Selective Removal of ZnO Nanoparticles from Water Using 3-aminopropyltriethoxysilane (APTES) and Monitoring by Meso-tetra(carboxyphenyl)porphyrin (TCPP)

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Abstract
Metal oxide nanoparticles (MONPs) such as TiO2 and ZnO have been engineered for various industrial manufacturing processes. Among MONPs, environmental exposure to ZnO nanoparticles may cause health concerns about their significant toxicity. This leads to a desire of efficient methods for their removal in the aqueous environment with facile detection. In this work, 3-aminopropyltriethoxysilane (APTES) was chosen to treat aqueous suspensions containing ZnO and other metal oxide nanoparticles. APTES first formed a thin surface layer on ZnO nanoparticles and continued in branching polymerization to link up with adjacent APTES-ZnO nanoparticles. Eventually, a web-like sediment settled down onto the bottom and was confirmed to be APTES-ZnO conjugation by FT-IR. A high removal efficiency over 99 % w of ZnO nanoparticles in aqueous suspension was attained using 2.0 % by volume of APTES. The sedimentation was selective towards ZnO nanoparticles due to electrostatic interaction with ZnO to form a sturdy condensation coagulate. Other MONPs (Al2O3, CaO, CeO2, CuO and TiO2) did not form any web-like sediment with APTES but could co-precipitate with the ZnO nanoparticles. Meso-tetra(carboxyphenyl)porphyrin (TCPP) could be added as an indicator to co-precipitate with the sediment, with its color changing from red purple to bright green during the formation of APTES-TCPP-ZnO sediment. A filter paper or membrane placed at the bottom greatly facilitated the disposal of all sediments at a low cost.

Keywords ZnO nanoparticles · APTES · TCPP · Selective sedimentation · Wastewater treatment · Environmental toxicity

1 Introduction
Numerous advances of nanoscience and nanotechnology have been reported in recent years on the use of metal oxide nanoparticles (MONPs) in enzymatic biosensors [1] and enzyme-linked immunosorbent assay [2]. The excellent and photocatalytic ability of TiO2 and ZnO nanoparticles has been utilised in various organic pollutants removal [3,4]. The highly unique chemical and physical properties also promotes a massive production of MONPs for industrial manufacturing of consumer products, which leads to the inadvertent release of MONPs to the natural aquatic environment [5]. This scenario raises great concerns because ZnO, TiO2 and CeO2 all exhibit toxicity towards microorganisms even though their bulk materials are generally considered to be non-toxic [6]. The toxicity is mainly due to induction of reactive oxygen species (ROS) that can lead to lipid peroxidation, DNA damage, and protein denaturation [7]. Ivask et al. identified the most toxic MONPs to be ZnO and CuO with average IC50 values of around 20 µg/mL against three mammalian cell lines (human alveolar epithelial cells A549, human epithelial colorectal cells Caco2, and murine fibroblast cell line Balb/c 3T3) at 24 h [8]. Jain et al. also reported in-vitro genotoxicity and cell death (on Chinese hamster lung fibroblast cells V-79) after exposure to 1-20 µg/mL ZnO nanoparticles for 6 h [9].

Most of the conventional wastewater treatment methods may not target the removal of MONPs and leaves a significant level of nanoparticles breakthrough (2-96 % of ZnO and 0-4 % TiO2) even with ultrafiltration simulated advanced treatment [10]. Thus, a simple detection and removal method towards MONPs is needed to test and treat wastewater. The recent common removal of MONPs is based on the enhanced coagulation and flocculation in the aqueous sample. While a
single coagulant such as alum may not serve the best for MONPs removal, Sun et al. proposed the combination of enteromorpha polysaccharide and polyaluminum chloride can result in a 95 % removal of ZnO nanoparticles along with Zn$^{2+}$ [11]. You et al. also stated the combination of polyaluminum ferric chloride and cationic polyacrylamide is capable of removing both TiO$_2$ and ZnO nanoparticles [12, 13]. Some organic molecules such as sodium dodecyl sulfate, nonylphenol ethoxylate and humic acid are proven to facilitate the coagulation of ZnO nanoparticles when using ferric chloride as a coagulant [14, 15]. However, these methods are lack of selectivity towards one specific MONP.

Colorimetric detection has unexpectedly emerged as a research focus area in the field of analytical chemistry. Compared with instrumental methods of analysis, colorimetric methods offer many advantages such as adequate sensitivity, good selectivity, great convenience, low cost, as well as fast turnaround [16]. For the detection of metal oxide nanoparticles in aqueous suspension, surface reactivity of different metals can be the basis for selectivity in the development of novel colorimetric methods. Liu et al. carried out a comprehensive investigation of common MONPs for their ability to adsorb DNA, quench fluorescence, and release adsorbed DNA in the presence of target anions [17].

Among several present studies in MONPs removal, most of them rely on traditional coagulation and filtration methods, which is labour intensive and lack of selectivity. In this study, a novel screening test of MONPs was developed for the specific detection and removal of ZnO among several other transition metal oxides in aqueous suspension. 3-aminopropytriethoxysilane (APTES), a popular silanization grafting agent on MONPs to introduce amino groups, was used as a removal agent to settle down the nanoparticles and form a sturdy layer for one-step removal. This depends on the polymerization feature of APTES to entrap ZnO nanoparticles in its complex, whereas monolayer of APTES on MONPs surface has a more common applications in biosensors [18], catalyst immobilization [19], drug delivery [20, 21] etc. Though the toxicity of APTES may be a concern, the resultant grafting on MONPs shows low cytotoxicity and high thermal stability [22]. Meso-tetra(carboxyphenyl) porphyrin (TCPP) is a porphyrin derivative that has been proved to produce unique fluorescence emission with ZnO nanoparticles [23]. The present test was based on specific colorimetric development from TCPP and obvious coagulate sedimentation of APTES-TCPP-ZnO. Analytical UV-visible spectroscopy and EDX were used to confirm the presence and estimate the quantity of ZnO nanoparticles. Both the colorimetric reagent TCPP and the coagulation agent APTES displayed excellent selectivity toward ZnO nanoparticles. The proposed method can be applied for convenient ZnO removal in the absence or presence of other MONPs in wastewater.

2 Materials and Methods

2.1 Chemicals

3-aminopropyltriethoxysilane (APTES), meso-tetra(4-carboxyphenyl)porphyrin (TCPP), CaO nanoparticles (<160 nm, 98 %), CeO$_2$ nanopowders (<25 nm), CuO nanopowders (<50 nm), TiO$_2$ nanoparticles (21 nm, >99.5 %), ZnO nanoparticles (<50 nm particles, >97 %) were all obtained from Sigma-Aldrich (Oakville, Ontario, Canada). Mixed cellulose ester (MCE) filter membrane (0.45 μm) was purchased from Millipore (Bedford, Massachusetts, US).

2.2 Removal of MONPs

The standard sample was prepared by dispersing individual MONPs in distilled deionized water (DDW) using an ULTRASONICS ultrasonic processor 300 W at a concentration of 1 mg/mL. A stock TCPP in ethanol was prepared at 1.0 mg/mL. For the removal of MONPs in aqueous suspension, a mixture of APTES (2 %) and TCPP stock (5 %) were added to treat the standard MONPs samples. The treated samples were then set at room temperature for coagulation and sedimentation over 24 h. The filter paper/membrane-assisted removal was done by placing a piece of filter paper or MCE membrane on the vial bottom to collect APTES-ZnO sediment.

2.3 Characterization

The resultant dispersion of APTES and TiO$_2$ nanoparticles mixture sample and the sediments scratched out from APTES-ZnO nanoparticles sample were studied using scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) analysis. The absorption spectra of ZnO nanoparticles, both the initial dispersion and the final supernatant after sedimentation, were measured on a Thermo Scientific GENESYS 10S UV-Vis spectrophotometer with a slit width of 1.0 nm. The UV-Vis spectrum of APTES-TCPP-ZnO sediment was measured directly from the vial wall.

The Fourier transform infrared (FTIR) spectra of APTES-ZnO and TCPP-APTES-ZnO conjugate were obtained using the Agilent Cary 630 spectrometer in the range of 650 – 4000 cm$^{-1}$. The APTES-ZnO and APTES-TCPP-ZnO sediments were washed with DDW, dried at room temperature, and mixed with KBr to prepare disks for FTIR analysis.

2.4 APTES Dosage and Efficiency

To study the effect of APTES dosage on ZnO removal, five standard 1.0 mg/mL of ZnO nanoparticle dispersions were
treated with 0.5 % - 2.5 % v of APTES. A series of ZnO nanoparticles in aqueous dispersion at various concentrations (0.1 - 2.0 mg/mL) were also prepared for spiking with 2 % by v of APTES. The removal efficiency was then determined by UV-Vis spectrophotometry. Interference by other MONPs with the selective sedimentation was studied by similar treatment of ZnO mixture with MONPs in 1:1 mass ratio.

3 Results and Discussion

3.1 Role of APTES

Addition of APTES by itself to the aqueous samples containing MONPs will experience a hydrolysis first on the epoxy group and result an increase of pH from 7 to 10 at the surface of ZnO nanoparticles [24]. This pH range exerts a maximum prohibition to the possible release of free metal ions for MONPs. For TiO₂ and ZnO nanoparticles that are more sensitive to the dissolution pH will experience an aggregation. Then, as of the multilayer APTES condensation that Bhushan et al. (2009) proposed, APTES will condensate on the surface of all MONPs and branch with other MONPs particles in high water content (Scheme 1) [25]. The higher degree of APTES branching condensation with ZnO nanoparticles is the leading cause forming a web-structured sediment. During the sedimentation, the accumulated APTES-ZnO on the vial bottom is immobilized by APTES condensed on the glass surface. Despite vigorous vortex, the sediment did not get dispersed and resuspended in the supernatant. However, there were no web-like sediments produced by APTES in other MONP dispersions.

3.2 Role of TCPP

Upon the addition of both APTES and TCPP into the aqueous samples containing MONPs, TCPP as an indicator appeared to be green only in the presence of ZnO (Fig. 1a). After a 24-hour period of sedimentation, the vial of ZnO nanoparticles revealed a clear supernatant sitting on top of a green sediment with a web-like microstructure adhering onto the vial bottom (Fig. 1b). The bright green color produced by TCPP can be related to the interaction with ZnO nanoparticles in the porphyrin center. This ZnO-TCPP complex can be co-precipitated by APTES through either the electrostatic interaction or hydrolysis between TCPP’s carboxyl (COOH) group and NH₂ during the sedimentation process. The addition of TCPP show no influence on the sedimentation but can be used as a convenient visual indicator for the majority of ZnO removal. The supernatant of APTES-TCPP-ZnO sample was later verified by EDX to comprise no significant amount of Zn.

3.3 Mechanism of Selectivity

When APTES is coated on MONPs, the surface density (mass per unit area) of APTES permits a different ratio between NH₂ groups and metal OH groups. Moreno et al. (2020) used a computational method to find the binding energy of common aquatic heavy metals (As(OH)₃ and Cd(OH)₂). Low APTES coverage on SiO₂ nanoparticles was favourable for As adsorption while high APTES coverage favored Cd adsorption [26]. This approach allows selective adsorption of heavy metal ions by adjusting APTES coverage as high NH₂ surface density facilitates adsorption by electrostatic interaction. The coverage can be adjusted to maximize the adsorption of MONPs since the surface charge of each nanoparticle is different. The
extent of APTES polymerization results in a specific pore size granting a preferable adsorption toward ZnO nanoparticles. The electrostatic interaction between OH surface groups on ZnO and NH$_2$ groups on APTES allows the formation of a stable and sturdy complex structure for sedimentation.

### 3.4 Characterization of APTES-TCPP-MONPs

#### 3.4.1 SEM Images of APTES-TCPP-MONPs

The SEM images (Fig. 2) show the overall morphology difference of the APTES-TCPP sediments produced by TiO$_2$ nanoparticles and ZnO nanoparticles. Although they both exhibited the branching polymerization of APTES, the APTES-TCPP-ZnO sediment possessed a more uniform web-like microstructure (Fig. 2a). According to EDX analysis results, the APTES sediment had a relatively consistent distribution of Zn content throughout the web-like microstructure (Fig. 3). In contrast, Ti content was only detected in a few spots of the APTES-TCPP-TiO$_2$ sediment (Fig. 4). This result suggests that the branching polymerization of APTES with TiO$_2$ in the presence of TCPP happened slower than the aggregation/agglomeration of TiO$_2$ nanoparticles themselves. Consequently, most of TiO$_2$ nanoparticles formed agglomerates during the APTES branching polymerization.

#### 3.5 FTIR Spectroscopy

The FTIR spectra of APTES, APTES-ZnO and APTES-TCPP conjugate are shown in Fig. 5. APTES exhibits a peak at 958.5 cm$^{-1}$ corresponding to the Si–O bond, while the peak at 2928.8 cm$^{-1}$ is attributed to the methylene group (CH$_2$). When APTES condenses on ZnO nanoparticles, a peak at 992.4 cm$^{-1}$ indicates the formation of Si–O–Si bond. The peak at 2926.1 cm$^{-1}$ also represents successful conjugation of APTES onto ZnO to form a sediment. The spectrum of APTES-TCPP-ZnO has a modest broad enhancement from 1650 to 1000 cm$^{-1}$, due to stretching vibrations of C=C and C=N in the porphyrin ring. Noticeably, the peak at 1384.5 cm$^{-1}$ can be attributed to stretching vibrations of C-N.

#### 3.6 UV-Vis Spectra

As presented by the UV-Vis spectra in Fig. 6a, TCPP exhibits a sharp absorption peak at 415 nm, and ZnO nanoparticles have a broad absorption peak from 250 to 360 nm. The freshly prepared mixture containing APTES, TCPP and ZnO nanoparticles shows a combination of TCPP and ZnO absorption peaks. However, after sedimentation over 24 h, both the absorbance peaks of TCPP and ZnO diminish for the clear supernatant. The UV-Vis spectrum of the precipitate showed a shift of TCPP peak from 415 nm to 440 nm; and an enhanced absorbance from 550 nm to 650 nm, which explained the presence of green color. This is strong evidence that supports...
the co-precipitate of TCPP during the removal of ZnO in the aqueous sample. On the other hand, the UV-Vis spectra of other MONPs in APTES/TCPP mixture shows no TCPP peak shift after 24 h (Fig. 6b).

Fig. 2 Scanning electron microscopy (SEM) image of APTES-TCPP sediment with TiO$_2$ nanoparticles (A) and with ZnO nanoparticles (B).

Fig. 3 Scanning electron microscopy (SEM) image (A) and energy dispersive X-ray (EDX) map (B-D) of APTES/TCPP-ZnO sediments from three different sites.
3.7 UV-Vis Calibration Curve of ZnO Nanoparticles

The calibration curve of UV-Vis absorbance versus the concentration of ZnO nanoparticles was first constructed using standard suspensions of ZnO nanoparticles in water. The UV-Vis spectra (Fig. 7a) indicate a detection limit down to 0.01 mg/mL where the absorption peak at 360 nm remains distinguishable. Figure 7b shows the standard calibration curve of ZnO nanoparticles to be linear between 0.01 and 0.5 mg/mL. This calibration curve can be used for estimating the removal efficiency up to 99 % when 1.0 mg/mL ZnO nanoparticles aqueous suspension was treated with APTES.

3.8 Removal Efficiency

The removal efficiency is measured by the UV-Vis spectra of ZnO nanoparticles in aqueous suspension before and after treatment with APTES. As APTES shows nearly no absorbance, the UV-Vis spectrum of ZnO should not be affected upon the addition of APTES (Fig. 8). After 24 h of sedimentation, the spectrum exhibits a significant decrease such that the absorbance peak at 360 nm is not differentiable from the
Therefore, the removal efficiency can be estimated to be >99% by taking the detection limit of 0.01 mg/mL as the final ZnO concentration.

### 3.9 Effect of APTES Dosage

When 0.5%–2.5% v of APTES were used to treat 1.0 mg/mL ZnO nanoparticles in aqueous suspension, Fig. 9a shows the UV-Vis spectra of ZnO nanoparticles after 24 h. By treating with 0.5% and 1.0% APTES ratio, significant agglomerations were observed in both sample, which initiated a decrease in ZnO absorbance from 4 to 1.8. However, full sedimentation only starts occurring from 1.5% APTES treatment (Fig. 9b). The removal efficiency reaches 50% with 0.5% APTES and...
maintain at 99 % in sample treated with 1.5–2.5 % of APTES (Fig. 9c). Thus, the optimal APTES dosage for sedimentation is determined to be 1.5–2.0 %.

3.10 Maximum Sedimentation Capacity of APTES

In Fig. 10, the resultant UV-Vis spectra after ZnO nanoparticles treatment show the reoccurrence of ZnO absorbance in 2.5 mg/mL ZnO nanoparticles suspension. Though 1 % v APTES cannot afford the removal of 1.0 mg/mL ZnO nanoparticles, the 2 % v APTES can reach a maximum removal capacity of 2.0 mg/mL ZnO nanoparticles. Interestingly, a completely sedimented APTES-ZnO conjugates aqueous sample could repetitively remove additional dosages of ZnO nanoparticles within its maximum capability.

3.11 Effect of Other TMONPs

While no sedimentation of other MONPs was observed upon addition of APTES, their potential interference with ZnO sedimentation was determined individually by testing 1:1 mass ratio mixture with ZnO nanoparticles. Figure 11 shows the separation outcomes of each mixture, where both TiO$_2$ and CaO nanoparticle mixtures were coagulated but failed to form a sediment adhering to the vial bottom. CeO$_2$ formed a less structured sediment on the vial bottom and some nanoparticles remained suspending in the supernatant. Neither CuO nor

![Fig. 9](image1.png) UV-Vis spectra (A), sedimentation effects (B) and removal efficiency (C) of ZnO nanoparticles dispersion treated with 0.5 %–2.5 % v of APTES

![Fig. 10](image2.png) UV-Vis spectra of 0.5 mg/mL to 2.5 mg/mL of ZnO nanoparticles dispersion treated with 2 % v of APTES for 24 h

![Fig. 11](image3.png) UV-Vis spectra of ZnO and other MONPs mixture after 24 h sedimentation using APTES. Sedimentation effects are visible for CuO, CeO$_2$ and Al$_2$O$_3$ (inset)
Al₂O₃ nanoparticles have any influence on the sedimentation structure. The UV-Vis spectra show that all five MONPs have relatively low or insignificant intrusion to reduce the sedimentation of ZnO nanoparticles using APTES (Fig. 11). Thus, this method could be applied for the simultaneous removal of other toxic MONPs during the sedimentation of ZnO nanoparticles.

### 3.12 Membrane-assisted Removal

To study the surface adhesion of APTES-ZnO sediment for facile disposal, a filter paper or mixed cellulose ester (MCE) membrane was placed on the glass vial bottom to collect the APTES-ZnO sediment. Figure 12 shows the appearance of APTES-ZnO deposited on either the filter paper or MCE membrane in a thin layer. The MCE membrane affords a condensed structure of deposit and thus can be retrieved from the water on top and regenerated by ultrasonic cleaning for reuse.

### 4 Conclusions

In this work, a simple method using APTES and TCPP was developed to simultaneously detect and remove the presence of ZnO nanoparticles in aqueous suspensions. APTES was found to afford selective removal of ZnO nanoparticles among other MONPs (Al₂O₃, CaO, CeO₂, CuO and TiO₂) in aqueous suspensions through branching polymerization. A web-like sediment that confirmed by FT-IR to have APTES-ZnO conjugation settled down onto the container bottom with high removal efficiency over 99 %. A colorimetric indicator of ZnO nanoparticles, TCPP, turned to bright green only in the presence of ZnO and can also verify the completion of removal. The best removal efficiency was found in 2.0 % of APTES by sample volume, which can afford the removal concentration up to 2.0 mg/mL of ZnO nanoparticles. When the sample was treated along with other MONPs, CeO₂, CuO and Al₂O₃ nanoparticles have no interference to the sedimentation effect, whereas CaO and TiO₂ nanoparticles prohibit the formation of adhered sediment layer but still facilitate the coagulation and removal. The settling feature is not selective to surface, therefore with a filter paper or MCE membrane placed on the container bottom, a facile disposal can be achieved by discarding the paper or regenerating the membrane. In the future, this method can be improved by adding a secondary surface reagent to facilitate a faster sedimentation.

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### Authors’ Contributions

EPCL initiated the idea for this review article, WZ performed the literature search and drafted the article, and EPCL critically revised the work.

### Data Availability

Not applicable.

### Code Availability

Not applicable.

### Declarations

#### Conflict of Interest
The authors have no conflicts of interest.

#### Ethics Approval
Not applicable.

#### Consent to Participate
Not applicable.

#### Consent for Publication
The authors give full consent for publication of this work.

#### Research Involving Human Participants and/or Animals
This manuscript does not contain any studies with human participants or animals performed by any of the authors.

#### Informed Consent
Informed consent was obtained from all individual participants included in the study.
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