

Quantum Dots in Waste Water Treatment- Review Article

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Abstract:- The effluents present in the water resources leads unqualified for various domestic and irrigation purposes. The waste water treatment purely depends upon the volume of contaminants. The objective of the study was to gives a detailed discussion about the chemical methods and different types of QDs involved, examining their effluents removing efficiency, the selectivity and sensitive detection of various chemicals present in the contaminated water bodies.

Keywords:- Graphene QDs, CdS QDs, Photolysis, Photoelectron catalysis, photon shielding effect.

I. INTRODUCTION

Water is globally considered as most crucial component for the endurance of life, nevertheless the fresh water resources are endangered by human activities. The gradual industrialization discharged innumerable quantity of chemicals leads to various diseases, damages the ecosystem and threatens the global life[1].The released pollutants mixed with ground and surface water impairment the human health and the ecosystem. Moreover, clean and pure water is the fundamental need for the human's healthy life. Thus, it is required to process the polluted water for several purposes like drinking, irrigation and industrial processes. Researchers follow several treatment methods to obtain the fresh water [2]. The presence of pollutant even in low quantity pollutes the water and soil aggravatingly [3]. The hazardous and carcinogenic effect decides the type of pollutants [4]. Organic compounds are the important pollutants released from the manufacturing unit[5]. These organic pollutants deplete the dissolved oxygen cause a risk to human health [6].

It is reality that the heavy metals are non-biodegradable, likely to cause carcinogenic effects on human beings lead to alter the gene expression and oxidative stress in living organisms by combining with dependent protein [7]. However, the extended use of organophosphorus compounds in agriculture fields percolated into water resources that reduce the grade of water rigorously. The surface water mixed with trace of chemical substances that contaminates the drinking water potential [8]. The spillage of petrochemicals and oil from industry and urban discharge plays a vital role in the contamination of marine water [9]. Most industries need a good amount of fresh water for proper functioning, however the effluents discharged from the industries causes side effects to human health [10].

Owing to this, the quality of the water is declined and it is desirable to inhibit the contaminants by exploitation of affordable and high efficiency water treatment technologies.

Moreover, the most permeative challenge should be preserve the existing fresh water bodies to meet the growing water demands [11] and in the next forty years the demands on water will increase gradually due to global population [12]. It can be achieved by better water treatment technologies like adsorption, RO purification, UV purification, coagulation and floatation. The working principle of these technologies differs from one another in terms of degree of pollutants, maintenance and operation. During the last two decades significant quantity of research is focussed on the potential application of quantum Dots in water treatment emerged and ignited tremendous research interest due to its unique properties.

II. QUANTUM DOTS

The semiconductor nano crystals are recently emerging nano materials best known as Quantum Dots (QD) which have large surface to volume ratio, zero dimensional specific inorganic metals with nano scale size particles having optical and electronic properties in which the excitation of electrons between valence band to conduction band is confined in three spatial directions, which has an ability to produce extreme bright fluorescence that helps to detect the single particle [13, 14, 15]. However, this quantum confinement effect, the outstanding property that increase of band gap energy with decreasing of nanoparticle diameter below certain value makes the quantum dot as artificial atoms and the measure of the energy gap depends on the size of QDs [16].It can be said that, very few number of atoms in QDs separates the energy levels in considerable degree, results the existence of atomic like wave functions [17].

Fluorescent carbon based nano material possessing unique electronic properties along with large surface area, reducing and oxidizing ability recognized graphene as a most important component in novel sensing platforms [18, 19]. The electronic properties of graphene has given an origination of graphene based sensors that can detect charge changes in different concentration media there by, helping in identification of surface functional groups and adsorbates at small level [20]. Undoubtedly, in these QDs one can identify abundance surface groups which are capable of strong photoluminescence (PL).The most

effective light effect of PL is always for a discussion. Since the observed PL centre have Quantum confinement effect conjugated domains and surface edge state encompassed within the structure. The unified effect of the above two states are taken for a greater impecunious of the study of graphene QDs [21].

The UV region of the visible light is the focus of absorbing graphene QDs. The concept of photoluminescence (PL) is stable within the UV light yet, it shows weak photo-bleaching [22]. This effect may be due to surface state and quantum size effect of the PL emission in graphene QDs. It has to be understood that the influence of single or multi layers in graphene QD is taken into concern [23], as a PL can also be quenched through selective doping of specific cations, anions or chemical groups [24,25]. Collaborating these features, it is evident that graphene QDs serve as effective sensors for PL detection by “turn-off” model. 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 denote the fact that within the blue green region of the spectrum a striking energy band of PL characteristic of graphene QD is observed [26].

III. WASTE WATER TREATMENT

The ionic form of hydrogen sulphide reduces the oxygen concentration in water leads to nervous system damage in human beings. It was required to find out the suitable techniques to treat the water for human and irrigation purposes. Comparatively methods adopted with QDs techniques are excellent water purification performance [27,28]. The selectivity and sensitive detection of H₂S in waste water is made possible through the strong bond created with doping element and consecutively followed by reduction which affects the intensity of fluorescence, which is not common ion found in water resource [29]. Ag-doped CdS QDs capped by MercaptoAceticAcid (CdSAg-MAA QDs) with size 3.3 nm, pH 5.0, limit of detection 3nM and Relative Standard Deviation is 0.54% served as an effective fluorescence probe due to their exact band edge of 2.4 eV that provides the high photo catalytic activity for enhanced chemical transformation [30]. However, the poor photochemical stability is overcome by doping the CdS along with the semiconductor of the element. At this stance, the doping of CdS QDs with Ag is taken as a popular and effective example owing to the high exchange current density with low activation energy of Ag [31,32]. At the same time, the co-stabilizing agents increase the detection selectivity for H₂S in the waste water. As a major predicament of reality, graphene QDs combined with Cu²⁺ have been used as the fluorescence probe for sulfide detection [33]. This fluorescence probe is highly selective and sensitive for S²⁻ in any water sample that contains anionic interferences with a limit of detection of 0.10 µM.

The coloured materials in water was treated through direct UV photolysis and ozonation techniques that study the use of QDs in waste water that take the colouration of the reaction of reactive blue 137 and toluene if it gets to mix in that water. The catalytic potential of the QDs were studied with the assistance of CdSe/ZnS core-shells. It was investigated that QDs acts as an additional pollutant rather the catalyst [34]. Further the semiconductor QDs Zn or Cd exhibits inhibitory effect upon UV radiation. In fact the photon shielding effect of the semiconductor QD is observed as it diminishes the efficiency of photolysis. Moreover, the illumination of semiconductor particle by UV light causes the electrons transferred from the valence band to conduction band that creates an electron-hole pair at the semiconductor nano particle surface. Simultaneously, the Photo generated electrons are able to react with adsorbed electron acceptor which can be taken as dissolved oxygen from its protonated form.

At an estimated analysis, it is found that 16 % semiconductor QD consisting of Cd or Zn helps to reduce the concentration of the colour after 60 minutes of a reaction. It is observed that the physical properties and reactivity of nano particles vary to a larger extent as a function as a function of size [35, 36]. Ahmad et al investigated the biofouling, major disadvantage of Forward Osmosis for the first time using integrated GQDs with size 3.4 – 8.8 nm in polyamide (PA) layer of thin film composite (TFC) membrane in which the water contact angle falling drastically leads to the decrease in solute and water permeability ratio. The resulting Thin Film Nanocomposite (TFC) shows excellent antibacterial behaviour. It is observed that the reference of GQDs integrated with polyamide matrix adds the essence to the hydrophilic attributes of the TFC membrane there by bringing a change to the antifouling attributes that determines the characteristic properties of forward osmosis being done with the bacteria [37]. The anti biofouling property of *Escherichia coli* showed that the GOQDs-PVDF (polyvinylidene fluoride) exhibits excellent biofouling resistance rather than other modified PVDF membranes. The TFC membranes are effective in biofilm formation when compared to the graphene oxide membrane [38].

Furthermore, the homogeneous CdTe capsulized wurtzite structure of ZnO nanorods with band gap 1.5 eV that is fabricated through layer-by-layer exhibits an excellent photovoltaic effect, serves as a potential matrix for degrade phenol from waste water. The incorporation of CdTe with ZnO enhances the photocatalytic efficiency of ZnO. This is done through the process of photoelectron catalysis which works on strong absorption of visible light creating the degradation efficiency is 75%. The photocurrent efficiency depends on the length of nano rod exclusively. The CdTe-ZnO composite degrade phenols more effectively through photoelectrocatalytic technique [39]. Besides that, the resultant photoluminescence (PL) creates quenching that separates the charge carriers between ZnO and CdTe [40, 41]. This leads to optimization of CdS QDs by means of Fractional Factorial Design (FFD) technique which

enhanced using sodium thiosulfate which serves as a substitute for TiO_2 due to the effective photocatalytic activity. The enhanced constituent attribute is the reusing constancy of the coloured compounds under the visible radiation in this process [42]. Further, the superoxide and $\cdot\text{OH}$ serve as the participating intermediates leads to the degradation of dyestuff [43,44].

The reference to fluorescent chemosensors was of great importance as they work upon the ions in solution to a greater degree [45]. The presence of Fe^{3+} and Hg^{2+} ions can be easily detected using fluorescent N-GQDs and SN-GQDs in waste water through solvothermal method. The fluorescent is proportional to the variation of excitation wavelength but remains stable at a pH range of 3.5 -9.5, below this limit the fluorescence intensity decreases and above this range it increases [46].

The intriguing properties of carbon QDs degrade the coloured pollutants upon irradiation with infrared and visible light [47]. Here in as previously referred the low photoluminescence of CQDs/ TiO_2 composite nano fibres could remove the entire methylene blue within a short period of time 95 minutes which was a faster rate in comparison to pristine TiO_2 nano fibre. An assessment on photo catalytic activity which decreases with the consecutive cycles was brought into reference [48]. Another mechanism that reflects on trapping of electro-hole pairs at the surface of OH radicals brings the degradation of cationic dyes in solution. The SnO_2 QDs fabricated with Mesoporous Silica Nanoparticles (MSN) in relevance to cationic dye behave as a potent adsorptive in the removal of dye ions from the factory waste water. At the same time, the concentration of ammonia and size of the molecular particle is taken for study specifically with 0.3 mL of NH_3 . In the recyclable experiment on dye degradation process SnO_2 QDs are found to be very favourable. This process follows pseudo second order kinetics in its techniques and greater negative zeta potential of -48.05 mV is found in existence of QDs in the bulk of SiO_2 material [49].

Another interesting concept in this waste water treatment would be the study of photo catalytic fuel cells which play an important role in the waste water treatment. In this fuel cells are excellent source for harvesting solar energy is created using 1.2 μm CdS fabricated with 10 nm TiO_2 . Light is a source of irradiation of photo anode in this mechanism thereby forming water in the presence of O_2 in the waste water and at the same time converting the contaminant into electrical energy or H_2 fuel. In such a photo catalytic fuel cell a possibility for formation of electricity was confirmed. The process conformation was enhanced with electrode reaction using acetic acid electrolyte. It is interesting to note that the power density of maximum production accounting to 3980 mW/cm^2 can be produced with enhanced electrolytic conductivity of 63.1 mS/cm [50].

An analysis on pharmacopanies on the production of steroid drugs with residual discharge into the water bodies for taken into study. It is because the consumption of such water knowingly or unknowingly by human is life threatening. The solar light intensity of 75.6 k lux is used to degrade these pollutants to 97%. Along with solar cell intensity, 0.25-0.75 g/L concentration of catalyst is taken in combination to treat 10-40 mg/L of pollutant solution which decreases the pollutant effect gradually and consequent cycles extended by adding 0.5 g/L of TiO_2 QDs. The effective functioning of the catalyst in these depends on the active site with higher concentration of photo catalyst along with pH range from 3-4.4 in the solution [51].

IV. INORGANIC POLLUTANTS

The CdSe/CdS core-shell QDs modified with mercapto ethanol as a fluorescence sensor investigate the presence of Cu^{2+} binds on the surface of the QDs results the displacement reaction with correlation coefficient of 0.9921 [52]. The defects of organic probe as the fluorescence were overcome by the inorganic probes owing to its rapid response time and stable fluorescence. The capping of CdS-MAA (Mercaptoacetic acid) QDs with thiourea detect Pb, Hg and Cu ions present in sewer water [53]. Consequently CdTe-MPA (CdTe-3Mercaptopropionic acid) QDs have excellent photo stability, anti-bleaching properties, real time and on-site detection recognize uranyl ions with fluorescent linear concentration range from 0 to 520 nM with pH 6.5-7.4. MPA was very toxic at low concentration conversely; toxicity was reduced at high concentration [54]. Whereas, CdTe/ZnS capped with MPA at pH 7.4 detect copper ions selectively and quantitatively with relative standard deviation 0.23% and limit of detection 1.5×10^{-9} M. The toxicity of the QDs were limited with aid of Zn doping [55]. The discharge of uranium and their compounds from nuclear power plants were harmful to living organisms. It was vitally necessary to devise an acting technique to recognize and purify the water polluted with the harmful chemicals. Comparatively CdTe-MPA QDs with size 4.2 nm determine the uranium content in waste water at neutral condition with lower detection limit of 4 nm than the CdS/MAA QDs. The short time on-site detection shows its ability towards the uranium compounds. Whereas, the negatively charged impurities in lake water decline the recovery rate of uranyl ions [56].

The relatively low electrocatalytic activity of nitrogen doped GQDs were further enhanced by doping with carbon nano tubes recognized the collection of inorganic pollutants from sewer water in addition with the targeted impurity Cr(VI) ions. The selective detection of Cr(VI) ions solely depend on the pH of NGQDs [57]. N-doped graphene quantum dots decorated N-doped carbon nanofibers (NGQD@NCNFs) with pyrrolic -N exhibits electrocatalytic activity with highest quality detection of nitrite ions with detection limit 3 μm . In a relative manner the particle size was larger than the pristine NGQDs. The doping of carbon nano fibers with nitrogen speed up the rate of electron transfer. The sensitivity towards the

hypochlorite was evaluated by comparing the effect of surface coating on different types of QDs. The inert polymer coated QDs possess high sensitivity towards HClO whereas the reactive coated QDs reduces the sensitivity of HClO. QDs-polyCO₂ was the potential material for the investigation of HClO than QDs-LACNMe₂, QDs-LAC-NHMe and QDs-poly-NHMe. The exchange of ligands and surfacing does not affect the size of the QDs. Comparatively, alkylamines are better scavenger for HClO than the thiols [58]. The traces of GO can be recovered using GQDs utilizing ultrasound energy where the pH was maintained at 7. Considering the solvent, water shows excellent fluorescence effect than methanol. For the detection of GO the organic impurities from the water should be removed using NaOH solution [59]. The pristine GQDs detect the Cu²⁺ ions, in which the metal ions turn off and the biothiols cysteine turn on the Photoluminescence of pristine GQDs [60]. Instead of altering the capping layer the changing of crystal size recognized the ionic impurities from water selectively. GSH (Glutathione), a peptide identifier capped CdTe QDs had no quenching effect on alkali and alkaline earth metal ions [61].

Furthermore, MES-CdSe QDs (2-mercaptoethane sulfonate-CdSe) detect the cyanide anions via partially dynamic quenching, due to its toxicity the pH was maintained higher than 9.0 [62]. The colour of the fluorescence depends on the size of the CdTe QDs, The larger QDs emit red and smaller one emits green fluorescence and the colors can be seen with naked eye. The continuous change of colour was observed with varying concentration of copper ions [63]. The quantum yield of N-GQDs were extremely higher than GQDs. The π -rich chelator ligninsulfonate improve the fluorescence while detecting the Fe³⁺ ions selectively with limit of detection 0.5nM. The fluorescence effect of SL/GQDs are outstanding in neutral condition, the selective detection was caused by the greater thermodynamic affinity and the quick chelating effect of iron ion with the QDs [64]. The excitation dependent PL was observed in GQDs associated with polyaromatic hydrocarbons and the outstanding behavior was tuning the wavelength and the range of emission wavelength [65]. The photoluminescent (PL) GQDs with size 5-10 nm was a potential sensor for Fe³⁺ and H₂O₂. The sensing of Cr(VI) using N-GQDs follow the reduction to Cr(III) [66]. The undoped GQDs exhibits surface action for Fe³⁺ quenching, whereas, the N-GQDs possess static and dynamic quenching [67].

V. CONCLUSION

The functioning of Quantum Dots on the investigation of various kinds of contaminant in the wastewater and their performance were discussed. The degradation ability depends on the doping of materials on QDs. Conversely, every technique brings forth excellent result for distinct impurities.

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