

A Review on the Removal of Dye, Pesticide and Pathogens from Waste Water Using Quantum Dots

Kalaiselvi Velayutham Anand, Sandy Subala Anand, Sumathi K. Sripathi,
and Antony Lucia Merin Stanish

ABSTRACT

The industrial pollutants in water bodies tend to unsuitable for living organisms and irrigation uses. Water contamination is exaggerating at regular pace and the universe is holding carcinogenic agents. Therefore, there is a necessity of immediate action to generate a potential and efficient technology for water management. By means of this, quantum dots (QDs) have emerged as an effective probe for the removal process. This review discusses the methods for removing and degrading the coloured components, pesticides, pathogens from waste water and contaminants removal ability of QDs.

Keywords: Carbon Quantum Dots, Chemiluminescence, Methylene Blue, Photo catalyst.

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Kalaiselvi Velayutham Anand*

DMI St. Eugene University, Lusaka,
Zambia.

(e-mail: anandvelu4@gmail.com)

Sandy Subala Anand

DMI St. Eugene University, Lusaka,
Zambia.

(e-mail: sibilandy@gmail.com)

Sumathi K. Sripathi

DMI St. Eugene University, Lusaka,
Zambia.

(e-mail: sumathiksripathi@gmail.com)

Antony Lucia Merin Stanish

DMI St. Eugene University, Lusaka,
Zambia.

(e-mail: luciamerin31@gmail.com)

**Corresponding Author*

I. INTRODUCTION

Water management is a universal question nowadays with the growing demand of freshwater caused by increasing population, domestic usage, and emerging industrial needs. Waste water treatment is the basic and fundamental process to stay clear from polluted water for human consumption. The water bodies are contaminated due to the pollution from discarded items such as coloured materials, pesticides, herbicides, pathogens and heavy metals due to human utilization. Therefore, efficient technology and methods have been implemented for the effective removal of pollutants from sewer water. Several technology and procedures are being adopted for removing and degrading the contaminants during the purification process[1]. Various processes were identified for the development of water purification technologies including coagulation, sedimentation, filtration, chemical purification, ion exchange, reverse osmosis, etc. Even though few water treatment methods are established, the efficiency of the nanomaterials in the water purification could be improved by developing novel filtration membrane, high surface area adsorbents, and other processes [2]. The objective of all these processes is the removal of contaminants from water and to provide clean water. Since nanotechnology emerges,

it has a vital role in waste water treatment due to the ability of biological tomography, particle sensing and heavy metal detection. Different form of water treatment procedures is generated by several research groups around the world by making various nanomaterials into the water treatment process [3]. Numerous nanomaterials have been attempted to validate the removal efficiency and to reduce the cost of the overall process. Even though the commercially available nanomaterial has been utilized for water purification process, several research groups are in the process of synthesizing or developing various nanomaterial systems to improve the efficiency by obtaining various morphologies and different hybrid system. The use of semiconductor nanocrystal or QDs is beneficial over other materials in terms of luminescence, photostability and photocatalyst. The purification performance may vary with parameters such as pH, doping agent and the QDs used for the purification process. The fresh water polluted with coloured impurities from industries become more likely to health issues such as hemolysis, high blood pressure, and respiratory disorder in living organisms [4]. The coloured impurities or dyes are classified into anionic, cationic and nonionic. The dyes used in fabric industries discharged into fresh water bodies leads to contamination of water. These dyes dissolved in water

and produce intense colours with acidic properties. These colourants consume the oxygen in the water [5].

Dyes discharged into water bodies from various manufacturing unit, such as leather, food industry, paper, cosmetics, pharma companies etc. The textile and dyeing industries use large quantities of dyes and expel these colourants into ecosystem as water pollutants. These toxicants are unsafe to living organisms, thus it should be removed from the water resources in order to make it suitable for consumption. These dyes are non-biodegradable and stable to light. They are resistive towards aerobic digestion and meant for the hard groups to be eliminated from the industrial wastewater [6].

Microorganisms and pesticides pose a threat to the universe due to their bio accumulative feature which has negative impact on the environment and human health [7]. By and large, the hazardous chemical detection was tedious and expensive process. However, graphene nano materials in bio sensing techniques plays an important role due to the unique and excellent electronic and optical properties [8].

Photocatalysis is an essential factor for large number of ecological and energy concern at the moment. Herein, semiconductors generally play this role due to their band gaps in the process of absorbing light over a wide range of spectra. This is achieved by the semiconductor in which the absorbed energy should be equal to or larger than the band gap in order to form electron hole pair. Nanoscience research has a strong influence on the development of novel and more influential catalysts through the pattern and properties through with energy gap, composition and modification [9, 10]. Since nanotechnology emerges, QDs are promising materials for photo-catalysis, ions sensing, biological imaging and heavy metal detection.

II. QUANTUM DOTS

Quantum Dots (QDs) are zero dimensional semiconductor nano crystals which is responsible for the light absorption and emission. The optical properties are further enhanced by fencing the core material with semiconductor material which limits the chemical attack. Since the last two decades these materials gain much attention due to the optoelectronic and optical properties [11,12]. A substantial quantity of research is focusing on utilizing the optical properties of QDs in several devices. The distinct feature of QDs is quantum confinement which is observable when the QDs size is small [13]. The important characteristic to be considered in QDs is doping when it is used for technical purposes such as optoelectronic, magnetic and biological applications [14], [15]. The relative position and amount of the dopant decides the optoelectronic and optical properties of QDs [16], [17]. The surface to volume ratio has significant effects on the optical properties [18].

The high cost of inorganic QDs is replaced by cost effective graphene quantum dots (GQD) and carbon quantum dots (CQD). Additionally, the excellent solubility, atoxic, good surface grating and stable photoluminescence making them as a potential candidate in technological applications. CQDs are very small carbon nanoparticles with

high quality photoluminescence, greater degree of stability and conductivity. Owing to its unique properties it has received a wide attention among the researchers [19]-[21]. In general, CQDs can be synthesized by conventional methods such as electrochemical oxidation, laser ablation, hydrothermal/solvothermal treatment, microwave irradiation and arc discharge [22], [23].

The quantum confinement and edge effects the GQDs causes it as a potential candidate in several research fields [24]. Besides, they have unique properties such as low toxicity, greater solubility, chemical stability, photoluminescence stability and excellent surface grating etc. [25], [26]. Further, graphene QDs with intrinsic structures exhibit different selective quenching phenomena there by, making it possible to detect various ions and chemical groups. This concept denotes the fact that within the blue green region of the spectrum a striking energy band of PL characteristic of graphene QD is observed [27].

III. DYE REMOVAL

The fresh water resources are contaminated with the dye stuffs released from the textile, leather and cosmetic industries, results the reducibility of sunlight and prevent the photosynthesis of hydrophytes [28]. Photo catalytic approach is the long familiar method to get rid of these dyes. For example, the N doped CQDs bear distinct properties such as carbon work function reduction, enhancing photoluminescence emission ability and desirable electronic and optical properties. In this sense, N doped Carbon QDs/TiO₂ composites, photodegrade 86.9% of Methylene Blue (MB) compare with pristine TiO₂, it was 53.8% due to the high charge separation in CQDs/TiO₂. It follows dye photosensitization mechanism [29]. In the degradation of fast Green (FG), the cationic dye in the presence of bimetallic Fe@Ag CQDs synthesized by reduction method shows a band gap of 1.9 eV. The low saturation magnetization value shows that their ferromagnetic behavior does not depend upon the non-ferromagnetic Ag. The free radicals produced by Ag attack the adsorbed dye molecules causes the degradation of FG follows pseudo first order kinetics [30]. Whereas the Fe³⁺ doped Zn QDs degrade Methyl Violet (MV), the band gap for the doped QDs are increased due to the internal pressure of Fe³⁺ ions. The decolourization efficiency is decreases with increase in concentration owing to the occupancy of dye molecules at the surface of the catalyst that decreases the number of photons [31]. The photo catalyst behaves different manner in dissimilar medium and the bigger band gap enhances the photocatalytic activity [32]. The Fe³⁺ control the size of the progression of ZnS thus shows a blue shift in UV-Visible spectra. The reduction in sample absorbance than ZnS shows the importance of doping with Fe ions and it was examined by the decolourization of Victoria Blue R (VBR) with different mole fractions. The rate constant for decolourization of VBR decreases with increasing of concentration [33]. The band gap energy connects closely with the photocatalytic activity [34] and the dye molecules acts as the filter in greater amount causes the decrease in

degradation efficiency. This can be prevented by fixing the optimum concentration and 8 mg of capped ZnS QDs removes the VBR effectively [35]. Furthermore, ZnS QDs synthesized by chemical precipitation method using water as the solvent possess the particle size of 3 nm with zinc blende structure shows the most eminent photocatalytic activity against malachite green at pH 8 and 0.80g/L within 2 hrs [36]. CQDs/N-ZnO decolourizes malachite green, Methylene Blue and fluorescein contaminants to a greater extent under ordinary light of intensity $33 \times 10^3 \pm 5000$ lx. Anti-photo corrosion property of CQDs increases the recycling tendency. Moreover, the band gap of 3.10eV depicts the broader absorption capacity [37]. The GQDs modified with graphene increases the surface charges and surface area in water system induces high remotion, reusability and adsorption selectivity and high dispersion stability due to the electrostatic repulsion afforded by GQDs. This improved surface area break up the harmful coloured pollutants from water. The number of rings in the molecule decides the equilibrium adsorption performance irrespective of the nature of dye. In addition to that, Rhodamine B and Eriochrome Black can be desorbed from the QDs with the help of ethanol and ethylene glycol [38]. The CdSe QDs follows first order kinetics while degrading the coloured compounds such as basic violet 16, Basic Blue 41 and Acid Blue 92. The starch doped CdSe QDs photodecolourize 80 % of malachite green and methylene green within three minutes in the ratio of 1:1000 catalyst and dye using MCR-ALS technique. This photo catalyst does not aggregate even after a long period of time due to the large number of hydroxyl group in complex carbohydrate [39]. The N-GQDs doped into TiO₂ increases the decolourization performance of methylene blue to 85% due to the excitation and transfer of electrons from N-GQDs to TiO₂ which forms oxygen and hydroxyl free radicals that oxidize the dye [40].

The GQD/TiO₂ nanotubes attained by hydrothermal method exhibits yellow fluorescence give rise to the size and functional groups at the surface. The enormous vacancy defects on the QDs leads to the excitation of wavelengths [41]. The raw chemical compound determines the particle size of the QDs. For instance, SnO₂ QDs possess two different sizes with glutamic acid and aspartic acid due to the nature of the molecule present in amino acids [42]. The impregnation of vertically aligned TiO₂ with GQDs exhibits superior and highly stable photo decolourization of methylene blue even after numerous cycles [43].

IV. PESTICIDE

It was proved that QDs can detect the pesticides even the existing concentration is below the regulatory limit. There is an advantage of doped QDs such as prolonged emission life time and less cytotoxicity over the undoped QDs [44]. The silica incorporated QDs are employed in creating fluorescence sensors to detect pesticides that, increase the chemical stability and decrease the photo bleaching effect [45]-[47]. The conjugation of QDs with macrocyclic molecules with cavities entails the pesticide detection.

Moreover calix[n]arene used as the receptors for pesticide selectively by changing the size of calix[n]arene. For instance, CdTe designed with p-sulfonatocalix [4] arene are employed for the detection of fenamithion and acetamiprid [48].

The incorporation of GO into NGQDs enhances the ElectroChemiluminescence (ECL) ability extremely with low onset potential. The behavior of ECL with S₂O₈²⁻ as a co reactant shows a strong ECL and the intensity is increases with increase in concentration of coreactant. The multipurpose chemical pentachlorophenol (PCP) is the very toxic pollutants. The permitted level in potable water is 9.85 ng/mL [49], [50]. Graphene Oxide fabricated NGQDs exhibits excellent ECL in which graphene oxide (GO) behave as an immobilization platform and exaggerate the signal. The presence of Pentachlorophenol (PCP) decrease the ECL intensity through the oxidation into chloranil and the Relative Standard Deviation is (RSD) down to 2.2 % at pH 8.0 with limit of detection 0.03 pg/mL confirms its potent reproducibility [51]. When the magnetic silica beads/graphene quantum dots/molecularly imprinted polypyrrole (mSGP) capsulize with silica shows magnetic properties in addition with water dispersibility, selectivity and photoluminescence. mSGP is highly sensitive towards tributyltin than mono and dibutyltin. It is a potential composite to detect tributyltin in sea water with limit of detection 42.56 ppb [52]. The insecticide Oxamyl (N, N-dimethylcarbamoyloxyimino-2-(methylthio)acetamide) enters the human body inhibits the function of human body enzyme. GQDs adsorb the maximum oxamyl at 250 rpm during agitation and this chemisorption follows pseudo second order kinetics. The removal efficiency increases with increase of temperature up to 40°C at 100 mg /L of oxamyl, on account of its strong interaction between the active site of the pesticide and QDs [53]. Moreover, the matrix effect affects the determination of organophosphorus pesticide (OPP) in low concentration level. This effect is suppressed by Magnetic Dispersive Solid Phase Micro Extraction (MDSPME) which separates the pesticide and pre concentrate out of actual sample in single step in which Fe reduced GQDs were used as a sorbent. One of the major advantages of this technique is takes place without any solvent. The extracting tendency is controlled by the type and volume of desorption solvent. Therefore, acetone is used as adsorption solvent owing to its desorption efficiency of 3.5 mins irrespective of the type of OPP. The rGQDs possess very few polar functional groups at the surface enhances the extraction efficiency [54]. The environmental issues due to the use of diniconazole as fungicide and plant growth regulator can be detected using mMIP@CDs/QDs of which the low accessibility of binding site was resolved by MIP [55].

V. PATHOGENS

Microorganisms spreading through water are the causes of dreadful diseases like cholera, typhoid, Diarrhea. The detection of such pathogens is highly important in many fields of engineering sciences and molecular biology. The

current detective technology needs modification or enrichment of the target pathogens in the sample. The unique properties of QDs such as broad absorption and narrow emission spectral profile, resistance to photo bleaching, larger Stokes shift value, composition and size dependent absorption and emission, high molar extinction coefficient value and good quantum yield make it as an excellent material for detecting and identifying the microbes even in a tiny measures [56]. For instance, the water soluble CdSe QDs excite the single wavelength, modify the optical system that measure the fluorescence and create a comfortable path to detect the pathogens [57]. This QDs exhibits extremely higher fluorescence intensity, luminosity and possess high stability than Fluorescein isothiocyanate and Tetramethyl Rhodamine Methyl Ester. Moreover, the binding of the above said QDs takes place at the top layer of the microorganisms [58]. Bio conjugated QDs open up a wider path in the exploitation of pathogenic detective system [59]. For the sensitive detection, the solid phase was formulated using the Immunoglobulin G (IgG) polycarbonate membrane in addition with bio conjugated QDs. It was identified that the immunoassay for this system is extremely sensitive [60]. The three different colours are emanate from different QDs size. The ternary CdSe QDs/ graphene /TiO₂ composite exhibits photocatalytic antibacterial activity against E. coli under visible light, in which graphene/TiO₂ furnish support for the CdSe QDs. The photocatalytic activity against the bacteria damage the cell membrane and discharge the intercellular components [61]. The TiO₂ nano tube increases the sensitivity of CdS QDs.

The GOQDs-Polyvinylidene Fluoride (PVDF) membrane exhibits more desirable bacteriocidal and antibiofouling properties were studied by testing E. coli bacteria of which the flux drop was 67.5% at 12 hrs filtration. The spectral studies reveal the covalent bond formation between GOQDs and PVDF/The anti-biofouling property is decided by means of hydrophilicity which is evidenced by the flux drop of 24.3% [62].

The CQDs prepared from rice straw possess high light emitting capacity; sensitive and specific in bacterial surface and water solubility detect the pathogens effectively [63]. The duple properties photo catalytic and bactericide of CQDs/TiO₂ was investigated by comparing the properties with pristine TiO₂. The pristine TiO₂ acts as a photo catalyst upon irradiation with UV light. Whereas the fabricated QDs exhibits low recombination rate and operate as a photocatalyst under sun light that produce electron hole pairs [64].

VI. CONCLUSION

In conclusion, the studies on QDs shown that GQDs, CQDs and inorganic QDs have significant effect on sewer water treatment. Fe³⁺ ion doped ZnS QDs remove 98% of the dyes from the polluted water effectively and N-GQDs doped TiO₂ bleach the methylene blue efficaciously than the pristine TiO₂. Additionally, CQDs/TiO₂ was the cost effective and efficient photocatalyst for the waste water treatment.

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Dr. K. V. Anand pursued his Ph. D in the year 2014 from Bharathidasan University, Tiruchirappalli, Tamilnadu, India. He is currently working as a Lecturer in the Institute of Virtual and Distance Learning (IVDL) under DMI St. Eugene University, Lusaka, Zambia. To his credit he has published research papers in reputed international journals. His main research work focuses on stress biology. He has 6 years of teaching and research experience.

Dr. A. Sandy Subala pursued her Ph. D in the year 2012 from Acharya Nagarjuna University, Guntur, Andhra Pradesh, India. She is currently working as a senior Lecturer in the Institute of Virtual and Distance Learning (IVDL) under DMI St. Eugene University, Lusaka, Zambia. To her credit she has published research papers in reputed international journals. Her main research work focuses on Liquid crystal. She has 6 years of teaching and research experience.

Dr. Sumathi K. Sripathi is a doctorate from Madurai Kamaraj University, Madurai, on a multidisciplinary concept of academic study. She is at present working as a Senior Lecturer in the Institute of Virtual and Distance Learning of the DMI St. Eugene University, Lusaka, Zambia teaching Biology and allied applications. She has published research papers in multidisciplinary percepts in reputed international journals. Her research work focuses on sustainable development and womanism. She has 37 years of teaching experience with 5 years of research evaluation.

Ms. S. Antony Lucia Merin is working as an Assistant Lecturer in DMI – St. Eugene University, Zambia. She has completed Bachelor of Engineering in the field of Computer Science in Engineering (CSE) at St. Xavier's Catholic College of Engineering, Anna University, Chennai, India. Her Master of Engineering in the field of (CSE – Networking) at Rohini College of Engineering and Technology, Anna University, Chennai India.