

# Phyto-mediated Nano-Ingrained Acid-Modified Carica Papaya Seed for Adsorptive Sequestering of Malachite Green and Congo Red from Solutions

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**Abstract:** Usable water is a scarce resource worldwide. Dyes are one of the agents that reduce water usability. Therefore, dyes need to be removed from environmental waters. In this study, two adsorbents: acid-modified Carica papaya seed (APS) and acid-modified Carica papaya seed (APS)-Zinc oxide nanoparticle (APS-ZnO) were prepared to sequester malachite green (MG) and Congo red (CR) from solutions. The adsorbents were characterized using Scanning Electron Microscopy and FTIR techniques. Adsorbent surface chemistry, adsorbate complexity, hydrogen-bond acceptor count, covalent-bond count, and molecular weight influenced adsorption. The adsorption capacities of the APS and APS-ZnO for MG were 13.87 and 32.57 mg/g, and the APS for CR was 11.98 mg/g. The data fitted the Freundlich isotherm and pseudo-second-order kinetics for all the systems. The processes were thermodynamically feasible with negative values of Gibbs free energy ( $\Delta G = -ve$ ). The APS and APS-ZnO are prospects for the removal of MG and CR from aqueous solutions.

**Keywords:** nanoparticles; Carica papaya seed; acid; malachite green; Congo red; hydrogen bond acceptor.

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## 1. Introduction

Dyes are essential materials used in a range of industries. In the textile industry, dyes are applied to impart aesthetic hues to fabrics for economic and durability reasons. Dyes are also used in food, leather, paint, and pharmaceutical industries for various purposes. Among the most widely used dyes are malachite green (MG) and Congo red (CR) [1].

Malachite green is a bluish-green dye that is crystalline and water-soluble. It is cationic and belongs to the family of triphenylmethane dyes. It is a widely used colorant in several industries [2,3]. Congo red is an anionic diazo dye that possesses a benzidine group. It is used in microbiological staining, medical diagnosis, textiles, and as a pH indicator [4,5]. It is water-soluble and usually comes in red powdery form.

The high dispersibility of malachite green and Congo red contributes to their presence in waste streams. Usable water is a limited indispensable resource. Therefore, there is a need to treat used water for recycling and environmentally benign purposes. Many studies have

examined the removal of malachite green and Congo red from waste. Among the materials that have been employed as precursors for adsorbents or as adsorbents for removal of MG and CR aqueous solutions were: starch-based hydrogel [6], inorganic clays [7], metal-organic framework [8], *Opuntia ficus-indica*, magnetic biochar [9], chitosan-Zinc oxide composite, orange peel, base-modified *Artocarpus odoratissimus* leaves [10], and rice bran composite [11] and; waste biomass, powdered activated carbon [12], *Aspergillus parasiticus* [13], mycelial pellete, live and dead biomass of thermophilic *Aspergillus fumigatus* [14] and magadiite-chitosan composite beads [15].

Adsorption is an effective, efficient, economical, and environmentally viable process in wastewater management and treatment. However, using commercial activated carbon makes it comparatively expensive [16]. Therefore, researchers continue to search for and develop cheaper carbon-based adsorbents. *Carica papaya* seed is an abundant agricultural waste in this locality and has not been used as an adsorbent for treating MG- and CR-bearing waste streams. This constituted a research gap; hence, this study was conducted.

## 2. Materials and Methods

### 2.1. Chemicals and equipment.

Some of the chemicals used in this work are Malachite green (MG) (Color index: 42000; Lot No:130510;  $\lambda_{\max}$ :616 nm; Molecular weight:364.91 g/mol) supplied by Kem Light Laboratory, Mumbai, India, and Congo red dye (CR) (CAS:573-58-0;  $\lambda_{\max}$ :496 nm; Molecular weight:696.66 g/mol) supplied by Timstar Laboratory Suppliers Ltd, Green Lane, Wardle, Nantwich, England, Zn acetate, distilled water, HCl (aq) and NaOH (aq). The equipment used included Biobase B-UV 1800PC, a shaker (SHA-C), and a pH meter.

### 2.2. Properties and interactive (adsorptive) centers of the adsorbates.

The properties of Malachite green and Congo red (Figure 1) are presented in Table 1 below. The suspected centers for influencing adsorptive mechanisms are molecular weight, electrical charge,  $pK_a$ , solubility, hydrogen bond donor (HBD) ( $-NH_2$ ), hydrogen bond acceptor (HBA) ( $-N$ ,  $-O$ ), rotatable bond profile (RBF), topological polar surface area (TPSA), covalently bonded unit (CBU), complexity, and heavy atom count (HAC). These adsorbate profiles enhance or de-enhance the adsorptive quotient of the adsorbates to a large extent.

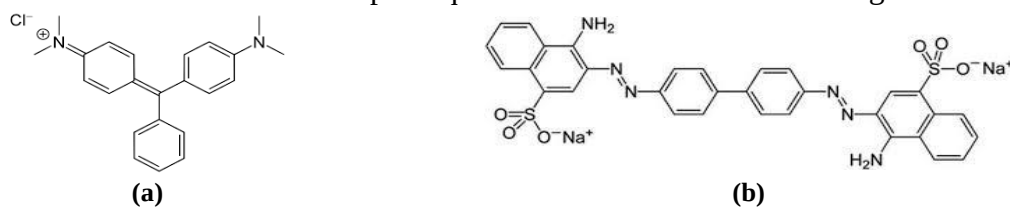


Figure 1. (a) Malachite green; (b) Congo red.

Table 1. Properties of Malachite green and Congo red [17].

| Name of adsorbate properties | Malachite green                                                                                        | Congo red                                                                                                            |
|------------------------------|--------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|
| IUPAC Name                   | [4-[[4-(dimethylamino)phenyl]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-dimethylazanium;chloride | disodium;4-amino-3-[[4-[4-[(1-amino-4-sulfonatophthalen-2-yl)diazenyl]phenyl]phenyl]diazenyl]naphthalene-1-sulfonate |
| Other Names                  | 569-64-2 (CAS); Basic Green 4; Malachite green chloride; China Green                                   | Congo red; 573-58-0 (CAS); Direct Red 28; C.I. Direct Red 28; Congo Red 4B                                           |
| Molecular Formula            | $C_{23}H_{25}ClN_2$                                                                                    | $C_{32}H_{22}N_6Na_2O_6S_2$                                                                                          |
| Molecular Weight             | 364.9 g/mol                                                                                            | 696.7 g/mol                                                                                                          |

| Name of adsorbate properties   | Malachite green                                                         | Congo red                    |
|--------------------------------|-------------------------------------------------------------------------|------------------------------|
| Electrical Charge              | +                                                                       |                              |
| pKa                            | pH (1.4)                                                                | 4.1 (25°C)                   |
| Toxicity                       | LD <sub>50</sub> 80mg/kg                                                | LD <sub>50</sub> 15200 mg/kg |
| Solubility                     | Soluble in methanol, ethanol, 4.0X10 <sup>+4</sup> mg/L (water) at 25°C | Soluble                      |
| Hydrogen Bond Donor Count      | 0                                                                       | 2                            |
| Hydrogen Bond Acceptor Count   | 2                                                                       | 12                           |
| Rotatable Bond Count           |                                                                         | 5                            |
| Topological Polar Surface Area | 6.2Å <sup>2</sup>                                                       | 233Å <sup>2</sup>            |
| Complexity                     | 516                                                                     | 1180                         |
| Canonicalized                  | Yes                                                                     | Yes                          |
| Covalently-Bonded Unit Count   | 2                                                                       | 3                            |
| Heavy Atom Count               | 26                                                                      | 48                           |
| Colour                         | Green crystal solid; blue-green in aqueous solutions                    |                              |

### 2.3. Preparation of acid-modified *Carica papaya* seed adsorbent (APS) and acid-modified *Carica papaya* seed-zinc oxide nano-adsorbent (APS-ZnONA).

The *Carica papaya* seeds used in this work were obtained from a local farm in Ede, Osun State, Nigeria. The seeds were removed manually from fresh ripe fruit, washed thoroughly with distilled water, drained, and air-dried for 7 days. The dried seeds were then ground into a powder and stored in an airtight container as raw *Carica papaya* seed (RPS). A 30 g of RPS powder was weighed separately in two beakers and soaked in 300 mL of 0.1 M HCl for 24 hours, adopting the method of [18], with slight modification. The treated RPS were then filtered, washed several times with distilled water until neutral pH was obtained, and dried in an oven at 75°C for 24 hours. The treated sample was then stored as acid-modified *Carica papaya* seed (APS). A 2 g of RPS was soaked in 100 mL of distilled water in a conical flask and heated at 60°C with constant stirring for 1 hour. The mixture was allowed to cool and then filtered using Whatman No 1 filter paper to obtain the extract. Zinc oxide nanoparticles (ZnO-NPs) were synthesized by adding 10 mL of freshly prepared RPS extract dropwise into 90 mL of 0.02 M Zinc acetate solution, with continuous stirring using a magnetic stirrer at 60°C for 5 hours. A few drops of 1.0 M NaOH were added during stirring to adjust the pH of the mixture to 12. The formation of ZnO-NPs was suspected to be due to the appearance of a milky precipitate and was confirmed to have maximum absorbance at a wavelength of 374 nm. This conforms with the absorption peak obtained in the literature, which is in the range of 360-380 nm [19,20]. The average particle size of the Zinc oxide nanoparticles (ZnO-NPs), as determined from TEM analysis, was 54 nm. A 100 mL solution of freshly prepared ZnO-NPs was mixed with 5.0 g of APS in a 500 mL beaker, stirred constantly with a magnetic stirrer for 5 h to ensure optimal interaction between the components. The resulting mixture was then oven-dried at 60°C for 15 h and labeled as APS-ZnO.

### 2.4. Characterization of adsorbents.

The adsorbents prepared were characterized using scanning electron microscopy, Fourier transform infrared spectroscopy, and the pH point of zero charge. The surface morphology of the adsorbents prepared (APS and APS-ZnO) was examined on a JSM-7800F scanning electron microscope (SEM). The beam of electrons generated from the emitter, usually in the range of 100 - 30,000 eV, passes through the lenses, which compress the spot.

The lenses then focus the electrons on the sample to generate a sharp image on the screen. FTIR Spectroscopic analyses of the adsorbents were carried out in the range 4000 to 400 cm<sup>-1</sup> using an IR Tracer-100 (SHIMADZU) to identify functional groups that may be responsible for the adsorbent's effectiveness.

## 2.5. Batch adsorption studies.

Batch adsorption experiments were performed to investigate the influence of various adsorption parameters on the adsorption process. The adsorption parameters studied were the effects of contact time, adsorbent dose, solution pH, adsorbate concentration, and temperature. Determination of the effect of contact time was carried out as follows: 0.1 g of APS was added to 30 mL of 50 mg/L each of MG and CR solutions, and 0.1 g of APS-ZnO was added to 30 mL of 50 mg/L MG in separate adsorption tubes. The solutions were shaken for the time range of 5-360 mins, and the samples were withdrawn at a predetermined time interval, filtered, and analyzed using a UV-VIS spectrophotometer. The effect of the adsorbent dose was determined as follows: doses (0.05-0.7 g) of APS were separately and serially added to 30 mL of 50 mg/L MG and CR, and the same serial doses of APS-ZnO were added to 30 mL of 50 mg/L MG. The adsorbate-adsorbent mixtures were agitated on a shaker (SHA-C) at 150 rpm for 300 mins at room temperature until equilibrium was attained. The mixtures were filtered and then analyzed for residual dye concentration using a UV-VIS spectrophotometer [21]. The effect of initial adsorbate concentration was investigated by adding 0.1 g of APS separately to 30 mL of different initial concentrations of 10-100 mg/L of each of MG and CR, and 0.1 g of APS-ZnO was added to 30 mL of initial concentrations of 10-100 mg/L of MG. The mixtures were then shaken at room temperature on a shaker, with other parameters held constant until equilibrium was reached. The mixtures were filtered, and residual dye concentrations were determined using a UV-VIS spectrophotometer. Also, the effect of temperature was studied as follows: Separate 30 mL of 50 mg/L MG and CR were agitated with 0.1 g APS, while MG solutions were only agitated with APS-ZnO at temperatures ranging from 30 - 60°C in a mechanical thermostatic water bath shaker. Shaking continued until equilibrium was attained, after which the mixture was filtered and analyzed for the concentration of unadsorbed dyes using a UV-VIS spectrophotometer [22].

## 2.6. Analytical methods.

The amounts of adsorbate adsorbed per unit mass of adsorbent from the analyses of the filtrates using UV-VIS spectrophotometer, adjusted to  $\lambda_{\max}$  496 nm for CR and 616 nm for MG were determined with the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where  $q_e$  is the quantity of dye adsorbed per unit mass of adsorbent (mg/g),  $C_0$  -initial dye concentration (mg/L),  $C_e$ -equilibrium dye concentration (mg/L),  $V$ -Volume of the solution (L),  $W$ - Adsorbent mass (g). The isotherm and kinetic models and thermodynamic equations employed in analyzing the data are given in Table 2.

**Table 2.** The isotherm, kinetic models, and thermodynamic equations [23].

| SN | Model             | Linear Equation                                      |
|----|-------------------|------------------------------------------------------|
| 1  | Isotherm Langmuir | $\frac{C_e}{q_e} = \frac{1}{KQ^0} + \frac{C_e}{Q^0}$ |
| 2  | Freundlich        | $\log q_e = \log K_f + \frac{1}{n} C_e$              |

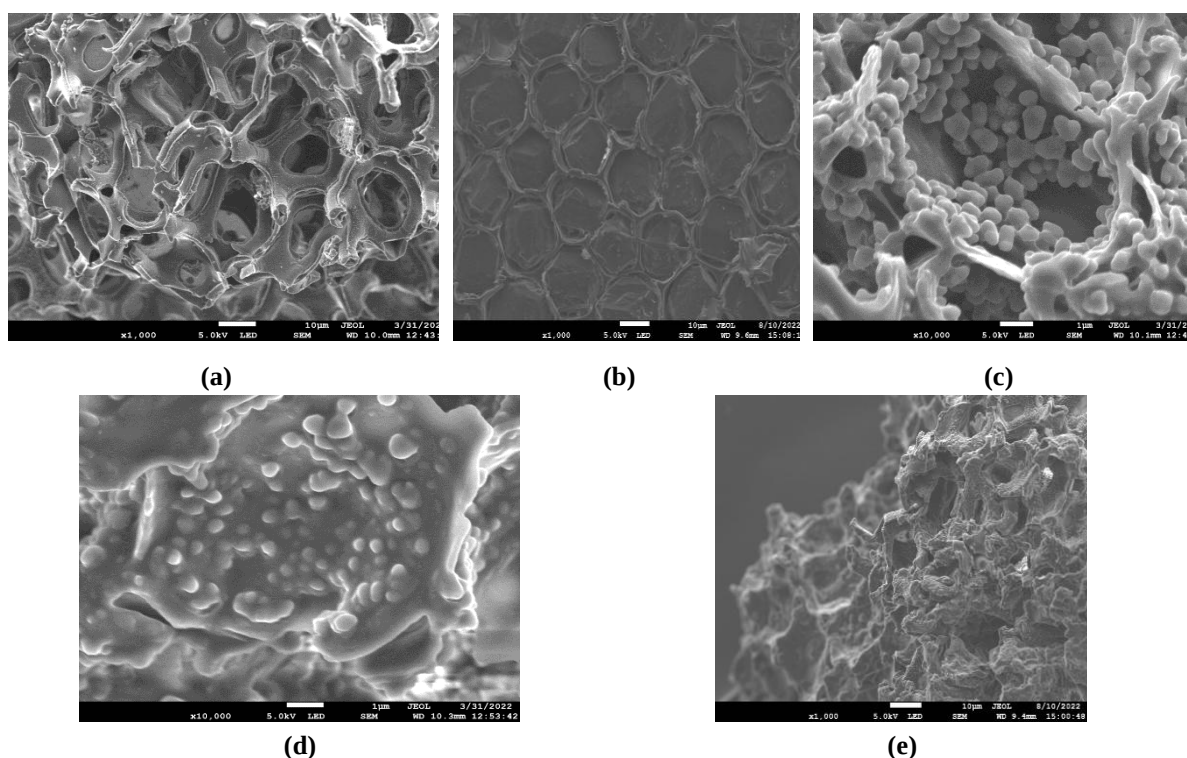
| SN | Model                                                       | Linear Equation                                                                    |
|----|-------------------------------------------------------------|------------------------------------------------------------------------------------|
| 3  | Dubinin–Radushkevich                                        | $\ln q_e = \ln(q_s) - (K_{ad}\varepsilon^2)$                                       |
|    | <b>Kinetic Model</b>                                        |                                                                                    |
| 1  | Pseudo-first order                                          | $\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$                                 |
| 2  | Pseudo-second order                                         | $\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$                                      |
|    | <b>Thermodynamic Equations</b>                              |                                                                                    |
| 1  | $\Delta G = -RT \ln K$                                      |                                                                                    |
| 2  | $\Delta G^0 = -2.303RT \log\left(\frac{C_{Ae}}{C_e}\right)$ | $\log \frac{C_{Ae}}{C_e} = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT}$ |

where  $C_{Ae} = (C_i - C_e)$  (mg/L) = amount of adsorbate adsorbed on adsorbent at equilibrium;  $C_e$  (mg/L) = amount of adsorbate in solution at equilibrium;  $R$  = gas constant (8.314 J/mol/K);  $T$  = temperature (K).

### 3. Results and Discussion

#### 3.1. The properties of adsorbents.

The properties of the adsorbents were established through the various characterization analyses mentioned earlier. These characteristics of APS and APS-ZnO may influence their adsorption capacities for MG and CR. The morphologies of APS and APS-ZnO before adsorption were revealed in the pictograms of scanning electron microscopy analyses in Figure 2. The pores were open, and the surface, as well as various sections of the pores, could adsorb adsorbates. It was apparent that there were alterations to the surface morphologies of the adsorbents after the adsorption.



**Figure 2.** Scanning electron microscopy pictograms of (a) APS before adsorption; (b) APS-ZnO before adsorption; (c) APS after adsorption of MG; (d) APS after adsorption of CR; (e) APS-ZnO after adsorption of MG.

The surface chemistry of APS and APS-ZnO was studied with the aid of FTIR spectroscopy. The sharp peak at, for APS,  $3362\text{ cm}^{-1}$  (Table 3, Figure 3) can be attributed to O-H stretching vibration of hydrogen-bonded alcohol. Also, the band at  $2342\text{ cm}^{-1}$  is assigned to  $\text{C}\equiv\text{C}$  stretching vibration of alkyne. The sharp band at  $1742\text{ cm}^{-1}$  is due to the carbonyl ( $\text{C}=\text{O}$ ) of carboxylic acid groups or esters, which is further supported by the band at  $1620\text{ cm}^{-1}$

<sup>1</sup> assigned to the C=O stretching vibration of a carboxylic acid with intermolecular hydrogen bonding. There was also a sharp peak at 1682 cm<sup>-1</sup>, which is assigned to the C=C stretching vibration of alkene, while the band at 1422 cm<sup>-1</sup> is attributed to the C-Cl group. The characteristic bands obtained for APS-ZnO were: a sharp peak at 3300 cm<sup>-1</sup> is assigned to the O-H stretching vibration of lignin, cellulose, and hemicellulose. Also, a band at 2920 cm<sup>-1</sup> is attributed to asymmetric and symmetric C-H stretching vibrations of alkanes. A sharp band obtained at 1682 cm<sup>-1</sup> can be due to the C=C stretching vibration of alkene. The peak in the region of 442 cm<sup>-1</sup> to 662 cm<sup>-1</sup> can be assigned to the Zn-O group in the nanoparticles used in coating the adsorbent. There were shifts in some bands, and new bands appeared. The band at 3362 cm<sup>-1</sup> for APS shifted to 3381 cm<sup>-1</sup> after MG adsorption and to 3400 cm<sup>-1</sup> after the adsorption of CR. There was a shift in the band at 1422 cm<sup>-1</sup> to 1440 cm<sup>-1</sup> after CR adsorption. Also, the band at 2342 cm<sup>-1</sup> was attributed to the C≡C stretching vibration of alkyne, which shifted to 2361 cm<sup>-1</sup> after the adsorption of CR dye. A new band at 2920 cm<sup>-1</sup> was assigned to the asymmetric and symmetric C-H stretching vibrations of alkane after the adsorption of the two dyes. After the adsorption of MG by APS-ZnO, there was a disappearance of the band at 2920 cm<sup>-1</sup> and the appearance of a new band at 1541 cm<sup>-1</sup> assigned to the C-O-H bending vibration [24-28].

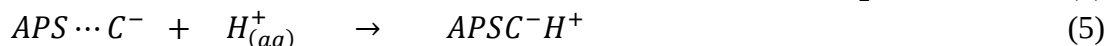
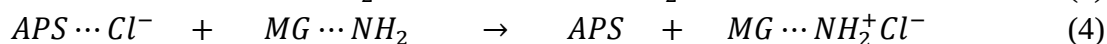
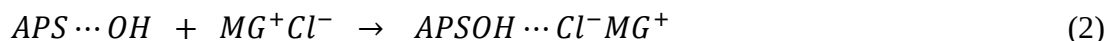
**Table 3.** FTIR analysis results.

| FTIR peaks (cm <sup>-1</sup> ) | Functional Group | APS                                         |                                 |                                             |                                 | APS-ZnO                        |                  |                                             |                                 |
|--------------------------------|------------------|---------------------------------------------|---------------------------------|---------------------------------------------|---------------------------------|--------------------------------|------------------|---------------------------------------------|---------------------------------|
|                                |                  | After MG <sub>ads</sub> (cm <sup>-1</sup> ) | Δ in peak λ (cm <sup>-1</sup> ) | After CR <sub>ads</sub> (cm <sup>-1</sup> ) | Δ in peak λ (cm <sup>-1</sup> ) | FTIR peaks (cm <sup>-1</sup> ) | Functional group | After MG <sub>ads</sub> (cm <sup>-1</sup> ) | Δ in peak λ (cm <sup>-1</sup> ) |
| 3362                           | O-H              | 3381                                        | +19                             | 3400                                        | +38                             | 3300                           | O-H              | 3281                                        | -19                             |
| 2342                           | C≡C              | 2342                                        | 0                               | 2361                                        | +19                             | 2920                           | C-H              | None                                        |                                 |
| 1742                           | C=O              | 1742                                        | 0                               | 1742                                        | 0                               | 2342                           | C-O              | 2361                                        | +19                             |
| 1682                           | C=C              | 1682                                        | 0                               | 1682                                        | 0                               | 1742                           | C=O              | 1742                                        | 0                               |
| 1620                           | C=O              | 1620                                        | 0                               | none                                        |                                 | 1682                           | C=C              | 1682                                        | 0                               |
| 1422                           | C-Cl             | none                                        |                                 | 1440                                        | +18                             | 1441                           | N-H              | 1441                                        | 0                               |
| 1042                           | C-O              | 1041                                        | -1                              | 1041                                        | -1                              | 662, 442                       | Zn-O             | None                                        |                                 |
|                                |                  | 2920 (C-H) (new peak)                       |                                 | 2920 (C-H) (new peak)                       |                                 |                                |                  | 1451 C-N, N-O, (new peak)                   |                                 |

Δ = change; λ = wavelength; none = disappearance; MG<sub>ads</sub> = MG adsorption; CR<sub>ads</sub> = CR adsorption.

As revealed in Table 3, the surface chemistry of the adsorbents that partook in the adsorptive interactions was: APS in adsorbing MG (O-H, C-H, and C-O); APS in adsorbing CR (C≡C, C=O, O-H, C-H, and C-O); and APS-ZnO in adsorbing MG (O-H, C-O-H, C-H, and C-O). The ZnO nanoparticles also impacted APS with additional peaks (functional groups) at 2920, 1451, 662, and 442 cm<sup>-1</sup>. These identified functional groups might influence the adsorption of MG and CR by APS and APS-ZnO. Interaction of a functional group with electron-withdrawing groups (e.g., F, -Cl, -Br) leads to shorter wavelengths and higher frequency, while the electron-donating group (e.g., O, -N) leads to longer wavelengths and lower frequency. Double-bond conjugation provides an electron-delocalization platform, which reduces electron density around the double-bond functionality. This phenomenon leads to weaker and longer double bonds (wavelength) and reduced frequency. In the adsorption of MG by APS, -OH frequency increased by 19 cm<sup>-1</sup> (Table 3). This implied that -OH interacted with the electron-withdrawing group. This electron-withdrawing group could probably be -Cl from the amine ion of MG. The frequency of -CO is lower by -1 cm<sup>-1</sup>. This reduction might be impacted through the interaction of -CO of APS and NH<sub>2</sub> of MG. The disappearance of 1422

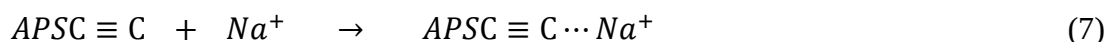
$\text{cm}^{-1}$  was suspected to be due to  $-\text{Cl}$  (from  $\text{HCl}$  activation) transferred to  $-\text{NH}_2$  of  $\text{MG}$ . The formation of a new peak at  $2920 \text{ cm}^{-1}$  could be attributed to a weak  $-\text{N}-\text{H}$ . The schemes of the interactions are:



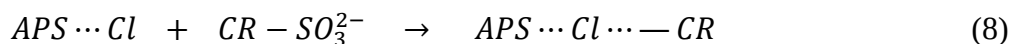
In the adsorption of  $\text{CR}$  by  $\text{APS}$ ,  $-\text{OH}$  frequency increased by  $38 \text{ cm}^{-1}$  (Table 3). The increase was attributed to the contribution of 2 sodium ions from  $\text{CR}$ :



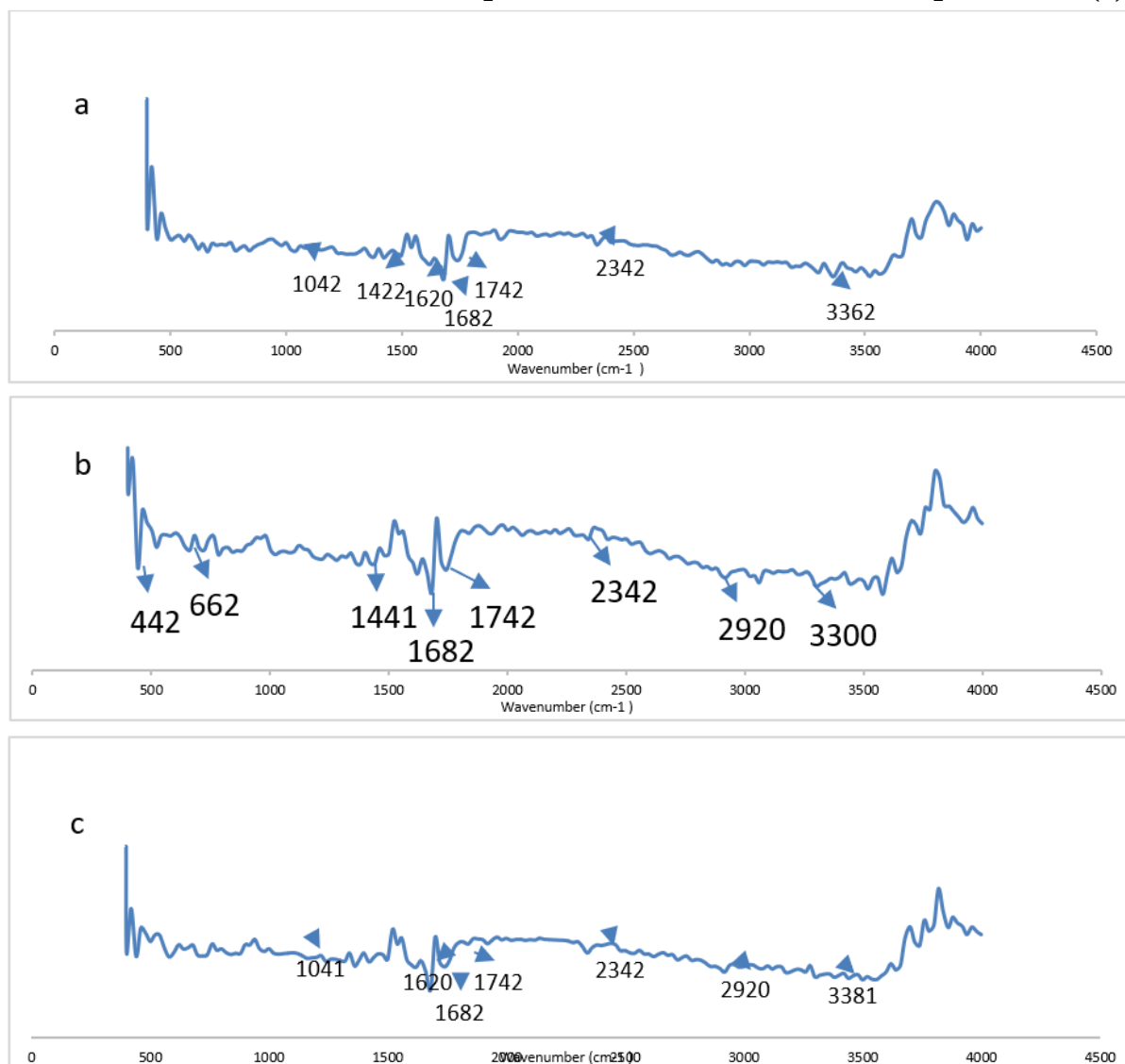
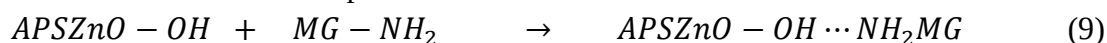
The peak at  $2342 \text{ cm}^{-1}$  shifted to a higher  $2361 \text{ cm}^{-1}$ , which was attributed to the interaction between  $-\text{C}\equiv\text{C}-$  and  $\text{Na}^+$ :

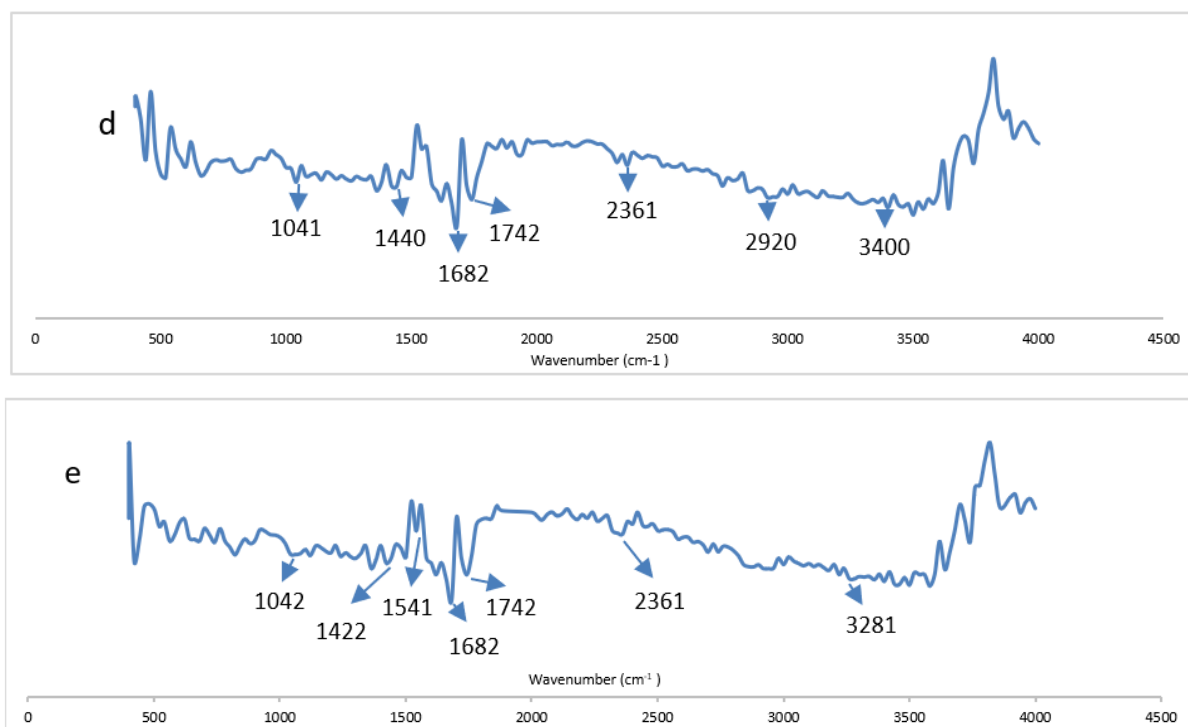


The  $\text{C}-\text{Cl}$  peak at  $1422 \text{ cm}^{-1}$  after interaction with  $\text{SO}_3^{2-}$  group of  $\text{CR}$  shifted to  $1440 \text{ cm}^{-1}$ :



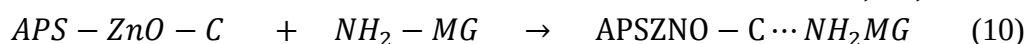
In the adsorption of  $\text{MG}$  by  $\text{APS}-\text{ZnO}$ , the  $-\text{OH}$  peak shifted to a lower frequency. The  $-\text{OH}-\text{NH}_2$  interaction could be responsible for this observation:





**Figure 3.** FTIR Spectra of (a) APS before adsorption; (b) APS-ZnO before adsorption; (c) APS after adsorption of MG; (d) APS after adsorption of CR; APS-ZnO after adsorption of MG.

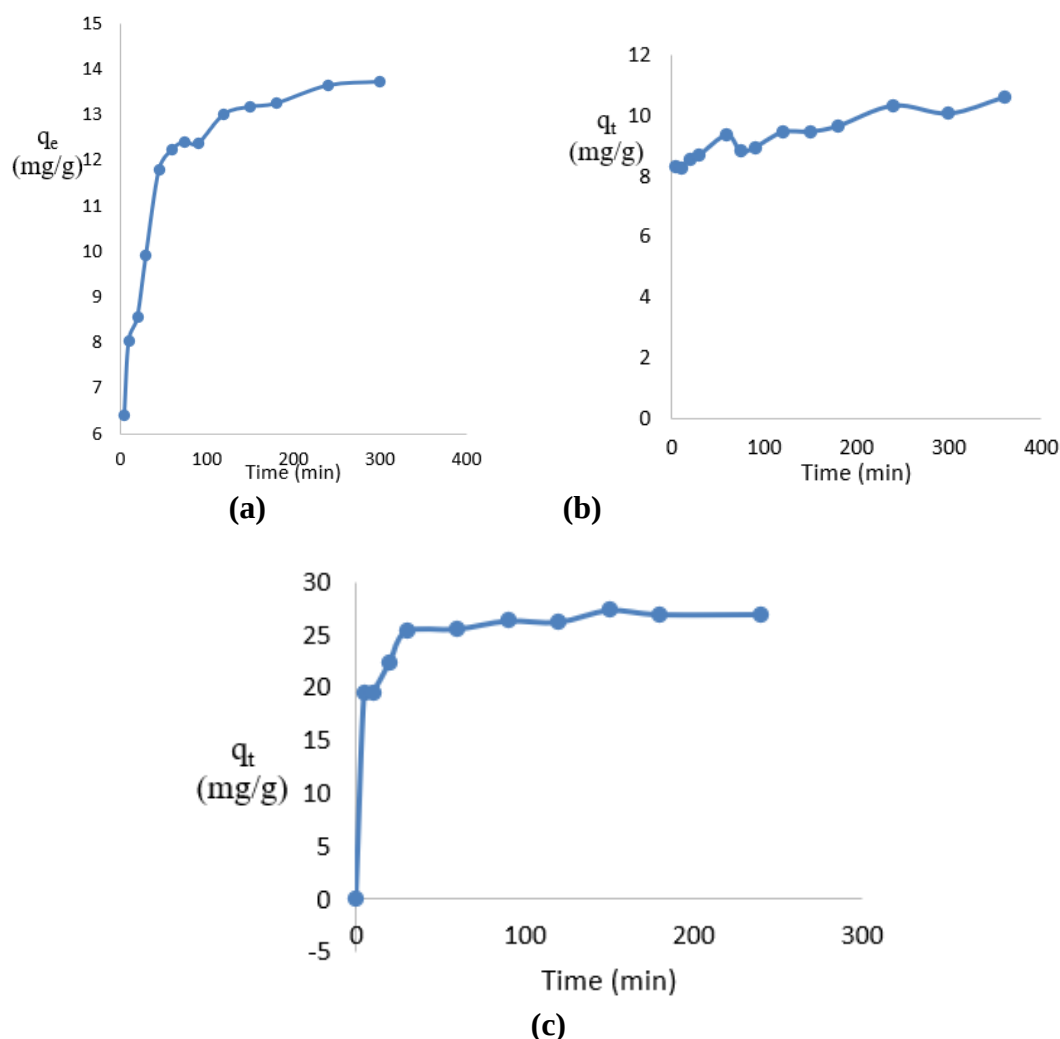
The peaks observed at 2920, 662, and 442  $\text{cm}^{-1}$  disappeared after adsorption of MG by APS-ZnO. There was the appearance of a new peak at 1451  $\text{cm}^{-1}$ . These developments were suspected to be connected to interactions between APS-ZnO and MG at C, Zn, and N centers:



### 3.2. Effects of adsorption parameters on adsorption of MG and CR.

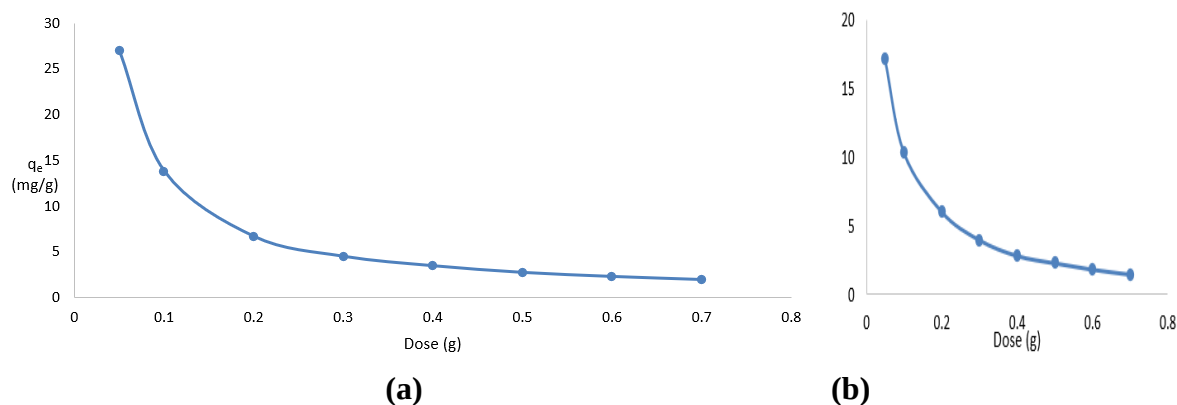
Effects of contact time, adsorbent dose, and temperature are among the parameters that determine how economical the adsorption process is, while effects of concentration and pH are guides to the process's operational effectiveness and efficiency [29]. Effects of contact time on adsorption of adsorbates by APS and APS-ZnO are presented in Figure 4. It was shown that the process was in three phases. The first phase was the phase where the adsorption was very fast, as indicated by the rapid increase in the quantity of dye adsorbed, and the second phase was where there was less rapid adsorption, and the third phase signified the attainment of equilibrium. In the adsorption of MG by APS, there was a rapid increase in  $q_t$  from 6.39 mg/g to 13.00 mg/g within the first 120 mins. After this,  $q_t$  increase was minimal until it reached its highest at 300 mins with  $q_t$  value of 13.71 mg/g (Figure 4a). The equilibrium time for the adsorption of CR onto APS was 360 mins with a capacity of 10.62 mg/g (Figure 4b). The equilibrium time for the adsorption of MG by APS-ZnO was reached at a shorter time of 150 mins with a capacity of 27.34 mg/g (Figure 4c).

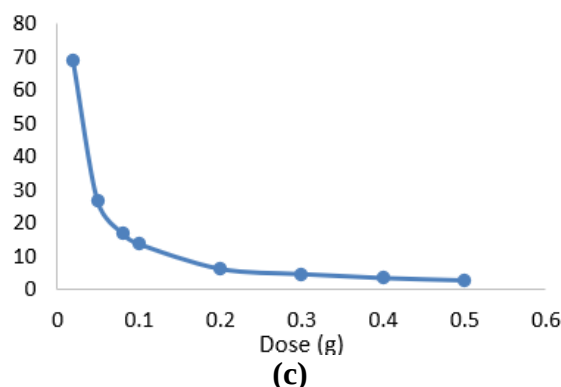
Adsorption that rapidly occurred in the first phase of the processes gradually slowed down until equilibrium was attained. Comparing the processes, the rate of adsorption of MG by APS-ZnO is halved, and the adsorption capacity doubles that of APS. Also, the APS-MG system, with little better adsorption capacity, attained equilibrium faster than the APS-CR system [30-32].



**Figure 4.** Effect of contact time on adsorption of (a) MG by APS; (b) CR by APS; (c) MG by APS-ZnO.

It was observed from the results that the quantity of dye adsorbed per unit mass of adsorbent ( $q_e$ ) decreased with increasing adsorbent dose for all the systems studied (Figure 5). For the adsorption of MG and CR by APS,  $q_e$  decreased from 26.96 - 1.95 mg/g and 17.15 - 1.48 mg/g, respectively, as the adsorbent doses increased from 0.05 g - 0.7 g. Similar observations were made for the adsorption of MG onto APS-ZnO, where  $q_e$  decreased from 68.98 - 2.77 mg/g as the adsorbent dose increased from 0.02 - 0.5 g. The adsorption capacity of APS-ZnO for MG at 0.02g is about 2.5x that of APS at 0.05g. These results revealed APS-ZnO as a higher performer for MG adsorption compared to APS and APS-MG system to APS-CR system across the adsorbent dose range.

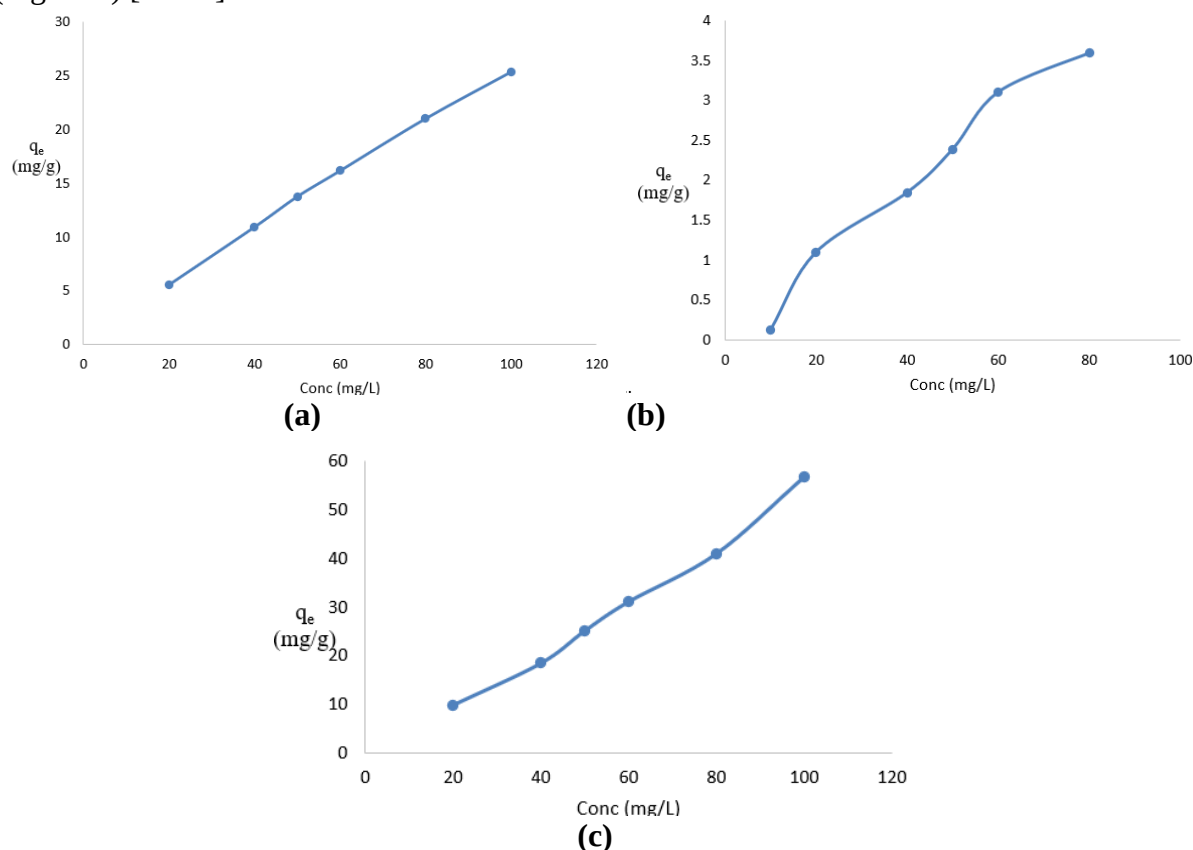




**Figure 5.** Effect of dose on adsorption of (a) MG by APS; (b) CR by APS; (c) MG by APS-ZnO.

It was also observed that the quantity of MG adsorbed by APS-ZnO is higher than that adsorbed by APS, showing that the nanoparticles enhanced the adsorption capacity of APS after incorporation.

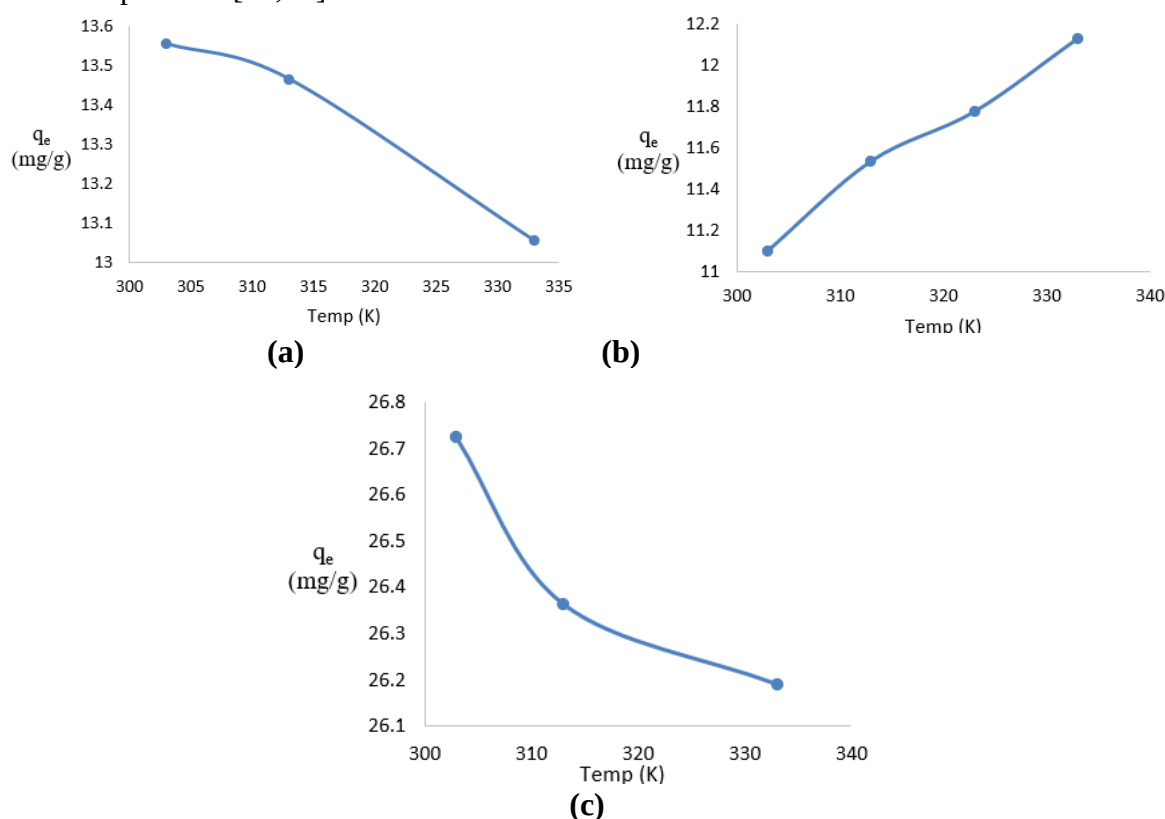
Concentration is one of the major driving forces that determine the transfer of adsorbate to the surface of the adsorbent in adsorption processes. There was an increase in the quantity of dye adsorbed per unit mass of the adsorbent ( $q_e$ ) as the initial dye concentration increased from 20 to 100 mg/L. The amounts of MG and CR adsorbed by APS increased from 5.58 to 25.36 mg/g and from 1.09 to 3.59 mg/g. The adsorption of MG onto APS-ZnO showed the same trend but with higher  $q_e$  values (9.86-56.78 mg/g) than all the other systems studied (Figure 6) [33-35].



**Figure 6.** Effect of initial concentration on adsorption of (a) MG by APS; (b) CR by APS; (c) MG by APS-ZnO.

It was observed from the results obtained that the amount of MG and CR adsorbed per unit mass of APS decreased from 13.56 to 13.06 mg/g and increased from 11.10 to 12.13 mg/g. There was a decrease in  $q_e$  (from 26.73 mg/g to 26.19 mg/g) with an increase in temperature

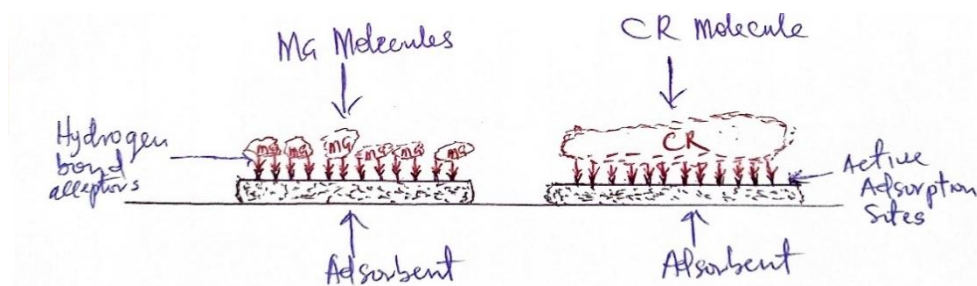
for the adsorption of MG onto APS-ZnO (Figure 7). The force of attraction between the dye molecules and the active sites on the surface of the adsorbent may also be weakened due to a rise in temperature [36,37].



**Figure 7.** Effect of temperature on adsorption of (a) MG by APS; (b) CR by APS; (c) MG by APS-ZnO.

Comparing the adsorption of MG and CR by APS through results of the effect of time, adsorbent dose, and adsorbate concentrations, the APS-MG system attained equilibrium earlier with a better adsorption capacity. The features of the adsorbates that seem to have been considered were complexity, topological polar surface area (TPSA), hydrogen bond acceptor count (HBAC), and atomic weight. The ratios of complexity, TPSA, atomic weight, and HBAC of MG to CR are 1:2.3, 1:37.6, 1:1.9, and 1:6. One molecule of CR occupied adsorptive sites for two molecules of MG in terms of complexity and atomic weight. The polar surface area of CR is significantly larger than that of MG. This was suspected to have implications for pore accessibility and adsorption. The HBAC played a key role in adsorbent-adsorbate functional group interactions. Six molecules of MG were adsorbed, while one molecule of CR was adsorbed (Figure 8). The temperature effect on the adsorption of MG and CR was opposing. The increase in temperature that favored CR uptake might have to do with its high molecular weight, which required higher energy for kinetic movement and diffusion from the bulk matrix to the adsorbent-solution interface. Comparing MG adsorption by APS and APS-ZnO, the latter performed far better than the former in both time and capacity. The deposition of ZnO nanoparticles on APS enhanced surface area with additional active adsorptive sites. The additional functional groups introduced by ZnO in APS-ZnO facilitated higher capacity. Both were affected similarly with respect to temperature, but APS-ZnO had a higher capacity. At room temperature, agitation alone was enough to kinetically drive the CR molecules onto the adsorption sites and attain maximum loading. As the temperature was elevated, the activation complex was further destabilized. Therefore, CR molecules in solution were hyperactive and could not bind to the adsorption sites. The early adsorbed molecules at ambient temperature

became disoriented at higher temperatures and desorbed from the adsorption sites into the solution.



**Figure 8.** Effect of adsorbate functional centers on adsorbent capacity.

### 3.3. Equilibrium isotherm studies.

The maximum MG and CR adsorbed per unit mass of APS ( $q_m$ ) were 13.87 and 11.98 mg/g, and APS-ZnO  $q_m$  for MG was 32.75 mg/g. For all systems studied, the dimensionless separation factor ( $RL$ ) was less than unity, indicating favorable adsorption. Based on the regression coefficient ( $R^2$ ), adsorption of MG and CR onto APS, and MG onto APS-ZnO, followed the Freundlich isotherm model, suggesting multilayer adsorption on a heterogeneous surface. The results also showed that the Dubinin-Radushkevich model better explained CR adsorption onto APS, with a mean free energy ( $E$ ) value less than 8 kJ/mol, which may indicate physisorption (Table 4). A similar report was also reported by [38]. The adsorption capacities of APS and APS-ZnO were also compared with other studies (Table 5).

**Table 4.** Isotherm terms of the adsorption of MG and CR by APS and APS-ZnO from aqueous solutions.

|                                             | MG      |         | CR      |
|---------------------------------------------|---------|---------|---------|
|                                             | APS-ZnO | APS     | APS     |
| Isotherm                                    |         |         |         |
| Langmuir                                    |         |         |         |
| $R^2$                                       | 0.9427  | 0.8337  | 0.9195  |
| $q_m$ (mg/g)                                | 32.57   | 13.87   | 11.98   |
| $K_a$ (mg/g)                                | 0.0517  | 0.0269  | 0.00403 |
| $R_L$                                       | 0.28    | 0.43    | 0.83    |
| Freundlich                                  |         |         |         |
| $R^2$                                       | 0.9978  | 0.9966  | 0.9781  |
| $K_f$ (mg/g)(L/g) <sup>n</sup>              | 2.129   | 1.289   | 0.0941  |
| $1/n$                                       | 1.1973  | 0.9349  | 0.8693  |
| Dubinin – Radushkevich                      |         |         |         |
| $R^2$                                       | 0.9511  | 0.9820  | 0.9826  |
| $\beta$ (mol <sup>2</sup> /J <sup>2</sup> ) | 4E – 06 | 1E – 05 | 5E – 05 |
| $q_0$ (mg/g)                                | 41.84   | 24.73   | 3.21    |
| $E$ (KJ/mol)                                | 0.3536  | 0.2236  | 0.1     |
| Temkin                                      |         |         |         |
| $R^2$                                       | 0.9444  | 0.8833  | 0.9658  |
| $A_T$ (L/g)                                 | 0.3987  | 0.3763  | 0.108   |
| $b_T$ (J/mol)                               | 99.97   | 261.01  | 1466.66 |

**Table 5.** Comparison of maximum adsorption capacities ( $q_m$ ) of APS, BPS, and other adsorbents.

| Adsorbent                                                       | Adsorbate       | $q_m$ (mg/g) | References |
|-----------------------------------------------------------------|-----------------|--------------|------------|
| Banana peel powder                                              | Congo Red       | 1.721        | [39]       |
| Native fungal biomass                                           | Congo Red       | 90.4         | [40]       |
| Tunics of the corm of the saffron                               | Congo Red       | 6.2          | [41]       |
| Cymbopogon winterianus                                          | Congo Red       | 3.5          | [42]       |
| Amino grafted biochar                                           | Congo Red       | 89.3         | [43]       |
| Gum Ghatti-acrylamide grafted copolymer coated zero-valent iron | Congo red       | 153.3        | [44]       |
| Azadirachta indica leaf                                         | Malachite green | 7.65         | [45]       |
| Lignin                                                          | Malachite green | 31.2         | [46]       |
| Walnut shell                                                    | Malachite green | 11.76        | [47]       |
| Catha edulis stem                                               | Malachite green | 5.62         | [48]       |

| Adsorbent               | Adsorbate       | $q_m$ (mg/g) | References    |
|-------------------------|-----------------|--------------|---------------|
| Lupinus albus seed peel | Malachite green | 20.90        | [49]          |
| Coal associated soil    | Malachite green | 89.97        | [50]          |
| APS                     | Malachite green | 13.87        | Present study |
| APS                     | Congo red       | 11.98        | Present study |
| APS-ZnO                 | Malachite green | 32.57        | Present study |

### 3.4. Adsorption kinetic studies.

The  $R^2$  values for pseudo-second-order kinetics obtained for the adsorption of MG and CR onto APS and MG onto APS-ZnO were higher than those of pseudo-first-order and Elovich kinetics models (Table 6). This implied that the rate-limiting step is chemisorption [51]. Further confirmation of this is the agreement of calculated adsorption capacities  $q_e$  (calc) for the Pseudo-second-order model with the experimental adsorption capacities  $q_e$  (expt).

**Table 6.** Kinetics parameters for the adsorption of MG and CR onto APS and BPS.

| Model                      | MG          |         | CR         |
|----------------------------|-------------|---------|------------|
|                            | APS         | APS-ZnO | APS        |
| $q_e$ (exp) (mg/g)         | 13.716      | 27.341  | 10.618     |
| <b>Pseudo-first order</b>  |             |         |            |
| $R^2$                      | 0.6329      | 0.7898  | 0.312      |
| $q_e$ (calc) (mg/g)        | 4.053       | 7.243   | 1.688      |
| $k_1$ (min <sup>-1</sup> ) | 0.0106      | 0.0147  | 0.0034     |
| <b>Pseudo-second order</b> |             |         |            |
| $R^2$                      | 0.9995      | 0.9996  | 0.9966     |
| $q_e$ (calc) (mg/g)        | 14.124      | 27.322  | 10.493     |
| $k_2$ (g/mg.min)           | 6.99 E – 03 | 0.0134  | 0.0122     |
| <b>Elovich</b>             |             |         |            |
| $R^2$                      | 0.9497      | 0.7928  | 0.6747     |
| $\alpha$ (mg/g.min)        | 13.423      | 26.396  | 1.108 E 06 |
| $\beta$ (g/mg)             | 0.5304      | 0.2428  | 2.0145     |

### 3.5. Thermodynamic studies.

Temperature is one of the important factors that affect the adsorption process because it determines its feasibility. The various thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) for the adsorption of MG and CR onto APS, and MG onto APS-ZnO were obtained from the slope and intercept of the plot of  $\ln K_o$  against the inverse of temperature,  $1/T$ . The results of the thermodynamic studies are presented in Table 7. The adsorption of MG onto APS and APS-ZnO was exothermic since  $\Delta H$  values were negative; the CR-APS system was endothermic. The value of  $\Delta H$  obtained for the adsorption of MG onto APS-ZnO was - 4.51 kJ/mol. This also confirmed the exothermic nature of the adsorption process. The feasibility and spontaneity of the adsorption process were further verified by the negative  $\Delta G$  values obtained.

**Table 7.** Thermodynamic parameters for the adsorption of MG onto APS-ZnO and APS and CR onto APS.

| Adsorbate | Adsorbent | Thermodynamic parameters          | Temperature (K) |        |       |       |
|-----------|-----------|-----------------------------------|-----------------|--------|-------|-------|
|           |           |                                   | 303             | 313    | 323   | 333   |
| MG        | APS-ZnO   | $\Delta G$ (kJmol <sup>-1</sup> ) | -3.94           | -3.92  | -3.91 | -3.89 |
|           |           | $\Delta H$ (kJmol <sup>-1</sup> ) |                 | -4.51  |       |       |
|           |           | $\Delta S$ (J/mol.K)              |                 | -1.87  |       |       |
| MG        | APS       | $\Delta G$ (kJmol <sup>-1</sup> ) | -3.29           | -3.38  | -3.47 | -3.57 |
|           |           | $\Delta H$ (kJmol <sup>-1</sup> ) |                 | -0.45  |       |       |
|           |           | $\Delta S$ (J/mol.K)              |                 | +9.35  |       |       |
| CR        | APS       | $\Delta G$ (kJmol <sup>-1</sup> ) | +0.39           | +0.05  | -0.29 | -0.64 |
|           |           | $\Delta H$ (kJmol <sup>-1</sup> ) |                 | +10.72 |       |       |
|           |           | $\Delta S$ (J/mol.K)              |                 | +34.10 |       |       |

The adsorption of MG and CR onto APS-ZnO and APS was spontaneous for all the temperatures studied except at 303 and 313 K for CR onto APS. However, as the temperature

rose to 323 K, the system became spontaneous. It was also noted that there was a lower degree of disorderliness at the sorbate/sorbent interface in the adsorption of MG onto APS-ZnO, which was reflected in the negative  $\Delta S$  value. Similar results were reported by [52].

#### **4. Conclusions**

Incorporating nanoparticles into the acid-modified *Carica papaya* seed (APS) adsorbent increased surface area and enhanced adsorption capacity for malachite green (MG) in solution. The physicochemical parameters of the adsorbates (MG and Congo red (CR)), including polar surface area, molecular weight, hydrogen bond acceptor count, covalent bond acceptor count, and complexity, were found to influence adsorption processes. Abundant types of adsorbent functional groups also enhanced adsorption. The isotherm, kinetic, and thermodynamic studies gave insights into types of adsorbent-adsorbate interactions, mechanisms of interactions, and heat movements within the processes.

#### **Author Contributions**

Conceptualization, G.A. A.; methodology, A.A.D.; formal analysis, A.A.D.; investigation, A.A.D; resources, A.A.D. and G.A.A.; data curation, A.A.D, and A.S.A.; writing—A.S.A; writing—review and editing, A.S.A.; supervision, A.D.O.; project administration, G.A.A.. All authors have read and agreed to the published version of the manuscript.

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#### **Informed Consent Statement**

Not applicable.

#### **Data Availability Statement**

Data supporting the findings of this study are available upon reasonable request from the corresponding author.

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#### **Conflicts of Interest**

The authors declare no conflict of interest.

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