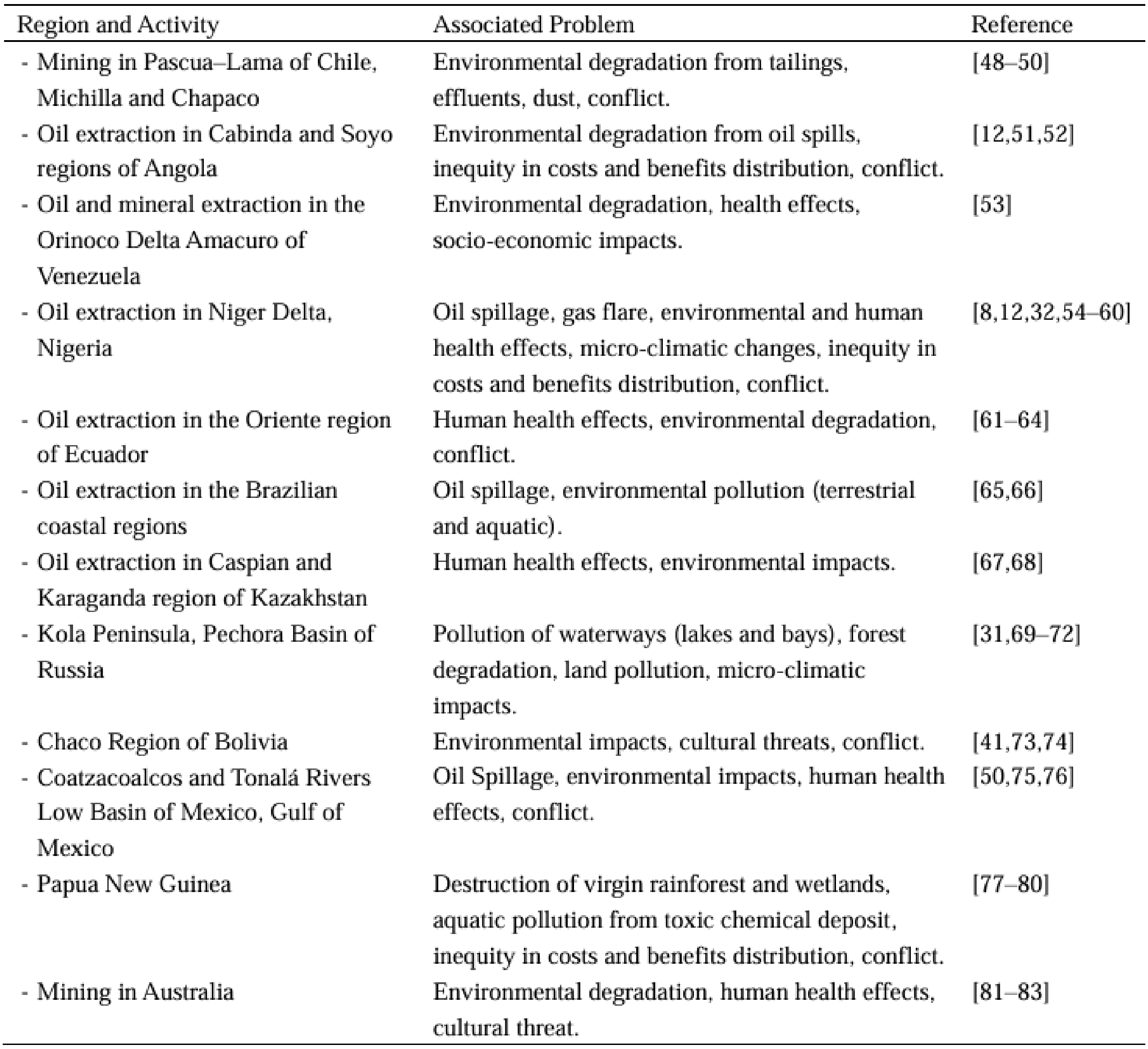
Although, there have been various definitions for rich ―resource regions‖ [18,21,22], Mineral Active Regions (MAR) here are considered those that have commercially extractable deposits of minerals or energy resources, often with historical production and on-going extractive activities, with reserves that can be used beyond their own needs. The value of the key functions of natural resources in relation to the value of resources exploited in the pursuit of economic prosperity determines the degree of exploitation, degradation, and destruction of natural capital [3,19,20]. Addressing the complexity of these regions, the paper investigates problems with their traditional management and raises the need for re-assessing these from a systems perspective.

2. Resource extraction dilemma

Mineral extraction has caused unprecedented impacts at different scales with detrimental effects on both humans and nature [2] and has been associated with a mixed legacy. Extraction activities come with significant environmental and human health effects [23,24], socio-cultural impacts [25–27] and ecosystem disruption and biodiversity losses in the areas where they take place [28–30], in addition to contributing to climate change [31,32]. Minerals, oil, and gas extracting regions experience similar socio-economic and environmental problems; with context-specific environmental problems also known to exist. For example; air pollution, toxic waste emissions, and acid rock drainage are prevalent in solid mineral extracting regions, while oil spills, drill cuttings/waste and gas flaring and venting are evident in regions where oil and gas extraction takes place. Uneven distribution of the benefits and environmental costs associated with the extractive activities is typical of these regions. Most frequently, national governments, investors, and shareholders share the benefits (in form of royalties, export earnings, taxes and rents), while local communities bare the environmental and social costs of the extraction of their mineral resources [2,33,34]. The capture of the resource wealth at the lowest cost possible, often through deliberate cases of negligence, is a serious threat to these regions. Key areas of suffering in these regions are power asymmetries and inequality [10,36], often a result of socio-political and economic exclusion, routed in vestiges of colonial-era laws and policy instruments complicit in the disempowerment of indigenous people [35]. Referred to as resource curse, this phenomenon has inspired a volume of theoretical and empirical research. Cases where resource export boom (oil as a typical case) prompt a rise in earnings leading to increased spending (public and private) causing the real exchange rate to appreciate so the non-traded sector becomes uncompetitive and consequently crowding out non-oil exports and ultimately slows down economic growth [10,37,38] are also captured by this theory. Boom-and-Bust cycles are typical of resource extraction economies, driven by profit and a tendency to thrive when demand is high, but followed by retraction as in the case of international mineral oil trade [13]. Sachs and Warner [39] have framed their argument of resource curse in relation to the crowding-out effect of entrepreneurial activity and innovation, with a rise in earnings from the natural resource sector which could stifle or disincentivise economic growth. Most researchers seem to agree with the resource curse phenomenon but often view it through different perspectives. Despite the variations in theories, the paradox is that natural resource wealth, key to economic growth and development based on conventional economic reasoning, has not delivered the benefits expected in most MARs.

The environmental impacts of extractive activities are significantly more distractive when taking place in ecologically sensitive mineral active regions. The failure to operationalise sustainability due to a lack of holistic accounting principles often with no environmental and social modifications leads to the depletion of resource stocks in these regions. The effects of extractive processes, aside from being cumulative, are characterised by high levels of technological, economic, geological and socio-cultural interactions, with associated uncertainties and ambiguities that increase the potential of often severe environmental and social impacts [40]. Oil and minerals have been contentious as point source and high-value commodities and their extraction is associated with significant loss of ecosystem services frequently at the expense of local people [41] who live in the periphery of the cash economy. Point-source resource economies often lack democratic and institutional development, which in turn hampers economic growth [36,42]. Generation of waste, environmental contamination, unequal distribution of benefits and costs, distortion of historical/cultural matrices and conflict plague these regions [41,43–45]. Systematic underinvestment in education, health care and infrastructure [46,47] is another characteristic of most MARs in the developing world. These characteristics drive resource decline and unsustainable growth with negative socio-economic and environmental consequences in most MARs. Examples of such regions with reference to these characteristics are presented in Table 1. They illustrate that resource extraction in these regions has been a challenge for communities, investors, policy makers and regulators, evoking the sustainability debate amongst stakeholders.

Table 1. Examples of mineral active regions and associated environmental, health and socio-economic impacts.



Region and Activity	Associated Problem	Reference
- Mining in Pascua–Lama of Chile, Michilla and Chapaco	Environmental degradation from tailings, effluents, dust, conflict.	[48–50]
- Oil extraction in Cabinda and Soyo regions of Angola	Environmental degradation from oil spills, inequity in costs and benefits distribution, conflict.	[12,51,52]
- Oil and mineral extraction in the Orinoco Delta Amacuro of Venezuela	Environmental degradation, health effects, socio-economic impacts.	[53]
- Oil extraction in Niger Delta, Nigeria	Oil spillage, gas flare, environmental and human health effects, micro-climatic changes, inequity in costs and benefits distribution, conflict.	[8,12,32,54–60]
- Oil extraction in the Oriente region of Ecuador	Human health effects, environmental degradation, conflict.	[61–64]
- Oil extraction in the Brazilian coastal regions	Oil spillage, environmental pollution (terrestrial and aquatic).	[65,66]
- Oil extraction in Caspian and Karaganda region of Kazakhstan	Human health effects, environmental impacts.	[67,68]
- Kola Peninsula, Pechora Basin of Russia	Pollution of waterways (lakes and bays), forest degradation, land pollution, micro-climatic impacts.	[31,69–72]
- Chaco Region of Bolivia	Environmental impacts, cultural threats, conflict.	[41,73,74]
- Coatzacoalcos and Tonalá Rivers Low Basin of Mexico, Gulf of Mexico	Oil Spillage, environmental impacts, human health effects, conflict.	[50,75,76]
- Papua New Guinea	Destruction of virgin rainforest and wetlands, aquatic pollution from toxic chemical deposit, inequity in costs and benefits distribution, conflict.	[77–80]
- Mining in Australia	Environmental degradation, human health effects, cultural threat.	[81–83]

3. Resource governance and management

Natural resources and the environment exist in a complex socio-ecological structure [84] driven by interactions between nature, technology and people. High levels of technological, economic and geological complexity characterise mineral extraction and influence intertemporal decisions [85] that cut across scales (spatial-temporal) and sectors (environment, social and economic). These intertemporal and sectorial interactions evolve to enhance the benefits derived from extractive activities or increase associated costs and environmental pressures. Historically, mineral resources management has been complex, with mineral extraction paradoxically a double-edged activity framed around economic development and environmental protection. Historical episodes of mineral extraction reveal inherent linkages and organic connections between extractive activities and society, one that holds economic potential that can sever a society from the constraints of nature [2].

Acheson [86] demonstrated three possible governance structures in resource management; provided by private property, government and community management. He argued that there is no cure-all solution to resource management; that is, while each of the groups can succeed, they can also fail depending on prevailing circumstances. Tarui [87] presented institutional management arrangements that include state property, private property, common property and open access resources management. He furthered his concept arguing that any of the institutional controls that predominate depend on the need and scarcity of the resource. This is based on the assumption that mineral resources are the driver of most economies, especially in developing countries [30], with most developed ones owning their advances to the exploitation of such resources in the past [2,88]. From Tarui‘s argument [87], the aim of resource exploitation is to meet states‘ economic needs. Examples of such states controlling mineral resources are oil and natural gas in Nigeria; oil, natural gas and diamonds in Angola; oil and natural gas in Brazil; oil, natural gas, gold and diamonds in Russia; diamonds, copper, nickel, and gold in Botswana.

Mining operations function within the formal and informal institutional frameworks of the country which hosts the mining project, and therefore inevitably acquire a political dimension, as well as strong links to its economy, ecosystem, and local communities. These communities unavoidably often come to depend on minerals production for employment, income, and broader development [89]. Resource extraction is multifaceted and has political, social and economic implications [90]. Natural resources shape and are shaped by political context, with numerous examples from mineral-rich countries demonstrating this across the world. This includes the _making and unmaking‘ of laws and policies governing resource ownership and extraction. Examples include cases from Angola [52], Bolivia [41], Ecuador [73], Nigeria [54,91], where policies have been designed to disenfranchise land owners of property rights to subsurface resources [92] through nationalisation and appropriation of natural resource wealth. Despite not being an exclusive reserve of national governments, resources management has been under their purview, creating revenue for national economies through taxes and resource rents [67,93,94]. The role of governments in resource exploitation and management has engendered counter posing challenges, with government often locked in opposing and conflicting interests; as agents of economic development and custodians of the environment [95,96].

Mineral resource active regions attract multiple players with diverse interests; including international investors, government agencies and local communities [90,97] resulting in multiscale and diverse interactions that are complex and often become problematic. Studies have been conducted at different scales: national, community and site levels to investigate the many problems MARs face and to evaluate traditional management approaches. However, studies at the regional scale, looking at interactions in a more holistic way are comparatively limited. Finer and co-workers [64] advocate that studies at regional level provide an avenue for proper delineation and for resource extraction to be coupled to other systemic impacts including characterization of extracting regions. This is supported by Solomon [9], who argues that regional studies can improve governance structures while engendering sustainable development. Indeed, sustainable development is better addressed at this level, as defined with context to the eco-regional scale [98]. Traditional management approaches place emphasis on economic rationality and environmental impact mitigation measures that are ad hoc, monodisciplinary and neither integrated nor holistic, thus the primary cause for the prevailing environmental problems we are left to deal with today. Robust management must take cognisance of the uncertainties and ambiguities not considered under traditional economic thinking. Coria and Sterner [99] have argued that environmental sustainability and economic prosperity present a scenario that is only comprehensible from a multifactorial perspective whilst acknowledging that resource development and environmental stewardship are not mutually exclusive. The ecological decline coupled with the socio-economic and political exclusion of communities in MARs demonstrate that traditional environmental and resource management approaches have failed to favour policy regimes that balance environmental and social components as non-mutually exclusive components of development. These shortcomings have prompted the development of unconventional approaches with the objective of ensuring sustainable resource extraction and maintenance of environmental quality. This has operated under different nomenclatures, although with the same core objective prompting research from both the academia and public sector to embrace the Ecosystem Approach (EA) for natural resource and environmental management. The report of the Millennium Ecosystem Assessment [19] has been instrumental in broadening knowledge and improving policymaking, however, emphasis on natural resource management has been on biodiversity in contrast to geodiversity. This position may have prompted Frank and co-workers [100] to argue that terrestrial minerals are part of the ecosystem of which their extraction brings disturbance to the natural environment compared to other ecosystem resources such as fisheries or timber. Integrated Resource Management (IRM) has evolved with aspects on social, economic, technical and institutional programs to ensure a robust resource management outcome; however, Bellamy and colleagues [101] argue that fragmentation and lack of a multi-disciplinary view alongside a high dependence on engineering, biophysical and economic standards tend to limit its application.

The need to manage the balance between mineral exploitation and environmental protection has led to the formulation of management tools (legal or regulatory standards and fiscal regimes) to ensure a sustainable extractive regime at MARs. This approach has its limitations [67] as regulatory standards are often about the need of management systems rather than requirements that characterise the system per se [102]. Cumulative socio-environmental and economic impacts of extraction and associated uncertainties are a real challenge to institutions of government and have drawn concerns across mineral dependent economies [9]. The absence of a sustainable solution as documented in most MARs is clear evidence that the problem has neither been understood by resource managers and policy makers nor have the right tools been deployed to understand and manage MARs from a systems perspective. A lack of an appropriate holistic framework to manage resources, enable the delivery of desired benefits, minimise ecological decay, trade-offs and cost borne by host communities, is often observed in MARs with traditional resources management. Depleting natural resources coupled with environmental degradation caused by extractive activities in many of these areas demonstrate the need for a change from current management practices and policies towards an integrated, holistic and purpose-driven approach that reduces environmental impacts and delivers resilience and sustainability. Features of traditional and systems-based perspectives are compared in Table 2. Understanding the characteristics of the MAR system could create foundational knowledge that could change interactions and create conditions that support a more sustainable system state.

4. Discussion

Mineral resource extraction stimulates multiscale interactions between numerous stakeholders, and is a source of economic gains and opportunities, as well as environmental and social impacts that evolve over time [103]. Natural resource management is characteristically complex and therefore a constraint to sustainable development [104]. Resource-environment-economy interactions in MARs are characterised by uncertainty and cognitive limitations that create complex incentives for policy.

Table 2. Traditional management approaches compared to systems-based thinking in resources management.

Traditional approach	Systems thinking approach
- Emphasis on conventional economic rationality	- Based on sustainability and seek sustainable - way out to persistent problems
- Rent-based	- Interest-based
- Sectoral, reductionist and lack of multi-disciplinary view	- Integrated, holistic and use of multiple perspectives
- High dependence on engineering and biophysical standards	- Understanding roots problems though soft approaches, and based on client perspective
- Emphasis on regulatory standards	- Emphasis on management systems
- Exclusion, top-down and end-of the-pipe modus operandi	- Integration, inclusion, collaboration, bottom-up and advocates win-win solutions
- Confounded by complexity	- Understand and manages complexity by thinking broadly to see interactions
- Focused on managing resources and meeting policy target	- Manage resource by managing people and their interactions resulting in learning outcomes
- Technical and expert knowledge-driven	- Stakeholder-driven and based on participatory approaches
- Results in depletion of natural resource and environmental degradation	- Aims to ensure resilience and sustainability of natural resources and environmental protection

Moreover, ecological and geological interactions mediated by humans in the quest for mineral exploitation have created complex environmental, resource and sustainability problems that are chronic and defy traditional thinking. For example, environmental, economic and social impacts of extraction have multiple and generational effects on both spatial and temporal scales [18]. Therefore, there is a clear need to harness and operationalise complexity, instead of ignoring it. When properly considered, complexity can be an opportunity rather than a threat [105]. The emergent environmental and socio-economic characteristics of MARs occasioned by mineral extraction coupled with the traditional sectoral and monodisciplinary management approaches create a complex situation because of the narrow focus on economic rationality that does not allow understanding of long-term and integrated systems management approaches. Addressing this complexity, there is an overarching need for retrospective understanding, scenario analyses and futures thinking as to understand the complex nature of interactions that exists in MARs, before any solutions are derived to manage natural resources. A conceptual diagram of the environment-social-economic nexus that exists in mineral active regions is presented in Figure 1. Addressing resource management challenges requires an understanding of the complexity of MARs by looking at the interactions and relationships between all system parts and redefining these challenges by looking at environmental and socio-economic problems as products of the interactions around the mineral extraction activity. The diagram illustrates mineral active regions as a system where interactions between its environmental, social, and economic components determine the impacts associated with the natural resources extraction.

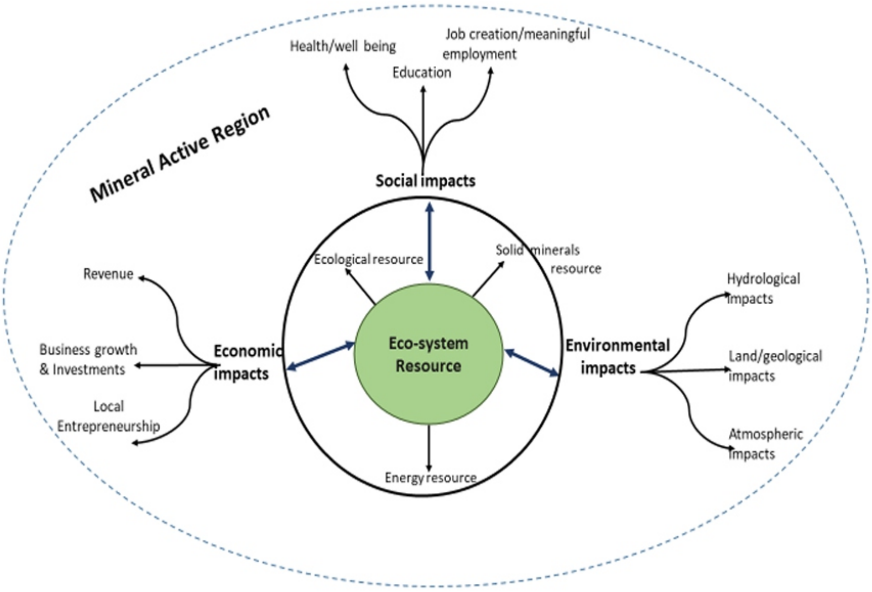


Figure 1. A preliminary conceptual model for system interactions in a MAR.

A holistic way to understand resource constructs is by its function and relationship [9]. This view sheds light upon an organic connection between humans, the environment, the economy and natural resources. Problems associated with resource extraction cannot be attributed to the latent subsoil assets but the conditions and configuration of interests developed around their exploitation [106]. One of the prevailing problems in traditional resources management is the lack of holistic integration of the economic activity with environmental, social, political and administrative issues, necessary for an effective governance regime [25,107]. Solving environmental problems associated with resource extraction lies in understanding their root causes, reaching optimal policies and engaging technical solutions [108]. For example, problem structuring methods that are participatory allow for understanding of the causes of problems [109] more effectively than the top-down or black box techniques that have been traditionally used. Managing natural resources is about managing people rather than the resource [110]. Inability to account for micro-level decision making in designing policies may result in a policy-resistant scenario where the system‘s response to policy implementation defeats the design purpose. Observed in many MARs are complex yet non-inclusive resource management structures that tend to create misperceptions and misrepresentations of most stakeholders involved. Perceptions of extractive companies predispose them to suffer from the lack of trust from local communities, a reaction often to their inability to influence issues concerning their future [111,112]. This leads to blame trading amongst the international extracting companies, local communities and the government, that often results in conflict with reputational liabilities [92]. Some scholars however consider conflict an integral part of the resource extraction regime [112]. Bebbington [74] explored this view by arguing that conflict can bring change that will enhance performance and that improved performance might deflate conflict. The theory offers a paradoxical interpretation, that raises the question: why should it take conflict to advance environmental policies as part of a management approach? Conflict-driven change is tenable when a result of learning process that could lead to improved performance, but at what cost? Often it sets in motion a chain of counterintuitive perspectives, in a state of physical and moral warfare with reputational and economic consequences for all involved.

Management must therefore be inclusive and consider all interests configured around resource systems by incorporating stakeholders‘ perception into the decision making. Management that is not holistic in problem conceptualisation and participatory in solution design can result in unexpected environmental and social impacts [40]. For example, after extensive research in the Niger Delta region of Nigeria; Jike [113] demonstrated that resource extraction patterns when left uncontrolled can lead to irreversible changes to regional ecosystems by affecting both the natural and socio-economic environment. Most of the studies conducted (for example in the Niger Delta, Nigeria) are sectoral and reflect discipline bias, either looking at environmental contamination and ecosystem effects arising from extractive activities [56,114], biophysical effects [59,115] or socio-economic dimensions [67,116,117]. Environmental issues should be considered an administrative predicament that must be holistically understood and not the reductionist and discipline-oriented approach that is ineffective and incomprehensive at managing resource and environmental complexities [3]. Environmental quality and natural resource management are inseparable factors that should be dealt with in an integrative system without setting arbitrary socio-economic or political boundaries. Resource development and environmental stewardship are not mutually exclusive as they can be simultaneously coupled with responsible resource management, underpinned on robust policy and effective regulation and can be undertaken to bring a maximum economic contribution and improved social condition with minimal environmental damage [27]. This can be achieved if resource regimes shift from reductionist rent-based to a holistic interest-based approach that is focused on ecological integrity, sustainable mineral extraction, community rights and redistributive equity. The need for systems thinking in understanding and managing complexity in MARs is a clear prerequisite for this.

Systems thinking offers an important cross-sectoral, interdisciplinary and diagnostic alternative for understanding interactions by improving communication and providing information on the vulnerabilities and resilience of MARs. Its application in resources management can avoid policy resistance and system collapse. It addresses the need to understand interdependences in mineral resource systems and how they can be leveraged to deliver win-win solutions for both the environment and society. Traditionally, developing environmental management plans has been the domain of highly trained experts, however, the mechanistic and non-deliberative nature of this approach has been associated to several failures and counterintuitive outcomes. Moreover, conventional policy regimes that evolved from technical domains to address environmental and natural resource problems can be deterministic, mechanistic and not adaptive to address multiscalar and cross-sectorial problems confronting this generation [118]. They involve management approaches that are focused on quantifiable and measurable impacts [18] without consideration of system relationships and interactions that reflect technical and soft principles underpinned by stakeholder constructs and interests. Systems thinking is purposed to advance environmental decisions that are robust [20] since it is conceptual and contextual and involves thinking, collection of data from clients, integration of stakeholders‘ mental models and communication. Consequently, this approach can reduce the opacity that expert or technical driven approaches present.

Systems thinking and system dynamics are central to tackling complex problems and have been widely applied to different fields including medicine and public health [119,120]; natural environment [121,122]; farming systems and agriculture [123]; and sustainability of renewable energy [124]. Mineral active regions are inherently complex, and therefore evidence-based knowledge is required for their management to deliver effective and result oriented outcomes. There are benefits for using a soft systems approach [107,125,126], that despite being principally qualitative, allows for quantitative data to be explored to gain an understanding of the system behaviour. This approach also allows unquantifiable or soft variables that influence environmental and resource decisions to be objectively captured [20]. It needs to be participatory and allow for creative problem structuring and embedding of stakeholder interest [127] by raising awareness of the consequences and benefits of system interactions. Achieved through mediated or group model building, it involves the use of mental models, conceptual models, situation mapping and rich pictures to scope and elicit information, build consensuses, deconstruct complexity and, consequently, enable participants to see things for what they are. Acknowledging that perceptions and understanding of things differ between stakeholders, systems thinking through transdisciplinary participation can enable collective representation and integration of different perspectives so as to improve overall understanding of the system. The path to sustainability for the mineral active region is through shared knowledge [128].

Environmental problems bordering resource extraction permeate every discipline and sector; and for that transdisciplinary approaches which are broadly based and holistic take preference to discipline-based and reductionist methods. The process builds on a conceptual model for a MAR, with defined system components (type of natural capital, natural resource accounting mechanism and principles, management institutions, environmental quality, biodiversity and ecosystems, geotechnical features, geopolitical condition, local and regional economy, socio-cultural features, human health effects) subsumed in the environmental, economic, social, and institutional sustainability tetrad (Figure 2). The main purpose of this representation of a MAR system is not to analyse the interactions but to facilitate the process of understanding the systems components of a MAR and explore the interactions that directly or indirectly drive sustainability problems.

The application of systems thinking in the management of MARs should therefore be further investigated because of its potential to deliver integrated and holistic solutions that could benefit all involved while maintaining ecological integrity. Investigating the systemic effects of mineral extraction in MARs; their contribution to the economic liberation of nations, attendant environmental and social impacts as well as the effect on the geopolitical landscapes of countries with natural resource assets, offer ways to address the complexity of these regions. Mineral extraction draws divergent interests and affects stakeholders differently in terms of cost and benefits distribution, while studies have shown that extractive industries‘ successes can be ensured when corporate interest aligns to regional and community interests and values. The awareness of the interdependences between the various players and sectors allows for the type of collaboration that could lead to a sustainable extractive regime [33]. This also requires taking down barriers such as weak laws and bad resource governance regimes, leaving behind reductionist, monodisciplinary and rent-based rationalities.

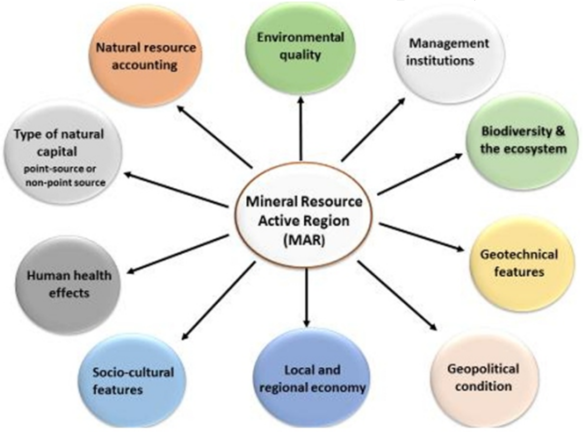


Figure 2. The conceptual systems representation of the components of a MAR.

5. Conclusion

System thinking in the management of MARs has the potential to deliver benefits through the understanding of the links between system components, their interactions, and interdependencies. Using conceptual models of the relationships and interactions that characterise MARs, and through a multidisciplinary approach, system tools can empower stakeholders enabling them to see these interactions and interdependencies. Critical gaps and barriers that undermine efforts to sustainable resource extraction and management become visible, allowing for more collaborative and participatory management. Accounting for spatial-temporal and sectorial issues, such participatory approaches involve gathering historical and contemporary views on MARs, creating a collective representation based on the integration of different perspectives. Systems tools treat mineral active regions as integrated catchments, complex systems open but with spatial and temporal boundaries. This does not mean that systems-based methodologies can provide an all-encompassing solution, instead, they enable stakeholders to redefine the problems they face and even make the need for management solutions obsolete.

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Conflict of interest

All authors declare no conflicts of interest in this paper.

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Combining electrochemistry and UV for the simultaneous wastewater decolorization and reduction of salinity

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ABSTRACT

Textile dyeing processes with reactive dyes consume high amount of water and generate wastewater containing residual dyes and salts. In this work, wastewater generated by a textile industry was treated by means of electrochemical techniques combined with ultraviolet irradiation. Five industrial wastewaters were collected in a textile mill and were treated at 10 A in an electrochemical cell. Full color removal was obtained after 10 minutes of treatment. The optimization of the electrochemical treatment was performed in order to select the most suitable conditions. Subsequently the decolorized effluents, which still contain salts, were irradiated with UV light to remove residual oxidants and were reconstituted for its reuse. This procedure enabled to reuse 70% water and 64% salt in the dyeing process. The chromatic coordinates of these dyed samples were evaluated with respect to reference ones. In all cases, samples dyed with the reused effluents showed colour differences into acceptance limit of the textile industry (DECMC(2:1) values lower than 1).

Keywords: *industrial textile wastewater; reactive dye effluents; effluent reuse; salt reuse; dyeing process; electrochemical treatment; UV irradiation*

1. Introduction

In 2030, industrial water consumption is expected to account for 22% of global water demand [1]. The water shortage and poor water quality in some industrial regions have caused the creation of new environmental policies focused on recycling and reuse of water [2].

Textile industry is one of the largest consumers of water due especially to their finishing processes such as dyeing and subsequent washing steps. High water consumption in textile industry has led to the treatment and reuse of its wastewater [2]. In addition to the presence residual dyes, textile wastewater is characterized by high organic and inorganic matters, turbidity, pH and in some cases, content of toxic chemicals [3].

Nowadays, biological [4–6] and physical-chemical processes [7,8] are used to remove dyes from textile wastewater. However, none of them enables water reuse in textile processes. On the other hand, advanced oxidation processes such as photo-Fenton [9] and photocatalytic [10] have been also studied. Although these methods provided high color removal, the treatment cost is their main limitation.

Electrochemical processes have also been tested to remove dyes from textile effluents. The process occurs via two pathways: direct anodic oxidation or indirect oxidation. In the direct oxidation, the electrolysis takes place directly on the anode whereas the base of the indirect oxidation is the electrogeneration in situ of the oxidant species that can degrade the pollutants [11]. The main advantage of the electrochemical treatment is that the electron is the only reagent required for the degradation of the pollutants.

Reactive dyes are the most consumed dyes in the textile industry. These dyes have high washing fastness as they react chemically with the fiber. However, part of reactive dyes can also react with water, generating the hydrolyzed form of the dye that cannot react with the fiber. Then, the hydrolyzed dyes are discharged with the wastewater [12]. To increase the affinity of the dye with the fiber, high amount of salt is added in the dyeing process. Between 0.6 and 0.8 kg of salt/kg of fiber is required, depending on the dye structure, shade and dyeing method [13]. As a result, the wastewater generated in the dyeing process with reactive dyes is characterized by high salt content. This represents an important disadvantage since there is no treatment that enables to destroy the salts. Currently, the treatments used for the removal of salts are based on obtaining a concentrate that must be subsequently removed as a waste. Therefore, wastewater from reactive dyeing process is suitable to be treated by means of electrochemical treatment. No chemicals should be added, as the treatment uses the salts already present in the effluent to generate the oxidant species [14] which destroy the chromophore groups of the dyes, according to the following reactions [15]:

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \tag{1}$$

$$Cl_{2(aq)} + H_2O \rightarrow ClO^- + Cl^- + 2H^+ \tag{2}$$

$$\text{Dye} + ClO^- \rightarrow \text{dye fragments} \tag{3}$$

According to the reaction (2), the chloride ion is obtained again at the end of the process and can be oxidized to reinitiate a new process. Some residual oxidants can remain in solution after the oxidation of dyes. The UV irradiation is applied to achieve its removal, providing a saline solution able to be reused in new dyeing processes.

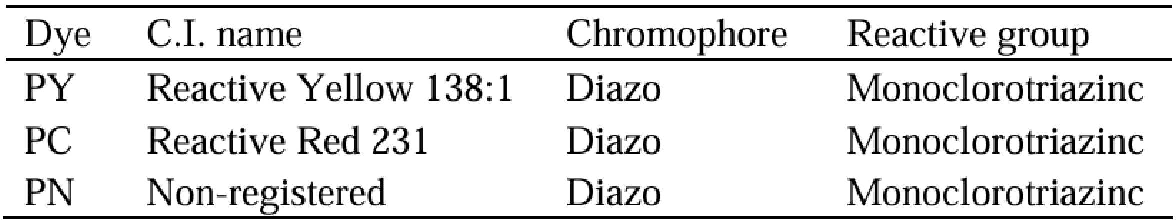
Taking these considerations into account, the aim of this work is to study the feasibility of the electrochemical techniques combined with UV to treat industrial effluents from the dyeing process with reactive dyes. Once the effluents have been decolorized by electrochemical treatment, are reused in new cotton dyeings. Finally, fabrics dyed with the reused effluent are evaluated with respect to references carried out with softened tap water.

2. Experimental

2.1. Reagents

Three reactive dyes (DyeStar) were selected for the study of effluent reuse: Procion Yellow H-EXL (PY), Procion Crimson H-EXL (PC) and Procion Navy H-EXL (PN). Table 1 shows the description of the dyes used in this study [12]. Sodium carbonate (Sigma-Aldrich) and sodium chloride (Scharlab) were used in the dyeing procedure. Finally, before the dyeing process, pH of treated effluents was adjusted with solutions of NaOH and Hcl.

Table 1. Description of the dyes used in this study.



Dye	C.I. name	Chromophore	Reactive group
PY	Reactive Yellow 138:1	Diazo	Monoclorotriazinc
PC	Reactive Red 231	Diazo	Monoclorotriazinc
PN	Non-registered	Diazo	Monoclorotriazinc

2.2. Wastewater

Five industrial effluents supplied by a textile mill were selected to be treated. They were collected from the jet dyeing process.

2.3. Electrochemical treatment assisted by UV

The effluents (0.5 L for each experiment) were treated in an undividable electrolytic cell. In all cases, the intensity was set at 10 A. The electrodes were made of Ti/PtOx, with 44.8 cm2 of active surface. The UV radiation was performed with a Philips TUV lamp PL-S UV-C at 254 nm and 9 watts.

2.4. Effluent reuse

Before reusing the treated effluent, a reconstitution step must be performed. The effluent reconstitution is carried out in the following steps:

Carbonates and bicarbonates are removed by acid addition and stripping.
Neutralization of the effluent by alkali addition.
Residual oxidants removal with UV irradiation.

Once the bath is reconstituted, the concentration of chloride ion should be quantified in order to determine to amount to be added in the reuse dyeing process.

The reuse dyeing tests were performed in a laboratory Ti-Color dyeing machine (Integrated Color Line) under the following conditions: 10 g of cotton fabric, dye concentration 3% o.w.f (over weight of fiber), liquor ratio 1:10 (1 g fiber/10 mL dye bath), 80 g·L−1 of NaCl and 16 g·L−1 of Na2CO3. The dyeing method is shown in Figure 1.

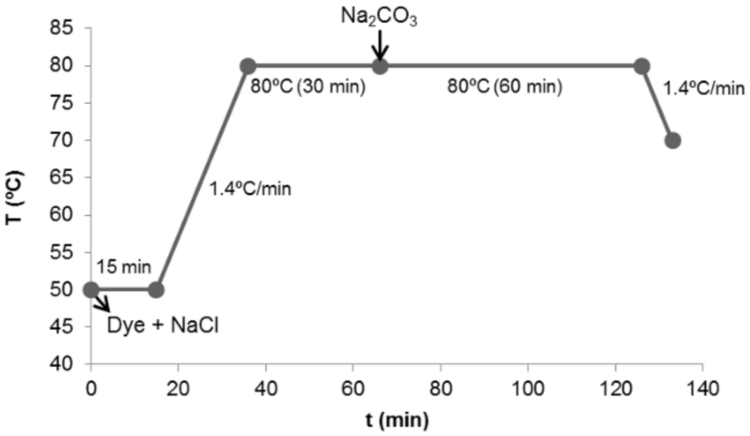


Figure 1. Dyeing method.

After the dyeing process, a washing process in nine steps was carried out:

1st–3rd: Cleaning with softened tap water at 50 ºC during 10 min.
4th: Soap cleaning with 2 g/L of COTEMOLL TLTR at 95 ºC during 15 min.
5th: Cleaning with softened tap water.
6th: Soap cleaning
7th–9th: Cleaning with softened tap water.

All the experiments were performed at liquor ratio 1:10.

2.5. Analytical methods and measurements

COD was determined according to the methods recommended by American Public Health Association [16]. The COD removal was calculated using the following equation:

$$COD\ removal\ (\%) = \frac{(COD_0 - COD_f)}{COD_0} \cdot 100$$

where COD_0 is the value before the electrochemical treatment and COD_f is the value after the electrochemical treatment.

The conductivity and pH were determined using a Conductimeter GLP 31 (CRISON) and a pHmeter GLP 21 (CRISON) respectively [16].

Color removal was calculated from the initial absorbance (A_0) and the absorbance at the end of the treatment (A_f) using the following equation:

$$Colour\ removal\ (\%) = \frac{(A_0 - A_f)}{A_0} \cdot 100$$

Absorbance was determined with a UV–visible spectrophotometer (UV-2401, Shimadzu Corporation) at the maximum wavelength of the sample visible spectrum.

The determination of Cl^- was carried out with Ion Chromatography ISC-1000 (Dionex) [16].

Finally, the quality of dyed fabrics was determined in conformity with the Standard UNE-EN ISO 105-J03 [17]. Total color differences ($DE_{CMC(l:c)}$) were calculated from lightness (DL^*), chroma (DC^*) and Hue (DH^*) using the following equation:

$$DE_{CMC(l:c)} = [(DL^*/lS_L)^2 + (DC^*_{ab}/cS_c)^2 + (DH^*_{ab}/S_H)^2]^{1/2}$$

For the measurements, a Macbeth Color Eye 7000A spectrophotometer was used. They were performed with the standard illuminant D65/10°. In general, a dyeing is considered into the acceptance range when the $DE_{CMC(l:c)}$ value with respect to a reference sample is lower than 1.

3. Results and discussion

3.1. Wastewater characterization

Before the electrochemical treatment, the effluents were characterized. The characteristics of each effluent are shown in Table 2.

Table 2. Characterization of samples of effluents collected from Jet process.

Initial Effluent	COD ($mg \cdot L^{-1}$)	Conductivity (mS/cm)	pH	Cl^{-} ($mg \cdot L^{-1}$)	λ_{max}
A	3518.9	57.5	10.9	24203.7	543.5
B	1515.4	83.1	10.6	66223.2	588.5
C	1099.0	88.3	10.7	39049.9	511.0
D	2450.5	129.0	10.5	69064.6	427.0
E	1811.0	124.1	10.7	65952.2	519.0

As can be observed in Table 2, the effluents from Jet dyeing process presented alkaline pH and high conductivity. In addition, the concentrations of Cl− are between 24 and 70 g·L−1, that represents a concentration up to 115 g/L of NaCl.

3.2. Electrochemical treatment

The efficiency of the electrochemical technique applied to treat textile effluents from Jet dyeing processes was determined by characterizing of treated effluent (Table 3).

Table 3. Characterization of effluents from Jet process after 10 min of electrochemical treatment.

Treated Effluent	Conductivity (mS/cm)	pH	COD removal (%)	Color removal (%)
A	63.0	10.6	11.9	100
B	77.7	10.2	0.0	100
C	87.1	10.7	0.0	100
D	128.1	10.7	51.4	100
E	120.6	11.2	8.3	100

In all cases, the effluents were totally discolored after 10 min. of electrochemical treatment (Figure 2).

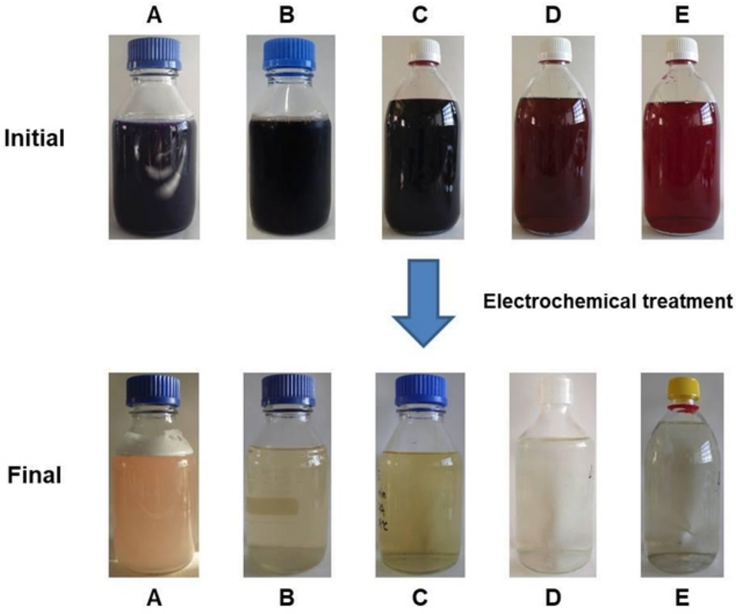


Figure 2. Electrochemical discoloration of textile effluents.

Regarding COD values, the reduction of organic matter did not follow a clear trend, as COD removal rates up to 51% were obtained. A full mineralization could be achieved with a longer treatment time [18]. However, other methods, such as biological treatments, are more efficient for this purpose. The electrochemical treatment is able to break down the poorly biodegradable organic molecules such as dyes into dye fragments, improving the biodegradability of the effluents [19].

Consequently, a full mineralization of the effluents could be achieved with a combination of electrochemical processes with conventional biological treatments.

At the end of the treatment, pH and conductivity values remained very similar to the initial ones. In some cases, these values are almost constant which evidences that the electrochemical treatment has little influence on them.

The concentration of residual oxidants at the end of the treatment is a key factor when the electrochemical treatment is carried out for reuse since they must be removed before reusing the treated effluent. Consequently, the treatment should be carried out at intensity high enough to achieve a good discoloration, but as lower as possible in order to avoid the generation of residual oxidants.

The optimization of the residual oxidants at the end of the treatment was carried out with the effluent C. It was treated at 2 A and 10 A, and the residual oxidants were determined in both cases. Results are presented in Table 4.

Table 4. Results obtained in the treatment of effluent C at different values of intensity and time of treatment.

Intensity (A)	Treatment time (min)	Color removal (%)	Residual oxidants ($mg \cdot L^{-1}$)
2	30	93	0
2	60	97	2
10	10	100	2000

As it was expected, decreasing the intensity resulted in increasing the time required to decolorize the effluent. However, the concentration of residual oxidants was also significantly reduced. On the other hand, the two trials at 2 A evidence that the first 30 minutes of treatment provided very high discoloration rate (93%) whereas in the last 30 minutes the color removal increased only in 4% (97% total color removal). Thus, when the time of treatment (and the power consumption) is increased twice, the color removal yield is only increased in 4%.

Taking into account these results, it was decided to carry out the reuse tests with the effluent C treated for 30 minutes at 2 A.

3.3. Effluent reuse

On the bases of our previous studies, the reuse process was carried out with 70% of decolored effluent, which also contains 64% of residual salt.

Cotton samples dyed with the 70% uncolored effluent was evaluated with respect to reference dyeings performed with decalcified water. Their chromatic coordinates and color differences (DECMC(2:1)) are shown in Table 5.

Table 5. Chromatic coordinates and color differences values.

Dye	DH	DL	DC	$DE_{CMC(2:1)}$
PC	−0.55	0.37	−0.37	0.76
PN	−0.11	0.22	−0.33	0.41
PY	−0.58	−0.29	0.67	0.93

It can be seen that $DE_{CMC(2:1)}$ values, which reflects the human eye perception, were lower than 1, the tolerance limit generally accepted by the textile industry (Figure 3).

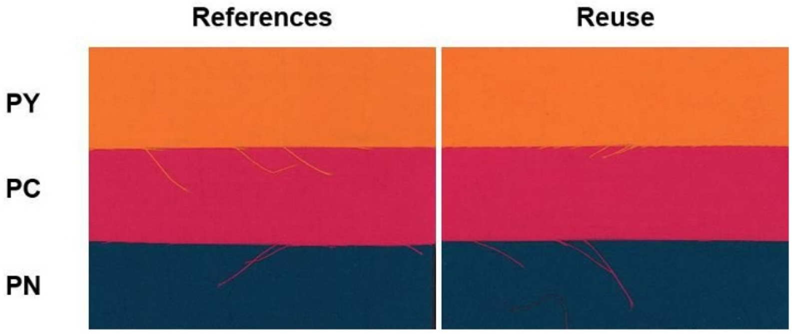


Figure 3. Results obtained in the effluent reuse study.

3.4. Advantages of the industrial implementation of the process

The combination of electrochemical technique with UV irradiation to treat and reuse textile wastewater has clear environmental and economic advantages.

According to the dyeing method, 10 L of water and 0.5 kg of salt are required to dye 1 kg of textile product. Consequently, the reuse of 70% of water and 64% of salt in the dyeing process result in a saving of 7 L of water and 0.5 kg of salt per kilogram of textile product.

A medium size textile mill can produce from 1–5 Tm of reactive dyed fabric per day. This would imply the generation of 10–50 m3 of exhausted dyebaths to be treated. The implementation of combined electrochemical and UV treatment will enable the company to save 7–35 m3 water and 0.5–2.5 Tm salt per day. In addition to the production process, the advantages on the wastewater treatment must also be considered. Thus, the reuse of the more colored effluents facilitates the treatment of the wastewater generated in other processes. Moreover, the conductivity of the discharged wastewater is reduced as a consequence of salt reuse. All this implies a reduction of discharge taxes and a better accomplishment of regulations.

As a result of the promising achievements obtained in this study, an industrial system combining electrochemical and UV treatment was designed to treat 4 m3/h in a textile mill in order to evaluate the industrial implementation of the technology.

4. Conclusions

Textile effluents collected from industrial reactive exhausted dyebaths were treated by means of an electrochemical treatment at 10 A. In all cases, the treatment provided 100% color removal. The residual oxidants were removed by means of UV irradiation. To reduce this step, the optimization of the electrochemical treatment was carried out and it was found that when the treatment is performed at 2 A, 93% color removal is obtained and the concentration of residual oxidants is minimized.

The effluent reuse study showed that 70% of uncolored effluents could be reused in new dyeing processes. Simultaneously, the reuse of 64% of salt was also achieved.

The results obtained in this study are promising for the textile industry since this sector consumes large amounts of water. The combined electrochemical and UV treatment enables the reuse of water and salt, which represents a significant advantage from both the environmental and economical points of view.

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For more information: www.ecuval.eu.

Conflict of interest

The authors declare there is no conflict of interest.

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Anaerobic co-digestion of swine manure and crude glycerol derived from animal fat—Effect of hydraulic retention time

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ABSTRACT

Crude glycerol (CG), an abundant by-product of bio-diesel production, has been identified as a suitable co-substrate for improving the biogas production of livestock manure through anaerobic digestion (AD). In this study, the potential of utilizing CG generated from the esterification of animal fats for biogas production was studied in both batch and continuous AD experiments, with emphasis on the importance of the hydraulic retention time (HRT). Batch experiments showed that the limiting step in the methane production rate during CG mono-digestion was the 1,3-propanediol uptake. Additionally, biochemical methane potential tests indicated that the addition of 1% w/w CG to swine manure-AD is more efficient in terms of percent of theoretical amount of methane obtained than the addition of 3% w/w. However, in continuous experiments, co-digestion of manure with 3% w/w CG did not exhibit any sign of inhibition within the HRTs tested (17–22 days). Moreover, a 222% increase of biogas productivity was observed with 3% CG supplementation at an HRT of 17 days, in contrast to a 146% increase at an HRT of 22 days. Based on this, and on the similar efficiency of soluble COD removal among the processes (ca. 93%), it was shown that it is possible to reduce the HRT without affecting negatively the efficiency of conversion of manure. Moreover, it was shown that CG from 2nd generation biodiesel based on animal fat, is a suitable feedstock for boosting the methane production of manure-based biogas plants.

***Keywords:** anaerobic digestion; manure; crude glycerol; co-digestion; biogas; methane*

1. Introduction

Anaerobic digestion (AD) is a widely applied waste management process for stabilizing the nutrient content of livestock manure, and ensuring a safer disposal and application to agricultural soils. An additional benefit of AD is that during the process, biogas is produced which is a renewable energy source. However, as a result of the low C/N ratio and the high dilution of manure, mono-digestion results into poor biogas production. In the last decades, the co-digestion of manure with other organic substrates has been successfully applied and undoubtedly improved the economic performance of biogas plants [1].

In recent years, a significant increase of biodiesel production through the esterification process of vegetable oils and animal fats has been evidenced [2,3], resulting in the generation of large amounts of crude glycerol (CG), the main by-product of biodiesel production. Crude glycerol has been identified as a suitable co-substrate for improving manure-based AD. Depending on the origin of the initial feedstock, CG is composed of glycerol (also called glycerin) along with impurities such as methanol, oils, salts, heavy metals, volatile fatty acids (VFAs) and water, that make its purification and commercialization a complex and expensive process [4]. Consequently, this substrate is highly available and not easily absorbed by the current glycerol market. On the other hand, it has a high carbon content and low nitrogen concentration that could balance the AD of manure and boost the biogas production.

Earlier studies have shown that an increase of 150–400% of biogas productivity is possible when adding CG to livestock manure [5,6]. On the other hand, at high CG concentrations, inhibitive effects such as accumulation of VFAs, overproduction of H2S and foaming phenomena have been reported [5,7], resulting in failure of the AD processes. These effects are a result of the impurities of CG, which are highly dependent on the origin of the substrate and any further processing. The majority of studies up to now have tested the co-digestion of manure with CG derived from the transesterification process of vegetable and cooking oils. However, CG originating from biodiesel production of animal fats and meat processing industry residues that often present high content of impurities [8] could be more inhibitory to the microbial community, and to our knowledge its co-digestion with swine manure has not been tested yet.

The aim of this study is to investigate the performance of co-digestion of swine manure with CG originating from the transesterification of animal fats. Initially, biochemical methane potential (BMP) tests were carried out for assessing the biodegradability of the substrates used and of their different co-digestion mixtures. Subsequently, continuous anaerobic digesters were operated with increasing supplementation of CG to swine manure AD at different hydraulic retention times (HRTs) for evaluating the importance of this factor on the stability and performance of the process.

2. Materials and methods

2.1. Substrates and inocula

The swine manure used in this study was collected from the Hashøj biogas plant in Sjealand (Denmark) and stored in sealed containers at −18 °C. Prior to use, each container was thawed and maintained at 4 °C. The Total (TS) and Volatile solid (VS) content of the manure used were 23.34 ± 0.24 g TS/L and 15.49 ± 0.43 g VS/L respectively, and the pH was 7.5 ± 0.1. The CG used was a by-product of the biodiesel production from butchery waste (based on animal fat categories 1 and 2 according to the EU regulation number 1069/2009 [9] and 142/2011 [10]) and was collected from Daka Biodiesel (Denmark). The specific characteristics of CG are shown in Table 1. The pH of the CG was equal to 1.5. The inoculum used for both the BMP tests and the continuous AD experiments originated from two bench-scale digesters operated with swine manure at mesophilic conditions (37 °C).

Table 1. Characteristics of CG *.

Component	Content
Moisture	10%
Ash	5%
Glycerol	75%
Fat	10%
Methanol	<1%
Sulphur	1–2%

*adapted from [11].

2.2. Biochemical methane potential tests

Two sets of BMPs were run. The first set comprised of BMP tests of CG at three different organic loadings, in order to test if any inhibitory effect occurred. The CG A, CG B, and CG C loadings corresponded to the following inoculum-to-substrate ratios (I:S): 4:1, 2:1 and 1:1, respectively (VS basis). The second set of BMPs was carried out for determining the ultimate CH4 yield of the swine manure alone, the mixture of 99% w/w swine manure and 1% w/w CG (1% CG), and 97% w/w swine manure plus 3% w/w CG (3% CG).

All BMP tests were set in 320 mL infusion bottles and were run in triplicates. In each set of experiments, BMP tests were also set only with inoculum and were used as blanks. The bottles were flushed with a mixture of 80% N2 and 20% CO2, sealed with rubber stoppers, secured with aluminum crimps and placed in an incubator at 37 °C. The CH4 production was monitored periodically until the end of the experiments. The CH4 production of the BMP tests of substrates was corrected for the residual production of the inoculum by subtracting the CH4 production of the blank tests. Liquid samples from the CG A, B, and C BMP tests were withdrawn periodically for monitoring the concentration of glycerol, 1,3 propanediol (1,3-PDO) and VFAs. Concentrations of soluble compounds were corrected for residual concentrations of the blank tests (containing only inoculum).

2.3. Continuous mode experiments

Two continuous stirred tank reactors (CSTR)-type digesters (3 L active volume) were used in the present study, both running under mesophilic conditions (37 °C). In order to ensure comparability of the two digesters, the initial inoculum was well mixed and distributed simultaneously to the CSTRs. Initially, the digesters were inoculated and left to acclimate for 2 days without any feeding. In continuation, both digesters were fed with swine manure (phase I), one with a HRT of 17 days (digester A) and the other one with a HRT of 22 days (digester B). After 30 days of operation, the feed of the digesters was changed to a mixture of 99% w/w manure and 1% w/w CG on a wet mass basis (Phase II, 30–78 days). Following phase II a mixture of 97% w/w manure and 3% w/w CG was initiated and lasted until the end of the experiments (Phase III, 79–120 days). In order to reduce errors associated to inhomogeneity of the mixture and ensure that no degradation of glycerol would occur prior to digestion, the mixture was prepared in a large container and subsequently divided into 2-L plastic containers and stored at −20 °C. The 2-L containers were thawed twice per week and added to the influent flasks of the digesters that were kept at 4 °C.

Both digesters were fed once per day by means of peristaltic pumps after rigorous mixing of the feed for 10 min. The stirring of the digesters was intermittent and took place every 3 hours for 10 min by means of overhead stirrers. The heating of the digesters was achieved by water jackets using a recirculating water bath. Biogas production was measured continuously with Ritter MilliGas counters (Ritter, Germany).

The digesters were monitored twice per week on the biogas composition in CH4, and weekly on the concentration of volatile fatty acids (VFAs), glycerol, 1,3-PDO, soluble COD, NH4 +-N content, and pH. Samples for TS and VS determination were taken weekly from the influent, inside the digesters and effluents. The biogas productivities and the CH4 yields of the two digesters at different phases were subjected to Student's t-test at a 95% significance level.

2.4. Analytical methods

The TS and VS content of the samples was determined following Standard Methods [12]. Soluble COD and Nh4 +-N were determined by means of HACH Lange kits LCK 514 and LCK 305 respectively after centrifugation at 10,000 rpm for 10 min and filtration through Whatman filters with a pore size of 0.45 µm. The total COD of the substrates was determined by HACH Lange LCK 914. VFAs, 1,3-PDO and glycerol quantification was done by means of an HPLC (Shimadzu, USA) equipped with a refractive index detector and an AMINEX HPX-87H (Bio-Rad) column at 63 °C. A solution of H2SO4 12 mM was used as eluent at a flow rate of 0.6 mL/min. The samples for the HPLC were centrifuged at 10,000 rpm for 10 min, filtered through 0.45 µm, acidified with H2SO4 (10% w/w), centrifuged at 10,000 rpm for 10 min and filtered through 0.20 µm. CH4 determination was done by a GC (Mikrolab Aarhus, Denmark) equipped with a packed column (6 ft. and I.D. 3 mm) and a thermal conductivity detector. N2 was used as a carrier gas and the injector, oven and detector were all set at 70 °C. All gas volumes are given at 20 °C, unless otherwise stated. All CH4 yields reported are expressed per g VS of substrate added.

3. Results and discussion

3.1. Theoretical CH4 yields of substrates

The theoretical CH4 yields of the substrates and their mixtures were calculated based on the COD measurements and assuming 0.35 m3/kg O2 at STP. The total COD of the swine manure was measured to be 29.00 ± 1.15 g/L, and of the CG it was 1255 ± 21 g/L. Thus, the ratios of g COD/g VS of manure and CG were 1.89 g COD/g VS and 1.52 g COD/g VS respectively. Finally, the theoretical maximum CH4 yield of manure was calculated to be 658 ± 50 mL/g VS and the maximum CH4 yield of CG was 573 ± 9 mL/g VS.

3.2. Ultimate CH4 yield of CG

The cumulative CH4 yields of the BMP tests of CG at different organic loadings are shown in Figure 1. As observed in the graph, all BMP tests presented a lag phase as almost no CH4 production was detected after 2 days of incubation. However a sharp increase of the CH4 production was detected after 5 days of digestion. Thereafter, only the lowest CG loading continued to produce Ch4 at a high rate, while the higher loadings presented signs of partial inhibition (reduced rates compared to CG A). The latter could be either due to overloading of easily degradable organic matter, or due to a higher concentration of inhibitory compounds such as salts [13].

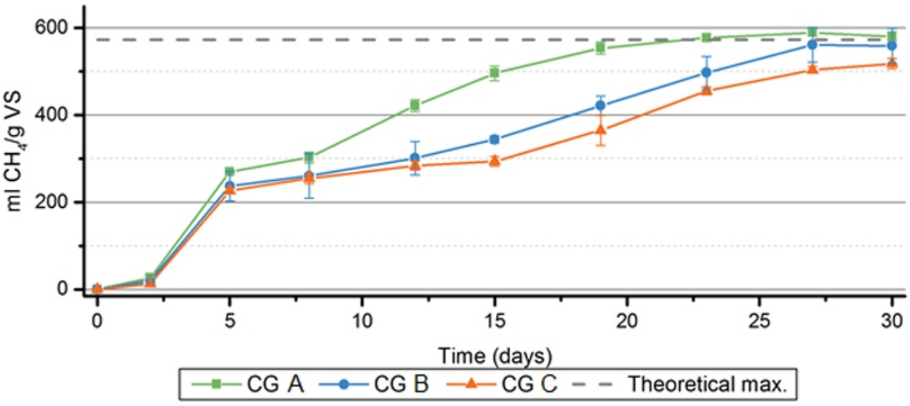

Figure 1. Cumulative CH4 yields of BMPs of CG at different organic loadings. CG A, B and C correspond to I:S ratio on a VS basis of 4:1, 2:1 and 1:1 respectively.

The evolution of the glycerol concentration in BMPs (Figure 2a) shows that glycerol was broken down to intermediate products after 5 days of digestion. The main intermediate was 1,3-PDO as it can be seen in Figure 2b, along with VFAs (Figure 2c), comprised mainly of caproic and acetic acid. The further degradation of 1,3-PDO has been suggested to be towards acetyl CoA [14]. The uptake of 1,3-PDO appeared to be the limiting step due to the slow consumption rate evidenced in all BMP tests (Figure 2b). Moreover, a minor peak of VFAs was detected in the BMPs with the lower organic loading (CG A) after 12 days compared to peaks after 19 and 23 days in the case of CG B and CG C, respectively (Figure 2c). These findings are in agreement to [15] who reported an increased inhibitory effect of 1,3-PDO in comparison to other intermediate products. Finally, after 30 days of digestion all BMP tests have reached an end producing on average 544 ± 29 mL CH4/g VS, corresponding to 94.9% of the theoretical maximum (section 3.1). This indicates that the entire substrate was consumed, as a 5% COD could be attributed to the fraction utilized by microbes for growing.

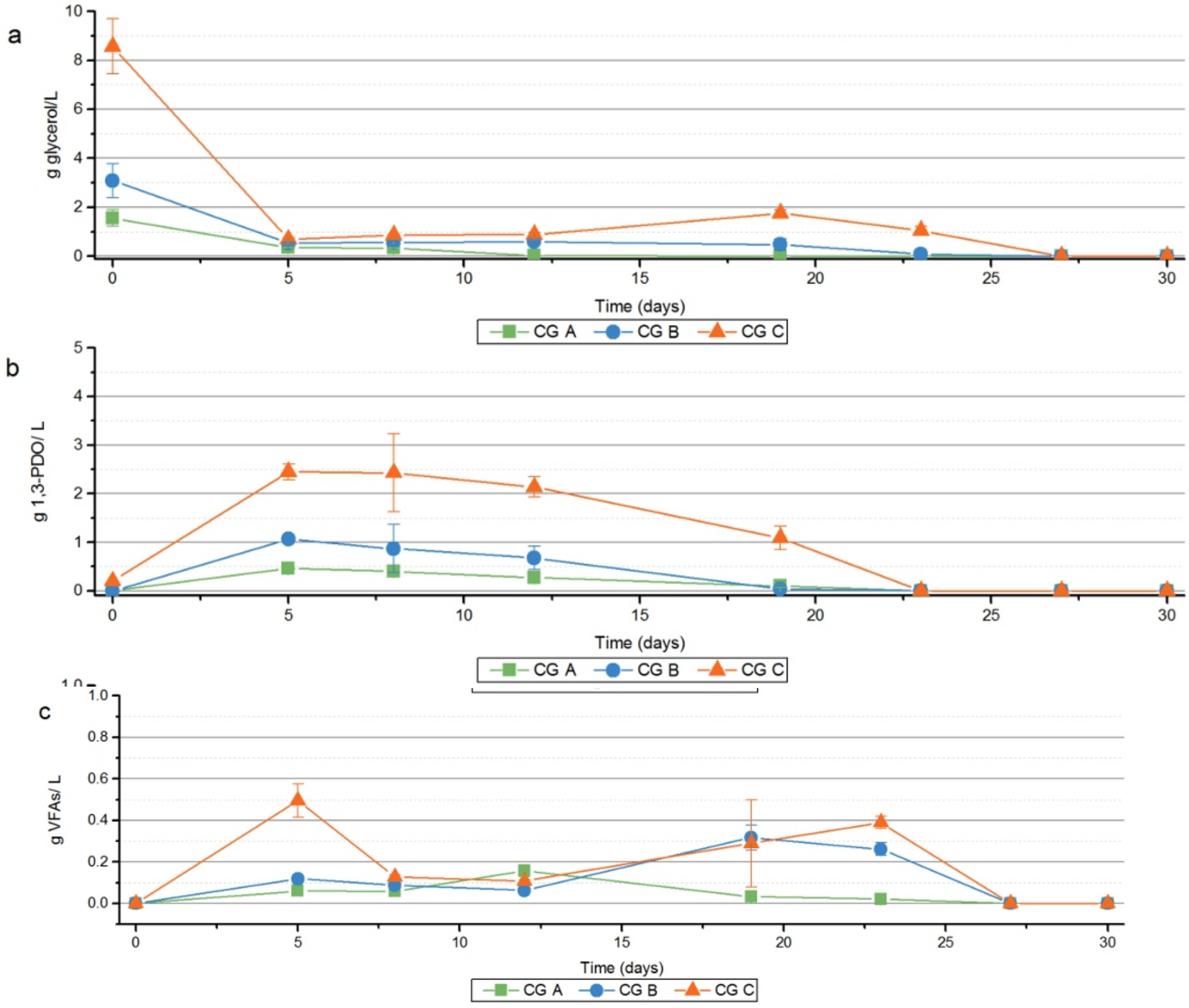

Figure 2. Evolution of (a) glycerol concentration, (b) 1,3-PDO concentration and (c) VFA concentration in BMP tests of CG at different organic loadings. CG A, B and C correspond to I:S ratio on a VS basis of 4:1, 2:1 and 1:1 respectively.

3.3. Ultimate CH4 yield of manure and CG mixtures

The second set of BMPs was carried out for determining the ultimate CH4 yield of swine manure and the mixtures of 1% CG and 3% CG that were subsequently fed to the continuous anaerobic digesters. The cumulative CH4 yield curves are presented in Figure 3, where it can be seen that all substrates were consumed rapidly. The ultimate CH4 yield of the swine manure reached 605 ± 15 mL CH4/g VS on average, while the 1% CG and 3% CG produced 639 ± 10 mL/g VS and 530 ± 11 mL/g VS of CH4 respectively. Thus the addition of 1% CG to manure resulted in a 6% increase of the CH4 yield. However, with the addition of 3% CG, a decrease of 12% of the ultimate CH4 yield was observed. Interestingly, the efficiency of the co-digestion of 99% manure with 1% CG was the highest in comparison to the other mixture and to manure alone, even though this mixture did not have the highest theoretical CH4 yield. More specifically, manure reached approximately the 91.9% of the theoretical CH4 yield (see section 3.1), while the 1% CG and 3% CG reached 99.7% (641 ± 36 mL CH4/g VS) and 93.5% (567 ± 30 mL CH4/g VS) respectively. This indicates that the co-digestion of 97% manure with 3% CG was probably partially constrained either from nitrogen limitation, or due to the presence of impurities that produced inhibition. N deficiency has been mentioned by [16] to be the reason why a supplementation of CG to sewage sludge, higher than 1%, did not result in improved efficiency. However, in contrast to sewage sludge, swine manure has a significantly higher N concentration that can permit the glycerol consumption. Thus, the lower efficiency of the 3% CG supplementation is probably a result of the impurities present in CG generated from the processing of animal fats for biodiesel production.

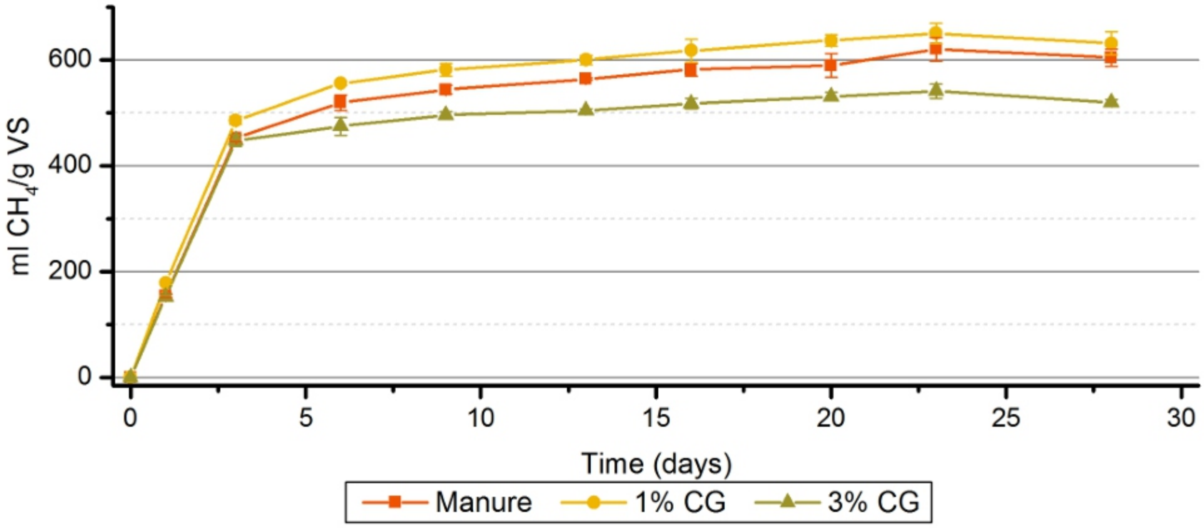

Figure 3. Cumulative CH_4 yields of second set of BMPs of manure, 99% of manure and 1% CG (1% CG), and 97% manure and 3% CG (3% CG).

3.4. Continuous AD experiments

BMP tests are very useful for providing information on the ultimate CH4 yield of different substrates and constitute the common approach for obtaining preliminary information regarding the incorporation of new feedstocks in industrial AD processes. However, continuous AD experiments can offer information on both the productivity and stability of co-digestion, which are more relevant to an industrial process where the HRT can be decisive on how well the process performs [17].

Additionally, inhibition effects that have been evidenced in batch tests might change, as accumulation of inhibiting factors is not favored in continuous experiments. Based on this, it was of interest to compare two co-digestion processes at different HRTs, for evaluating whether it was possible to reduce the HRT without affecting significantly the process stability and efficiency. The approach followed in this study was based on increasing the share of CG in consecutive steps, in order to permit adaptation of microorganisms to CG. During phase I, the two digesters were fed only with swine manure and the HRT of digester A and digester B was set at 17 and 22 days respectively. This permitted to compare the process performance of the co-digestion to the mono-digestion of swine manure at different HRTs.

During phase I, digester A was operated at an organic loading rate (OLR) of 0.97 g VS/L/day in comparison to digester B that ran with 0.75 g VS/L/d. As expected, digester B presented lower biogas productivity and higher CH4 yield compared to digester A (Table 2), as more time was allowed for the microbes to biodegrade the organic matter of manure. This resulted also in a slight increase of the Nh4 +-N concentration in digester B, probably due to an improved digestion of nitrogenous compounds such as proteins. The VFA concentration was slightly higher in digester A,though in both processes the VFA concentration was low enough (<0.5 g/L) to avoid a drop of pH. Overall, both processes were operated without any signs of instability and the reduction of soluble COD was similar among the digesters, corresponding to approximately 84%. The biogas productivity of digester A was 0.46 ± 0.02 L/L/d, similar to 0.41 ± 0.02 L/L/d observed from digester B. The CH4 content of the biogas produced in both digesters was the same, reaching 64.5%.

Following the addition of 1% CG after day 30, both digesters responded with an increase in the biogas productivity and no process instability occurred as indicated by the low VFA concentration and the stable pH values (Table 2). However, the biogas productivity of digester B was stabilized faster as it can be observed in Figure 4 and the glycerol concentration in digester A was 0.12 g/L after 3 days of mixture-based digestion in comparison to 0.04 g/L in digester B. After 1 week of co-digestion the glycerol concentration in both digesters was less than 0.03 g/L. Similarly, the 1,3-PDO concentration in digester A was 0.06 g/L and in digester B 0.04 g/L during the first week and thereafter no 1,3-PDO was detected. Consequently, it can be assumed that during the continuous process, microbes were adapted faster to 1,3-PDO than in the batch experiments. The CH4 content of biogas was significantly increased reaching 68.0% and 70.9% from digester A and B respectively. The biogas productivity from digester A in phase II was 0.81 ± 0.06 L/L/d, corresponding to a 76% increase as compared to phase I where the digester was fed only with swine manure. On the other hand, the increase of biogas productivity of digester B at phase II corresponded to 46% in comparison to phase I. These increments were of the same magnitude to the increase observed by Astals et al. [5] when adding 1% w/w of vegetable-oils-derived CG to swine manure at a digester with similar HRT (20 d), indicating thus that even when using CG generated from processing animal fats for biodiesel production (as used in this study) and when the supplementation is as low as 1% w/w, similar improvements can be obtained in manure-based AD processes.

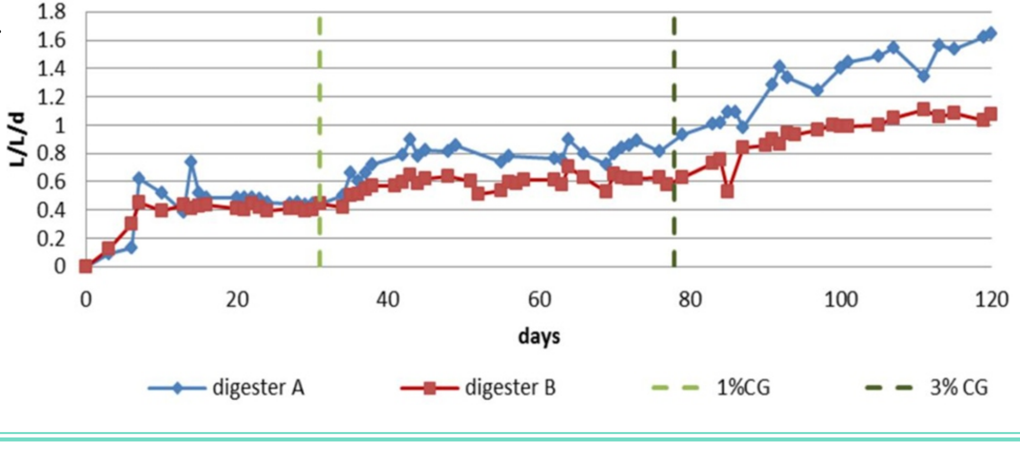

Figure 4. Biogas productivity of digester A and B (with HRT of 17 and 22 days respectively) fed with swine manure and an increased CG supplement.

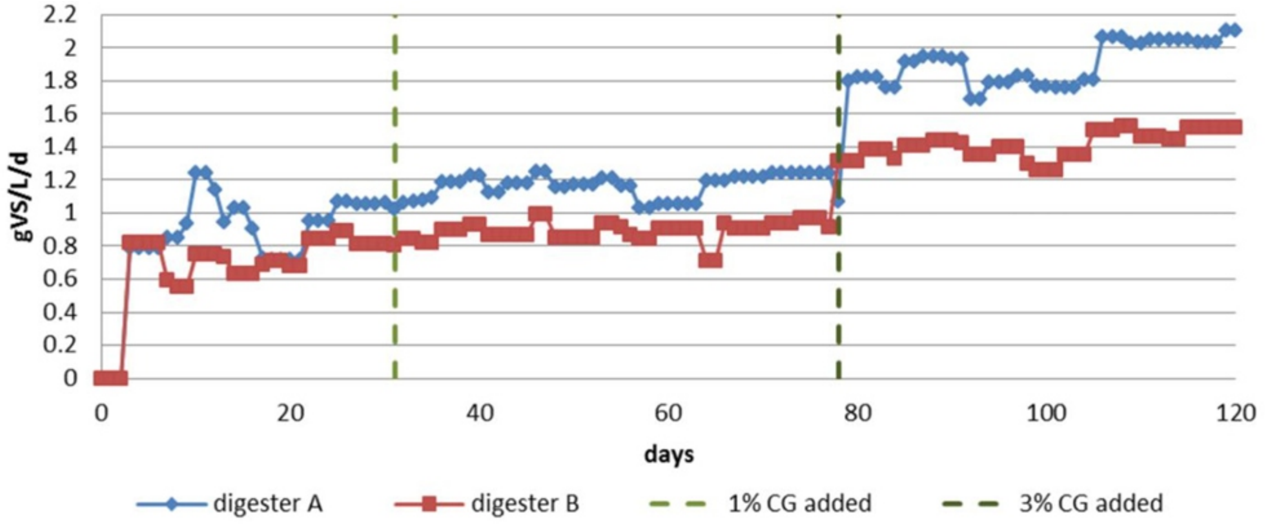

Figure 5. Organic Loading Rate of digesters A and B during the entire course of experiments.

On day 78, feeding of 3% CG mixture was initiated (phase III), resulting to a 2-fold increase of the OLR on both digesters as compared to phase I (Figure 5). Both digesters responded relatively fast. The biogas production started to increase sharply in both processes, and no signs of inhibition were observed as implied also by the very low levels of intermediate products, 1,3-PDO and acids (Table 2). The concentrations of both glycerol and 1,3-PDO remained lower than 0.001 g/L and no accumulation of VFAs was detected. However, the biogas productivity of digester B was more stable than the productivity of digester A that continued to increase for more than 20 days after the increase of the OLR (Figure 4). Overall, during phase III, digester A and digester B presented a 222% and 146% increase of biogas productivity.

Table 2. Average characteristics of digesters A and B during Phase I (manure only), II (1% CG added) and III (3% CG added)*.

Characteristic	Phase I (days 14–30)		Phase II (Days 43–76)		Phase III (Days 100–120)	
	Digester A	Digester B	Digester A	Digester B	Digester A	Digester B
g VS manure: g VS CG	100:0	100:0	65:35	65:35	38:62	38:62
Organic Loading Rate (g VS/L/d)	0.94 ± 0.16	0.75 ± 0.10	1.17 ± 0.07	0.91 ± 0.09	1.91 ± 0.13	1.42 ± 0.08
pH	8.3 ± 0.1	8.3 ± 0.1	8.3 ± 0.1	8.3 ± 0.1	8.2 ± 0.0	8.2 ± 0.1
NH_4^+-N (g/L)	2.24 ± 0.8	2.54 ± 0.3	1.96 ± 0.44	2.34 ± 0.06	2.16 ± 0.17	2.21 ± 0.21
VFAs (g/L)	0.42 ± 0.15	0.33 ± 0.15	0.43 ± 0.09	0.39 ± 0.15	0.33 ± 0.04	0.23 ± 0.02
Biogas productivity (L/L/d)	0.46 ± 0.02a	0.41 ± 0.02b	0.81 ± 0.06c	0.60 ± 0.04d	1.48 ± 0.13e	1.01 ± 0.07f
CH_4 yield (L/g VS)	0.33 ± 0.08a	0.35 ± 0.07a	0.48 ± 0.04b	0.47 ± 0.04b	0.48 ± 0.04b	0.48 ± 0.02b
Sol COD reduction (%initial)	83.6 ± 2.1	84.3 ± 2.0	90.2 ± 2.4	91.0 ± 2.9	92.7 ± 2.7	93.5 ± 2.4

*different letters next to the values indicate a significant statistical difference based on t-test with $p < 0.05$ (with same letters indicating a non- significant difference).

The CH4 yield of both processes reached 0.48 L/g VS at a 3% CG supplementation, which is similar to values reported in previous studies on co-digestion of manure with CG derived from vegetable oils. Usack and Angenent [18] ran a long-term co-digestion of cattle manure and CG and reported a CH4 yield of 0.55 L/g VS. However, in that study the share of glycerol in the mixture was lower as the feed ratio was equal to 62 g VS manure: 38 g VS glycerol, in contrast to this study where a ratio of 38 g VS manure: 62 g VS glycerol (Table 2) was achieved without process instability issues. Generally, the limits of CG concentration before having signs of process failure or reduced yields vary among studies. Lobato et al. incremented the CG content up to 8% v/v and evidenced an increase of the CH4 yield from 11 L/g COD to 17 L/g COD [19]. Amon et al. [20] found a 170% increase of the CH4 yield of manure mono-digestion by adding 6% CG. Astals et al. found a biogas yield equal to 0.78 L/g VS under mesophilic co-digestion with 4% w/w CG, corresponding to a 400% increase of biogas productivity and reported process instability at 5% w/w CG [5]. The same group increased the supplementation of CG up to 3% w/w CG and found a biogas yield equal to 0.47 L/g VS under thermophilic conditions [21]. In this sense, it is clear that not only the origin of the CG used may affect the efficiency of the co-digestion process but the process conditions (temperature, HRT, etc.) as well.

The effect of the HRT on the performance of the co-digestion of manure with CG was evaluated by comparing the data of the two digesters. The biogas productivity of digester A was found to be 35% higher than the productivity of digester B during phase II. Interestingly though, the CH4 yields of the two processes were similar during phase II, being these 0.48 L CH4/g VS for digester A, and 0.47 L CH4/g VS for digester B. A possible explanation for this could be that the CG added was quickly degraded by the microorganisms in both digesters as it is a more readily available carbon source, while a larger part of the organic content of manure was permitted to degrade in digester B due to its higher HRT. Thus, the high yield originating from CG covered the difference in the CH4 yields originating from the degradation of manure, making the difference in the CH4 yield among digesters less significant. Similarly, in phase III, only the CG was probably converted to CH4 in both digesters, resulting into the same yields. This hypothesis is also supported by the soluble COD reductions found (Table 2). Based on the soluble COD reductions of phases I and II, the expected CH4 yields were calculated to be 0.30 L and 0.39 L respectively in both digesters. However, in phase III, the expected CH4 yield based on the reductions of soluble COD observed were calculated to be 0.48 L. This means that during phase I and II, part of the particulate matter was hydrolyzed and contributed to the CH4 yield. On the other hand, at phase III, the share of CG was high and the expected CH4 yields coincide with the observed yields indicating that only the soluble matter was converted to CH4. This is in agreement with a previous study reporting that the addition of CG to manure may reduce the digestion efficiency of manure due to the presence of more favorable compounds for microbes [7]. This could also explain why the NH4 +-N content in digester B was higher than in digester A (especially during phase II), as the NH4 +-N probably originated mainly from manure components. Additionally, the removal of soluble COD achieved by digester B was found to be slightly higher than in digester A (Table 2). However, the difference among the two processes is not that significant. Based on these observations, it appears that a low HRT of 17 days can be applied without significantly reducing the extent of AD of manure.

4. Conclusions

The co-digestion of crude glycerol, CG, derived from the transesterification of animal fats with swine manure was shown to be an efficient way to improve the methane production of manure-based biogas plants. Batch experiments of CG mono-digestion indicated that the limiting step for CH4 generation was the uptake of the intermediate product 1,3-PDO. However, this did not appear to limit the continuous co-digestion of manure with CG. Continuous experiments showed no inhibition effects with concentrations up to 3% CG and reached a 222% increase of biogas productivity compared to manure mono-digestion. More importantly, in this study it was shown that decreasing the HRT from 22 days to 17 days allowed for a significant increase of the biogas productivity while not reducing the soluble COD removal efficiency importantly.

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Conflict of interest

All authors declare no conflicts of interest in this paper.

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