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### **Credit Author Statement:**

*Th. Babita Devi*: Conceptualization, Methodology, Data curation, Writing- Original draft preparation. *M. Ahmaruzzaman*: Supervision, Writing- Reviewing and Editing.

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### **Graphical abstract**



### Facile synthesis of rGO/Ag@AgCl core-shells nanocomposite and their multifunctional efficacy as a photocatalyst and antimicrobial agent for decontamination of water

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### Abstract

An environmentally friendly process for synthesis of rGO/Ag@AgCl Core-shells nanocomposite was developed by Bitter gourd leaf extract. The core-shell morphology was confirmed by STEM-EDX line profile and elemental mapping images. As-synthesized nanocomposite was utilized as photocatalyst for degradation of Clofibric acid (CA) and Naphthol Green B (NGB) from aqueous phase under solar irradiation. As-synthesized nanocomposites showed photodegradation up to 98% of CA and 98.7% of NGB within 40 and 30 min, respectively. Here, we also investigated the optimum amount of nanocomposites for the photodegradation process. ESR analyses confirmed that the active species such as hydroxyl and superoxide anion radicals were mainly accountable for the degradation of organic pollutants. The presence of rGO enhanced the catalytic activity of Ag@AgCl NPs. The as-prepared nanocomposite was also utilized for the removal of biological impurities against bacterial strains. Hence form the present study, it was confirmed that the synthesized rGO-Ag@AgCl nanocomposites act as a potential material for wastewater treatment.

Keywords: Reduced graphene oxide; Clofibric acid ; Naphthol Green B; photocatalyst.

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### 1. Introduction

Recently, the treatment of industrially polluted waste-water which is hard to remove from aqueous phase biochemically is a significant zone of research worldwide [1-2]. The paper, textile, and wood industries are mainly responsible for the pollution of water. Such types of industry are users of toxic elements, dyes, and solvents for dyeing. It was consumed above 60% of toxic dyes and many of them, containing one or more toxic and explosive chemicals for such type of purpose. Recently it was observed that Naphthol Green B dye used for the dyeing purpose. Naphthol Green B (NGB) dye, is a radical configuration consisting of conjugated double bonds containing delocalized electrons, which containing chromophore groups, such as azo (-N=N-), nitroso (-NO or N-OH), nitro (-NO<sub>2</sub> or =NO-OH), sulfur (C=S) [3]. Such azo dyes are very highly toxic, and their by-products (degraded) are carcinogenic and cause significant environmental and water harm.

Nowadays, the psychotropic drug is highly consumed for the treat symptoms of mental disorders such as depression, schizophrenia, bipolar disorder has a disability angiocardiopathy problem, such as coronary heart disease, high blood pressure, arrhythmia, and cardiac function failure [4-11]. Among those pharmaceutical compounds, Clofibric acid (CA) is utilized for the treatment of diseases, such as coronary heart disease, high blood pressure, arrhythmia, and cardiac function, and epilepsy. It is highly motile and very persistent in the environment (lakes and rivers) because it is non-biodegradable [12-13]. Thus, it is very important to remove such organic and pharmaceutical pollutants from the environment and water purification.

Adsorption process is commonly utilized for removal of such type of toxic drug from aqueous phase because of its simplicity and general applicability [14-16]. However, such type of method created some problems during separation efficiency. The formation of secondary by-products is

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the main disadvantages of the adsorption process. Nowadays, Sunlight-induced degradation process is one of the most simple and green approaches for removal, such type of toxic elements from aqueous phase [17].

From the literature, it was observed that  $TiO_2$  photocatalyst has been widely considered as a traditional photocatalyst because of its non-toxicity as compared with other metal nanoparticles (such as silver and gold) and long-term stability [18-20]. However, some drawbacks are associated with the practical application of  $TiO_2$  photocatalyst because of its high band gap. Therefore, several researchers carried out experiments to prepare very effective photocatalytic materials for removal of various contaminants from aqueous phase [21-22]. Recently, it was observed that hybrid NPs and nanocomposites have been used in different application [23-28]. But X-hybrid/nanocomposite (X=Ag/Au) were showed an excellent photocatalytic material for elimination of such noxious compounds. Recently, reduced graphene oxide is utilized as a phase matrix for the development of nanocomposites and its subsequent application for photocatalytic removal of various organic contaminants from aqueous phase [29-31]. The polluted water contains various types of unwanted pollutants, such as toxic elements, microbes, fungi, etc. Due to the high surface area of graphene, it can sufficiently absorb such toxic particles into the surface pores of rGO. The high specific surface area allows more metal ion (attached on the surface of rGO) to come into full contact with its inner surface and damages bacterial cell wall [32-35].

Hence, main objectives of this present investigation are summarized below:

(i) Fabrication and characterization of plasmon-induced reduced graphene oxide nanocomposites using various techniques.

(ii) CA (drug) and NGB dye was selected as target compounds and degraded these toxic compounds using as-synthesized nanocomposites.

(iv) To examine the antimicrobial activities of the synthesized rGO-Ag@AgCl nanocomposites. Herein, we report, for the first time, the preparation of rGO-Ag@AgCl nanocomposites using bitter gourd (medicinal plant) leaf extract.

The chemical structure of Clofibric acid and Naphthol Green B dye were given below:



### 2. Materials and Method

### 2.1. Materials

Reduced graphene oxide was purchased from Nanoshel LCC Punjab, India and Clofibric acid [2-(4-chlorophenoxy)-isobutyric acid] and Naphthol Green B (trisodium, iron (III), 5-nitroso-6oxidonaphthalene-2-sulfonate) were purchased from Merck Ltd. India. All solutions were prepared in double-distilled water.

### 2.2. Synthesis of reduced graphene oxide loaded Ag@AgCl nanocomposites (rGO-Ag@AgCl)

Ag@AgCl nanoparticles were synthesized using Bitter gourd leaf extract. The method for the preparation of Ag@AgClNPs was modified, as mentioned in previous work [36]. The MC leaf extract was added dropwise in 20 mL of AgNO<sub>3</sub> (0.001M) solution under stirred condition and

reaction mixture was changed into brown color within 10 min. About 30 mg of rGO was dispersed in 300 mL colloidal solution of Ag@AgCl NPs and stirred at room temperature for 24 h. After 24 h, brown color of nanoparticles was changed into a black and indicated formation of rGO-Ag@AgCl nanocomposites. The growth mechanism of rGO-Ag@AgCl nanocomposites was shown schematically (Scheme 1).

# 2.3. Photodegradation of hazardous dye and pharmaceutical compound rGO-Ag@AgCl nanocomposites as photocatalyst

The optimization study of catalysts also reported in this present work. The experiment was carried out by keeping a solution concentration of 10 ppm for both NGB and CA. To evaluate optimum amount of catalyst, the experiment was carried out by changing the amount of catalyst from (0.01 to 0.05) gm in 250 mL of NGB and CA solution. Here the catalysts were added in each 250 mL solution of NGB and CA solution and checked the catalytic activities. It was found that photodegradation efficiency increased with increase in catalyst amount from 0.01g to 0.025 g. However, the efficiency of photodegradation is decreased with increase in catalyst amount from 0.03 g to 0.05 g. The optimum amount of the catalyst was observed to be 0.025 g in the degradation of both NBG and CA from aqueous phase [37-39].

In a photocatlytic experiments, specific amount of photocatalyst (0.025 gm) suspended in 250 mL of 10 mg/L aqueous solutions of CA and NGB. CA and NGB solutions were kept in a dark environment under agitation for 30 min to achieve the adsorption-desorption equilibrium followed by exposure to sunlight (average solar radiation ~4.29 kWh/m<sup>2</sup>/day) for photodecomposition [37]. A total of 4 mL of NGB and CA aqueous suspensions were withdrawn, centrifuged and recorded by noting the absorbance at their respective  $\lambda_{max}$  after every 10 min.

### 2.4. Recycling of photocatalysts

The life span of a catalyst for a longer period leads to a considerable decrease of cost. It is very important to check the reusability of rGO-Ag@AgCl. The details of the recovery of the photocatalyst and their subsequent use in photodegradation were reported in our previous study [36]. The recovered catalysts were reutilized for photodegradation of NGB and CA upto fourth cycles, and their catalytic losses were also calculated.

### 2.5. Antimicrobial activities of rGO-Ag@AgCl nanocomposites

The biological activities of nanocomposites were also investigated by Kirby Bauer or Disc standard disc diffusion method. Here we used two different gram-negative and gram-positive bacteria like *Pseudomonas aeruginosa* (*P. aeruginosa*), *Escherichia coli* (*E. coli*), *Staphylococcus aureus* (*S. aureus*), and *Staphylococcus epiderminis* (*S. epiderminis*). The details of experiments for antimicrobial activities were reported in our previous study [40]. After 24 h of incubation, the zones of inhibition (mm) were calculated using standard scale. Here, code B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub> and B<sub>4</sub> were presented the *Staphylococcus aureus* (*S. aureus*), *Escherichia coli* (*E. coli*), *Pseudomonas aeruginosa* (*P. aeruginosa*), and *Staphylococcus epiderminis* (*S. epiderminis*). The Code 1 represents rGO-Ag@AgCl, Code 2 presents rGO and Code 3 AgNO<sub>3</sub> solution.

### 2.6. Characterization

The synthesized rGO-Ag@AgCl nanocomposites were well characterized by various analyses. Here we investigated the absorption pattern (UV-visible), Powder X-ray diffraction (XRD) patterns, morphology and diffracted ring pattern (TEM, AFM and SEM), the functional groups (FT-IR), element mapping (S-TEM, EDX and EDX line profile analysis), elemental composition and chemical status (XPS), radical determination (ESP), and the surface area and pore size of nanocomposites (BET). We adopted the same method and instrument as mentioned in our previous work [36].

### **3 Results and Discussion**

### 3.1. Ultraviolet-visible spectroscopy

The optical absorption properties of the synthesized Ag@AgCl/rGO nanocomposite were investigated using UV-Vis spectrophotometry and represented in Fig. 1 (a). The broad band centered at 460 nm was attributed to the surface plasmon resonance (SPR) of Ag nanoparticles. The UV cut-off in the range 280 – 320 nm can be ascribed to the photo-excitation of electrons from valence band (VB) to conduction band (CB) of AgCl and the sharp peak centered at ~230 nm can be assigned to the  $\pi$ - $\pi$ \* transition of aromatic C=C bonds of rGO. The surface plasmon resonance of Ag nanoparticles can induce enhanced light absorption capacity to the Ag@AgCl photocatalyst and the hybridization with rGO may increase the life span of photogenerated excitons by delocalizing electrons to the C=C backbone [40]. Therefore, Ag@AgCl/rGO is believed to have high light absorption capacity and low charge recombination rate which can synergistically enhance the photocatalytic property of the engineered nanohybrid.

Further, to determine the direct band gap energies of the Ag@AgCl/rGO nanocomposite, Tauc's theorem can be employed using the following equation [41-42],

$$(\alpha hv)^2 = A(hv-E_g)$$

where h is Planck's constant,  $\alpha$  is the absorption coefficient,  $\mathbf{v}$  is the photon frequency,  $E_g$  is the band gap energy and A is a proportionality constant. The X-axis intersection point of the linear fit of Tauc's plot gives an estimate of the band gap energy. The Tauc' plot showed two possible tangents corresponding to surface plasmon resonance of Ag nanoparticle and electronic

excitation of AgCl semiconductor nanoparticle (Fig. 1(b)). The calculated band gap energies for Ag and AgCl using Tauc's method were found to be 1.8 eV, and 3.7 eV respectively.

The conduction band (CB) and valence band (VB) positions of AgCl can be calculated from the following equation [43],

$$E_{CB} = X - E_c - 0.5E_g$$
$$E_{VB} = E_{CB} + E_g$$

where X is the absolute electronegativity of the semiconductor ( $X_{AgCl} = 6.07 \text{ eV}$  [43]), Ec is the energy of free electrons in hydrogen scale (4.5 eV),  $E_g$  is the band gap energy,  $E_{CB}$  and  $E_{VB}$  are the conduction band and valence band potentials, respectively. Accordingly, the  $E_{CB}$  and  $E_{VB}$  of AgCl were calculated to be -0.28 eV and 3.42 eV, respectively.

#### **3.2.** Morphology studies

#### 3.2.1. Scanning and Transmittance electron microscope

Surface morphologies of inner and outer surfaces of the nanocomposites were investigated by scanning and transmission electron microscope. Fig. 2 (a-b) demonstrates scanning electron microscope (SEM) and transmission electron microscope (TEM) images of rGO-Ag@AgCl nanocomposites. From SEM and TEM images, shape and average particles size of nanocomposites can be calculated. From the SEM image, spherical shape of nanocomposites was observed and calculated average particles size was found to be ~40 nm. TEM images of rGO-Ag@AgCl nanocomposites showed that a core-shell shape was formed. The core and shell structure was clearly identified by brightness differences between the silver and silver chloride of the particles. This was due to the difference of densities between Ag and AgCl atoms [44-45]. The core and shell NPs Ag@AgCl were further attached on the surface of the reduced graphene.

The calculated shell thickness and average particles size, from TEM image were 3 and 10 nm, respectively. Here the shell thickness was found to be 3 nm, therefore Ag core was also marked in plasmonic contribution [44-46]. Fig. 2 (c-d) displayed HR-TEM and SAED pattern of rGO-Ag@AgCl nanocomposites. The calculated d-spacing value from HR-TEM images corresponds to the (111) plane of Ag crystal and (222) plane of AgCl crystal respectively. The SAED pattern revealed the polycrystalline nature of the nanocomposites. The d-spacing values were calculated from the SAED pattern and observed to be 0.138, 0.195 and 0.0876 nm and corresponds to the lattice plane (400), (220), (620) of fcc structure of AgCl, respectively and 0.116 nm corresponds to lattice plane (222) of Ag (fcc) structure.

### 3.2.2. Atomic force microscope microscopy

Further, the core shell morphology was confirmed by AFM (Atomic force microscope) analysis. The AFM was performed in contact mode and image was returned in two forms: 3-dimension (3D) topography and 2-dimension (2D) scan as seen in Fig. 2 (e-d). In the 2D image of AFM the formation of core-shell morphology was clearly observed. The nanocomposites showed monodispersed and well separated from each other.

### 3.3. X-ray Diffraction Pattern analysis

Fig. 3 (a-b) displays XRD spectra of reduced graphene oxide (rGO) and rGO-Ag@AgCl nanocomposites. The XRD pattern of rGO showed a broader peak at 23.74° and 43.8° and appeared as the peak of graphite (amorphous) (JCPDS Card no.75 -1621). All peaks were corresponded to (002) and (101) planes of graphite with d-spacing values of 0.339 and 0.204 nm [47-48]. The peaks at 32.2°, 46.2°, 57.6° and 67° corresponded to the lattice planes of AgCl (planes (200), (220), (222) and (400)) and reflected the face centered cubic (fcc) structure of crystal (JCPDS File No: 131-1238). The remaining peak at 44.2° was due to the lattice planes (200) of Ag and reflected the

face centered cubic (fcc) structure of Ag (JCPDS file: 65-2871). The board peak at 24.74° corresponds to (002) plane of graphite. The JCPDS data number 225, demonstrated that NPs have a space group Fm3m (for Ag and AgCl) and edge lengths were found to be 4.079 and 5.549 for Ag and AgCl, respectively. The crystallite particle size of Ag and AgCl atom were calculated from the XRD spectra. The calculated average crystallite particle sizes were 12 and 25.5 nm for Ag and AgCl, respectively. The crystallite particle size of rGO was not determined because of amorphous structure.

# **3.4.** X-ray photoelectron (XPS) and energy dispersive x-ray (EDX) spectroscopy analysis

The elemental composition and chemical status of the nanocomposites were investigated by XPS and EDX analyses. Fig. 4 (a-d) displays XPS spectra of Ag (3d), Cl (2p), C (1s) and O (1s) respectively. Fig. 4 (a) shows the Ag 3d spectra and further Ag 3d region fragmented into the two components and coexist in Ag3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub> signals, respectively. These two peaks may be divided into two peaks at 366.55, 367.58 eV and 372.58, 373.58 eV, where the peaks at 366.55 and 372.58 eV for the Ag<sup>+</sup>, and those at 367.58 and 373.58 eV are attributed to metallic Ag<sup>0</sup>. Hence from the XPS spectra of Ag 3d, it was confirmed the presence of Ag<sup>0</sup> and Ag<sup>+</sup> in rGO-Ag@AgCl nanocomposites. The binding energies of Cl ( $2p_{1/2}$  and  $2p_{3/2}$ ) are approximately 197.76 and 196.24 eV. In XPS spectra of C1s, five deconvolution peaks correspond to the C=C (283.15 eV), C–C (284.7 eV), C–O (hydroxyl, 285.76 eV), C=O (carbonyl, 287 eV), and O–C=O (carboxyl, 288.2 eV) groups, respectively. The binding energies of O (1s) 531.8 and 532.3 eV are associated with oxygen in the states of C=O and C–OH/C–O–C, respectively. The survey spectra of rGO-Ag@AgCl were demonstrated in Fig. 4 (e).

Elemental compositions of rGO-Ag@AgCl nanocomposites were also investigated by EDX (Fig. 4 f).

The EDX spectra of rGO-Ag@AgCl nanocomposites show the presence of Ag, Cl, C, and O. The elements, such as C and O were from rGO reduced graphene oxide and Ag, Cl from precursor materials and MC leaf. Hence, from the EDX and XPS analyses, it was confirmed the formation of rGO-Ag@AgCl nanocomposites.

### 3.5. Functional group determination by FT-IR spectroscopy

Fig. 5 (a) shows the FT-IR spectrum of reduced graphene oxide and indicated the presence of peaks at 3280, 1696, 1550 and 1034 cm<sup>-1</sup>. These peaks can be assigned to the stretching vibration of C-OH (hydroxyl), stretching vibration of C=C, vibration of C=C (may be because of skeletal vibration of unoxidized graphite domains), and C-O stretching, respectively [49-50]. The peak assigned to C-OH was changed to 3289 cm<sup>-1</sup> in the spectrum of rGO-Ag@AgCl nanocomposites (Fig. 5 b). The peaks at 2923, 2359, were due to C–C stretch (in-ring) and C-O bond. The remaining peaks at 1640, and 1536 cm<sup>-1</sup> were assigned to -C=C asymmetric stretching of the aromatic ring, and C=N stretching, respectively. The appearance of peaks 1020 cm<sup>-1</sup> was due to the alkoxy C-C [51-52]. The presence of Cl (peak at 520 cm<sup>-1</sup>) was also observed in the FT-IR spectra of the. The appearance of peak at 520 cm<sup>-1</sup> was assigned for the presence of Cl in the assigned anocomposites.

### 3.6. STEM-HAADF imaging and EDX line analysis

Fig. 6 (a) depicted the STEM-HAADF micrograph of the rGO-Ag@AgCl nanocomposites. It was observed from Fig. 6 that the core was comparatively brighter than the shell. The arrangement of the core-shell morphology was further confirmed by elemental mapping executed using the Ag–La1 and Cl–Ka1 energies with the STEM-HAADF-EDX technique (Fig. 6 (b-c)). Major elements, such as carbon and oxygen of reduced graphene oxide were investigated by C–Ka1 and O-Ka1 energies (Fig. 6 (d-e)). The overlapped X-ray elemental mapping image (red

dots- represented-Ag and white dots- represented-Cl, green dots-carbon, and blue dots-oxygen) was represented in Fig. 6 (f). It was apparent from the figure (Fig. 6 (f)) that Ag was at the center and Cl (from AgCl) at the periphery. Further, it was surrounded by C and O. Hence, it was perceptible from all the micrographs that Ag is situated in core and was bounded by the AgCl shell. Fig. 6 (g) (EDX line profile) showed that the core was made of Ag (red line) and completely surrounded by the shell of Cl (from AgCl green line). The core-shell morphologies of Ag@AgCl were attached on the surface of rGO and also observed in EDX line profile (aqua color –carbon and violet color- oxygen).

### 3.7. BET analysis

The porosity and surface area of rGO-Ag@AgCl nanocomposites were also investigated in this present work by BET analysis. The activity of adsorbent in the adsorption process depended porosity and surface area of rGO-Ag@AgCl nanocomposites. High values of porosity and surface indicate good adsorption characteristics for elimination of hazardous dyes and pharmaceutical compounds. The surface area and pore size distribution (PSD) were calculated from N<sub>2</sub> adsorption data. The surface area of nanocomposites was found to be 630.67 m<sup>2</sup>g<sup>-1</sup> as evident from the BET analysis. The value of surface area indicates single point surface area of the nanocomposites. Fig. 7a displays the hysteresis loop of N<sub>2</sub> adsorption-desorption isotherm and follows Type-IV isotherm and demonstrated that as-synthesized nanocomposites are mesoporous (d=2-50 nm) in nature, with no pores opened at both ends. The calculated pore diameter was found to be 4.25 nm (Fig. 7b). From the BET analyses, it was confirmed that dye and pharmaceutical molecules were quickly accommodated on the mesoporous surface of the rGO-Ag@AgCl nanocomposites. Hence, surface area and PSD data of rGO-Ag@AgCl nanocomposites showed superior values for elimination of dye and pharmaceutical compounds.

## **3.8.** Removal of hazardous dye and pharmaceutical compound from aqueous phase using synthesized rGO-Ag@AgCl nanocomposites

The BET results (N<sub>2</sub> adsorption/desorption isotherms) showed that nanocomposites followed typical IV isotherm [53], and it was confirmed that rGO has a strong adsorption capacity. Here we also investigated adsorption ability of nanocomposites for exclusion of NGB dye and CA drug before sunlight irradiation. The reaction mixture was kept under magnetic stirring in dark conditions for the adsorption/desorption equilibrium study. Approximately, 35-40% NGB (dye) and 25-30% CA (drug) adsorption were detected following 1 h treatment in dark condition [54]. It shows that as-synthesized nanocomposites possess a higher adsorption capacity of dye and pharmaceutical molecules from aqueous phase. The adsorption process occurred on nanocomposites via a  $\pi$ - $\pi$  conjugation between CA and NGB molecules and aromatic regions of graphene.

The photocatalytic activities of synthesized nanocomposites were evaluated for the degradation of NGB dye and CA drug under solar irradiation. Fig. 8(a-b) showed photodegradation spectra of NGB and CA using rGO-Ag@AgCl nanocomposites as a photocatalyst under sunlight. The absorption spectra of NGB showed a prominent absorption band at around 715 nm and band intensity decreases with the addition of photocatalyst. From the absorption spectra, it was also found that color of the dye solution faded away with increase in radiation time and indicated the destruction of chromophore structure of the dye. The absorption spectra depicted that NGB dye was completely degraded completely within 30 min using rGO-Ag@AgCl.

Similarly, the photodegradation of CA was also investigated. Clofibric acid showed prominent absorption band at around 227 nm and characteristic band intensity decreases with addition of

the nanocomposites. The absorption spectra showed that CA was completely degraded within 40 min utilizing rGO-Ag@AgCl nanocomposites.

The photodegradation of NGB and CA obeyed the pseudo-first-order kinetics and shown in equation (1).

$$\ln (C_0/C_t) = kt....(1)$$

All the parameters were mentioned in our previous work [33]. Fig. 8(c-d) showed kinetics plot of ln [C<sub>0</sub>/C<sub>t</sub>] versus radiation time (t) for degradation of NGB dye and CA using rGO-Ag@AgCl nanocomposites as a photocatalyst. The plot gave a linear relationship, and hence, slope of the line represented the rate constant (k) for photodegradation. The rate constant for the degradation of NGB and CA were  $9.16 \times 10^{-2}$  and  $4.57 \times 10^{-2}$  min<sup>-1</sup> respectively. Moreover, the percentage degradation was calculated using the equation given below:

Percentage degradation =  $[(C_0 - C)/C_0] \times 100....(2)$ 

Here, parameter  $C_0$  and C presents concentration before and after degradation process. The percentage efficiency for degradation by solar irradiation was found to be 98.7 % for NGB and 98% of CA. Table 1 presents the result obtained from the photodegradation of NGB and CA.

### **3.9.** Recycle studies rGO-Ag@AgCl nanocomposites (photocatalyst)

The photocatalysts, rGO-Ag@AgCl were reused for the degradation of NGB and CA upto fourth cycles and the loss of their catalytic activity was also determined. Fig. 9 shows the investigation recycle properties of rGO-Ag@AgCl photocatalyst during photodegradation of NGB and CA under solar irradiation.

### 3.10. Probable degradation products of NGB and CA during photodegradation

The probable by-products during photodegradation of NGB dye were naphthalene (m/z 128), 2formylcinnamaldehyde (160.17), naphthoquinone (m/z 158.15), formaldehyde (m/z 30), O- phthalaldehyde (m/z 134), E-penta-2,4-diene (m/z 82.1) and ethane (m/z 28) [55-57]. The possible intermediates or by-products obtained from degradation of Clofibric acid are 2-(4-hydroxyphenoxy)-isobutyric acid (m/z 195), 2-or 3 hydroxyisobutyric acid (m/z 104), hydroquinone (m/z 110), isobutyric acid (m/z 88), 4-chlorophenol (m/z 125), 4-chlorocatechol (m/z 143), Hydroxybenzoquinone (m/z 124), p-Benzoquinone (m/z 108) etc. CO<sub>2</sub> and H<sub>2</sub>O were formed as a final product after complete degradation of CA and NGB [58-60]. Fig.10 (a-b) displayed the probable by-products formation during the photodegradation of CA and NGB using nanocomposites as a photocatalyst.

# 3.11. Probable mechanism of nanocomposites during the photodegradation of CA and NGB under solar irradiation

The plausible mechanism of enhanced photocatalytic degradation using rGO-Ag@AgCl nanocomposite can be proposed on the basis of heterojunction structure of rGO-Ag@AgCl. In the first step, when nanocomposites were dispersed in NGB and CA solution, molecules of dyes and drug were absorbed on rGO surface via a  $\pi$ - $\pi$  conjugation between NGB and CA molecules and aromatic regions of graphene. In second step, photon (due to the sunlight irradiation) with adequate energy falls on the surface of the catalyst. The presence of Ag nanoparticles in Ag@AgCl/rGO enables it to absorb visible radiation as indicated by the UV-Vis spectral analysis (Fig. 1 (a)). Most of the photoexcited electrons due to SPR of Ag cluster can transfer to conduction band of AgCl [43]. Also, under UV irradiation, electronic excitation can occur within AgCl semiconductor to generate electrons at CB and holes at VB.

A photogenerated electron-hole ( $e^ h^+$ ) pairs are formed on AgNPs surface under visible region because of SPR effect of Ag. AgCl nanoparticles cannot absorb visible light because of its high band gap (3.25 eV). Therefore, the photocatalytic characteristic of Ag@AgCl is ascribed due to the plasmonic absorption of metallic silver (Ag) nanoparticles. Then, plasmon-induced electrons of silver (Ag) nanoparticles transfer to the rGO nanosheets via the conduction band of AgCl and reduce oxygen. But plasmon-induced holes ( $h^+$ ) are retained on Ag NPs surface and react with water molecules to generate hydroxyl radicals [61-63]. Thereafter, these holes ( $h^+$ ) are transferred to the surface of AgCl surface and leads to the oxidation of Cl<sup>-</sup> ions to form Cl<sup>0</sup> atoms (radicals). This transfer takes place due to the high oxidation ability of the chloride ions present in AgCl. Meanwhile, electrons on rGO sheets react with O<sub>2</sub> and produces  $•O_2$  radical. Finally, the NGB and CA molecules adsorbed on active sites of rGO-Ag@AgCl and oxidized by active species, such as  $•O_2$  radical. In the entire system, rGO sheet acts as an electron mediator, and enhance the photocatalytic activity for separation and transfer of electrons [64-65]. This can be explained by the fact that rGO pieces may decrease the resistance of separation and transportation charge produced from Ag nanocrystal (whose surface plasmon resonance is susceptible to visible light) [65]. The probable mechanistic pathway of rGO-Ag@AgCl nanocomposites during the photo degradation of CA and NGB were displayed below and in Scheme 2.

$$\begin{array}{c} AgNPs + hv \Longrightarrow AgNPs^* \Longrightarrow AgNPs^- (e^{-}) + AgNPs + (h^+) \\ H_2O + h^+ \implies OH^- + H^+ \\ OH^- + h^+ \implies OH^- \\ AgNPs^- (e^{-}) + O_2 \implies O_2^- + AgNPs \\ Or \\ rGO (e^{-}) + O_2 \implies O_2^- \\ NGB \text{ or } CA_+ OH^- \implies Degradation \ product \ (CO_2 + H_2O) \\ NGB \text{ or } CA_+ O_2^- \implies Degradation \ product \ (CO_2 + H_2O) \end{array}$$

To detect the photogenerated radicals, such as super oxide anion radical in the photodegradation process, spin-trapping ESR method was utilized. Fig. 11 (a-b) displays the ESR spectra of

DMPO-superoxide anion radicals during the photodegradation of Naphthol Green B and Clofibric acid. The reagent like DMPO (5,5-dimethyl-1-pyrroline-N-oxide) is usually used for trapping radicals because of its capability of generating stable radicals such as DMPO-superoxide anion. Fig. 11 clearly showed the formation of superoxide anion radicals ( $^{\bullet}O_2$ ) [66]. It was reported that the active species like  $^{\bullet}O_2$  was mainly responsible for NGB and CA degradation. Therefore, ESR study evidently indicates the production of both the radicals. These radicals are accountable for NGB and CA degradation.

### **3.12.** Antimicrobial Test

The inhibition zones were calculated after 24 h of incubation and displayed in Table 2. From the antimicrobial test, it was observed that rGO-Ag@AgCl nanocomposites showed greater inhibition zones than that of rGO and AgNO<sub>3</sub> solution. Fig. 12 presents the photographic images of antimicrobial activities of rGO-Ag@AgCl nanocomposites.

### 3.13. Antibacterial mode of actions of rGO-Ag@AgCl nanocomposites

The probable mechanism action of rGO-Ag@AgCl nanocomposites was cited as "*insertion mode of action*". Here, the sharp edges of graphene nanosheets (*act as knives*) cut through cell membranes of bacteria, hence, the leakage of intracellular substrates causing eventually cell death [67-69]. Then hydrocarbon tails of the lipids and the lipophilic flat surface of graphene were attracted each other and then allow the graphene to sink in between the lipid tails, embedding the graphene nano sheets in cell membrane [70-71]. In next step, metal NPs (Ag<sup>+</sup>) were enter in the bacterial cell membranes, as a result their structural compositions were changed because of the interaction with the sulfate group of bacteria (*active site of enzymes*). As a result, few of the bacterial enzymes were blocked which is required for metabolism and electrolyte transport system for bacterial mechanism and finally weakens bacterial survival and deteriorates

its activity. The metallic nanoparticles affect the DNA backbone of the bacteria hindering its replication process, reduce its immunity by binding itself to the bacterial wall rendering structural imperfections within its cells. Therefore, metal ions also serve as defensive tool for minimizing bacteria proliferation and weakening bacterial development [72-74].

### 4. Conclusion

In summary, rGO-Ag@AgCl nanocomposites were successfully synthesized by loading reduced graphene oxide (rGO) on Ag@AgCl nanoparticles. TEM image showed core and shell morphology of as-synthesized nanocomposites and further, it was also confirmed by STEM and elemental mapping analyses. The synthesized nanocomposites were successfully used as a photocatalyst and antimicrobial agents. As-synthesized nanocomposites showed 98 % of CA and 98.7 % of NGB within 40 and 30 min, respectively. This indicates efficient catalytic activities of rGO-Ag@AgCl nanocomposites for elimination of hazardous organic pollutants from water and wastewater. As-prepared nanocomposite showed good antimicrobial activities against *Staphylococcus aureus (S. aureus), Escherichia coli (E. coli)), Pseudomonas aeruginosa (P. aeruginosa), and Staphylococcus epiderminis (S. epiderminis)* strains. The rGO-Ag@AgCl nanocomposites showed superior antimicrobial properties than that of rGO and AgNO<sub>3</sub>. The above studies established that the synthesized rGO-Ag@AgCl nanocomposites could be utilized as a potential material for wastewater treatment.

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### List of Schemes:

- 1. SCHEME 1 displays schematic diagram of the growth of rGO-Ag@AgCl nanocomposites
- 2. SCHEME 2 displays probable mechanistic pathway of rGO-Ag@AgCl nanocomposites during the photo degradation of CA and NGB

### List of Table:

- 1. TABLE 1 presented comparative analyses of the results obtained for the photodegradation of NGB and CA under solar irradiation in presence rGO-Ag@AgCl, Ag@AgCl-AC and Ag-AC of as photocatalyst.
- 2. TABLE 2 presented displays the results obtained from the antimicrobial test of rGO-Ag@AgCl, nanocomposites.

### **List of Figures:**

- 1. FIGURE 1 (a-b) displays the UV-visible spectra and Tauc's plot of rGO-Ag@AgCl nanocomposites.
- FIGURE 2 (a-f) displays the SEM, TEM, HR-TEM and SAED pattern, AFM image and 3D image of rGO-Ag@AgCl nanocomposites.
- 3. FIGURE 3 (a-b) displays the XRD spectra of rGO and rGO-Ag@AgCl nanocomposites.
- **4.** FIGURE **4** (a-d) displays XPS spectra of Ag (3d), Cl (2p), C (1s) and O (1s) respectively.
- 5. FIGURE 4 (e-f) displays XPS survey spectra and EDX spectra of rGO-Ag@AgCl
- 6. FIGURE 5 (a-b) presents FT-IR spectrum of reduced graphene oxide and rGO-Ag@AgCl nanocomposites.
- 7. FIGURE 6 (a-e) depicted the STEM-HAADF micrograph image, elemental mapping energies of silver (Ag–La1) chlorine (Cl–Ka1), Carbon (C kal1-2) and Oxygen (O Ka1) with the STEM-HAADF-EDX technique.
- 8. FIGURE 6 (f-g) depicted combined elemental mapping and STEM-EDX line profile images of rGO-Ag@AgCl nanocomposites.
- **9. FIGURE 7** (**a-b**) depicted Nitrogen adsorption desorption isotherm (BET) and Pore volume vs pore radius (using the BJH method) of rGO-Ag@AgCl nanocomposites.
- **10. FIGURE 8(a-b)** represented the absorption spectra of photodegradation of NGB and CA by solar irradiation using rGO-Ag@AgCl, nanocomposites as photocatalyst.
- **11. FIGURE 8 (c-d)** represented the plot of  $\ln [C_0/C_t]$  versus irradiation time (t) for the degradation of NGB dye and CA drug using rGO-Ag@AgCl, as photocatalyst, respectively.
- **12. FIGURE 8 (e-f)** showed the percentage degradation of NGB and CA with time using rGO-Ag@AgCl as photocatalyst.
- **13. FIGURE 9** displays the recycle studies of rGO-Ag@AgCl photocatalyst during the photodegradation of NGB and CA under solar irradiation.
- **14. FIGURE 10 (a-b)** displayed the probable by-product formation during the photodegradation of CA and NGB using nanocomposites as a photocatalyst.

- **15. FIGURE11 (a-b)** displays the ESR spectra of DMPO-hydroxyl and DMPO- superoxide anion radicals during the photodegradation of Naphthol Green B and Clofibric acid .
- 16. FIGURE 12 (a-d) displays the antimicrobial photographic images of Staphylococcus aureus (code B1), Escherichia coli (code B2), Pseudomonas aeruginosa (code B3), and Staphylococcus epiderminis (code B4) microbes using rGO-Ag@AgCl



SCHEME 1 displays a schematic diagram of the growth of rGO-Ag@AgCl nanocomposites



**SCHEME 2** presents probable mechanistic pathway of rGO-Ag@AgCl nanocomposites during the photo degradation of CA and NGB.



FIGURE 1 (a-b) displays UV-Vis spectrum and Tauc's plot of rGO-Ag@AgCl nanocomposite.

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**FIGURE 2** (a-d) displays the SEM, TEM, HR-TEM, SAED pattern, AFM image and 3D Morphology of rGO-Ag@AgCl nanocomposites.



FIGURE 3 (a-b) displays the XRD spectra of rGO and rGO-Ag@AgCl nanocomposites.



FIGURE 4 (a-d) displays XPS spectra of Ag (3d), Cl (2p), C (1s) and O (1s) respectively.



FIGURE 4 (e-f) displays XPS survey spectra and EDX spectra of rGO-Ag@AgCl



FIGURE 5 (a-b) presents FT-IR spectrum of reduced graphene oxide and rGO-Ag@AgCl nanocomposites.



**FIGURE 6** (a-e) depicted the STEM-HAADF micrograph image, elemental mapping energies of silver (Ag–La1) chlorine (Cl–Ka1), Carbon (C kal1-2) and Oxygen (O Ka1) with the STEM-HAADF-EDX technique.



**FIGURE 6 (f-g)** depicted combined elemental mapping and STEM-EDX line profile images of rGO-Ag@AgCl nanocomposites.



**FIGURE 7** (**a-b**) depicted Nitrogen adsorption – desorption isotherm (BET) and Pore volume vs pore radius (using the BJH method) of rGO-Ag@AgCl nanocomposites.



**FIGURE 8(a-b)** presents the photodegradation absorption spectra of NGB and CA by solar irradiation using rGO-Ag@AgCl, nanocomposites as a photocatalyst.



**FIGURE 8** (c-d) displays the plot of  $\ln [C_0/C_t]$  versus irradiation time (t) for the degradation of NGB dye and CA drug using rGO-Ag@AgCl, as photocatalyst, respectively.



**FIGURE 8 (e-f)** showed the percentage efficiency of NGB and CA with irradiation time using rGO-Ag@AgCl as photocatalyst.



**FIGURE 9** displays the recycle studies of rGO-Ag@AgCl photocatalyst during the photodegradation of NGB and CA under solar irradiation.





FIGURE 10 (a-b) displayed the probable by-products during the photodegradation of CA and NGB



**FIGURE 11** displays the ESR spectra of DMPO- superoxide anion radicals during the photodegradation of Naphthol Green B and Clofibric acid.



**FIGURE 12** (a-d) displays the antimicrobial photographic images of *Staphylococcus aureus* (code B1), *Escherichia coli* (code B2), *Pseudomonas aeruginosa* (code B3), *and Staphylococcus epiderminis* (code B4) microbes using rGO-Ag@AgCl

**TABLE 1** Comparative analyses of the results obtained for the photodegradation of NGB and CA under solar irradiation in presence rGO-Ag@AgCl, Ag@AgCl-AC and Ag-AC of as photocatalyst.

Compounds	Photo-catalyst	Amount	Time	Efficien	Rate
		added	(min)	cy (%)	( <b>min</b> <sup>-1</sup> )
		(g)			
Clofibric acid (CA)					
HO O (Clofibric acid)	rGO-Ag@AgCl	0.025	40	98	4.57×10 <sup>-2</sup>
Naphthol green B (NGB)					
NaO <sub>3</sub> S <sup>-</sup> Napthol Green B	rGO-Ag@AgCl	0.025	30	98.7	9.16×10 <sup>-2</sup>

Bacteria Name	Nanocomposites	Amount of nanocomposit es (mg mL <sup>-1</sup> )	Time of inhibition (h)	Zones of Inhibition (mm)
Staphylococcus aureus	rGO-Ag@AgCl (code 1)	1	24	4.5
(Code B1)	rGO (code 2)	1	24	2
Gram positive	AgNO <sub>3</sub> (code 3)	1	24	0.5
Bacteria				
Escherichia coli	rGO-Ag@AgCl (code 1)	1	24	7
(Code B2)	rGO (code 2)	1	24	3-4
Gram negative bacteria	AgNO <sub>3</sub> (code 3)	1	24	0
Pseudomonas aeruginosa	rGO-Ag@AgCl (code 1)	1	24	2
(Code B3)	rGO (code 2)	1	24	1
Gram negative	AgNO <sub>3</sub> (code 3)	1	24	0
Bacteria				
Staphylococcus epiderminis	rGO-Ag@AgCl (code 1)	1	24	6
(Code B4)	rGO (code 2)	1	24	3
Gram positive	AgNO <sub>3</sub> (code 3)	1	24	0
Bacteria				

TABLE 2 displays the results obtained from the antimicrobial test of rGO-Ag@AgCl, nanocomposites

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### **Highlights:**

- ✤ A core-double shell NPs were synthesized using Medicinal leaves extract.
- Synthesized NPs were utilized for photodegradation and antimicrobial activities
- ♦ A total of 98% of CA and 98.7% of NGB was degraded within 40 and 30 min, respectively.
- ✤ rGO-Ag@AgCl showed superior antimicrobial properties than that of rGO and AgNO<sub>3</sub>.
- ✤ Hydroxyl and superoxide anion radicals were responsible for photodegradation.

### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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