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Influence of Sol Gel Conversion on the Adsorption Capacity of Crab Shell for the Removal of Crystal Violet from Aqueous Solution

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Abstract: *The influence of concentration on the adsorption of crystal violet by crab shell (CS) and CaO nanoparticles (CaONP) produced from the shell by sol-gel method was investigated between an initial dye concentration range of 10 to 70 mg/L. The results indicated the equilibrium amount of dye adsorbed (Q_e) by CaONP and CS to increase with an increase in concentration while the percentage removal efficiency ranged from 92.67 to 99.22 % and from 49.33 to 98.67 % for CaONP and CS respectively. CaONP was a better adsorbent than CS. The adsorption of the dye on both adsorbents fitted the Langmuir and Freundlich adsorption models but better fitness was observed for the nanoparticles. The adsorption of the dye on both adsorbents was deduced to occur through cooperative adsorption while the mechanism of physical adsorption was proposed. The study concluded that CaONP and CS can be an efficient adsorbents for the removal of crystal violet dye from an aqueous solution if operational parameters are properly optimized.*

Keywords: *Water, contamination, remediation, crab shell, CaO nanoparticle*

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1.0 Introduction

Adsorption is one of the most applied and acceptable means of removing contaminants from aqueous media (Odiongenyi, 2020a-c, 2021). The aqueous system is a significant part of the environment as far as environmental pollution is properly referenced because of its capacity to serve as a medium for transporting contaminants into other components of the environment (including man, plant, animal soil and even the air). Adsorption can be facilitated through batch or column (continuous flow) methods and the primary purpose of the process at an industrial scale is to reduce the level of contaminants in discharge effluence to such an extent, that the discharge concentration is acceptable to the best environmental level. Several adsorbents have been tested, approved and applied for this purpose (Garg *et* al., 2022). However, part of the current protocol in the activation of waste management policies is resource recovery, reuse, or recycling, with the primary aim of reducing the volume of agricultural, domestic, or industrial waste to be disposed of (Eddy *et al*., 2022). In response to this call, several plants and animal shells have been used as adsorbents for the removal of heavy metal ions, dyes, antibiotics and other contaminants (Odoemelam and Eddy, 2009'Uchechukwu *et al*., 2015a,b).

Crab shell is one of the waste materials that have great potential as an adsorbent for the removal of varieties of organic and inorganic pollutants (Cai *et al*., 2019). The shell is rich in $CaCO_3$ which has also proven to be a good adsorbent (Jacob *et al*., 2018). Beyond the direct utilization of crab shells as adsorbents for the removal of contaminants from aqueous solutions, due to their $CaCO_3$ content, current hope is much appealing towards the conversion of the shell to nanomaterials (Eddy and Garg, 2021).

3.0 Materials and Methods

Samples of crabs were purchased from Oron market and the shell was removed, dried and crushed to powder form. Crab contains $CaCO_3$

and the method that was adopted for the synthesis was the sol-gel method. The process included the following steps :

(i) Preparation of homogeneous solution
(ii) the formation of 'sol' by hydrolysis,
(iii) the formation of 'gel' by condensation
(iv) drying of the formed gel. I

During the process, the $CaCO_3$ in the crab shell reacted with HCl to form $CaCl_2$ according to equation 1

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)} \quad (1)$$

The next step was the formation of a stable dispersion of colloidal particles of precursors in a solvent through a hydrolysis reaction. During the hydrolysis process (using NaOH), metal hydroxide was formed and the homogeneous solution of $CaCl_2$ solution was converted to a sol at ambient temperature (equation .2).

$$CaCl_{2(aq)} + 2NaOH_{laq)} \rightarrow Ca(OH)_{2(aq)} + 2NaCl_{(aq)} \quad (2)$$

The slow addition of NaOH resulted in a low rate of nucleation and encourages subsequent precipitation of $Ca(OH)_2$ one over another forming a highly crystalline gel. The condensation reaction produced small-sized particles interconnected to each other to form a rigid and highly crystalline inorganic network within the liquid. $Ca(OH)_2$ gel, which contained the solution. The solution was aged overnight at ambient temperature to form CaONP according to the following equation:

$$Ca(OH)_{2(aq)} \xrightarrow{\Delta} CaO + H_2O \quad (3)$$

Batch adsorption experiments were carried out as reported elsewhere (Odiongenyi, 2020a-b). The method was most useful for the investigation of parameters that affects adsorption such as initial dye concentration, period of contact, etc. In each case, the equilibrium amount of dye adsorbed was estimated using the following equation

$$Q_e = \frac{C_0 - C_e}{C_0} \times \frac{V}{m} \quad (4)$$

where Q_e is the equilibrium amount of dye adsorbed, C_o and C_e are the initial and equilibrium concentration of the dye (i.e inlet and outlet concentration) respectively. All concentrations experiments were measured using a spectrophotometer

All spectrophotometric measurements were carried out to estimate the concentration of the dye in the solution (using 721,P/N:A003 UV-visible spectrophotometer). The wavelength of maximum absorption was first obtained by scanning 50 ppm of the solution at various wavelengths. A calibration curve was developed through the measurements of values of absorbances of serially diluted solutions of the dye (crystal violet) according to the requirements of Beer-Lambert's law. The plotted graph is shown in Fig. 1.

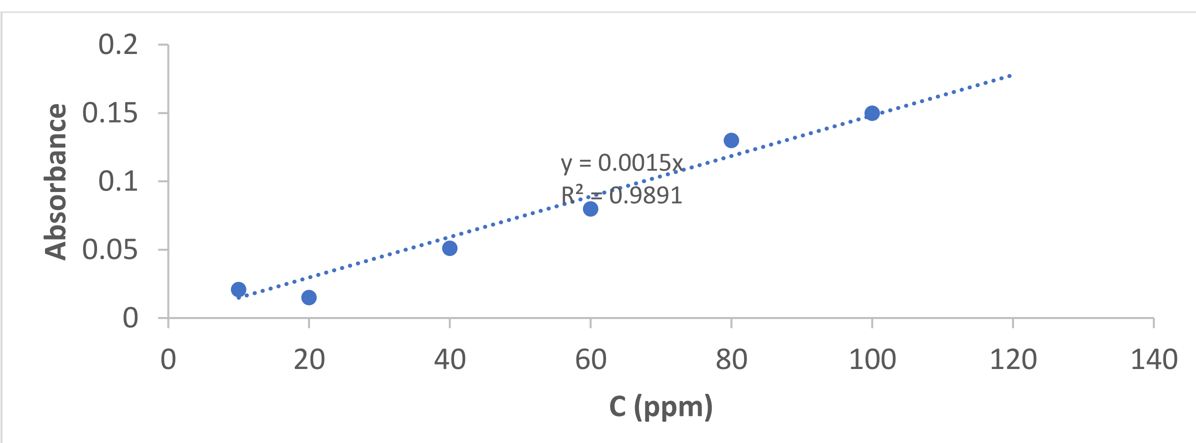

Fig. 1: Calibration curve for crystal violet dye

From the plot, it is evident that the Beer-Lambert's law was obeyed with R^2 values equal to 0.9891. Therefore, this plot was adopted as a reference for the determination of the concentration of the dye after absorption through extrapolation.

3.0` Results and Discussion

3.1 Effect of concentration

Fig. 2 shows plots for the variation of the equilibrium amount of dye adsorbed with the initial concentration of dye in solution. The Figure reveals that the amount of dye adsorbed by calcium oxide nanoparticle that was synthesized from crab shell (CaONP) and by the crab shell (CS) increases with an increase in concentration This is due to an increase in the amount of the adsorbate (crystal violet) approaching the vacant and active adsorption sites. Odoemelam *et al*. (2018) reported that given a fixed number of available adsorption sites that are activated, the rate of adsorption of dye would be strongly dependent on the concentration of the dye in the solution. Consequently, the more the concentration, the higher the rate. Similar observations have been reported by Ekop and Eddy (2009, 2010), Eddy (2009), Odoemelam and Eddy (2009), Uchechukwu *et al*. (2015, 2018) and Essien and Eddy (2015). Therefore, the adsorption of crystal violet dye unto CaONP and CS surfaces slightly followed a linear model with a slight deviation.

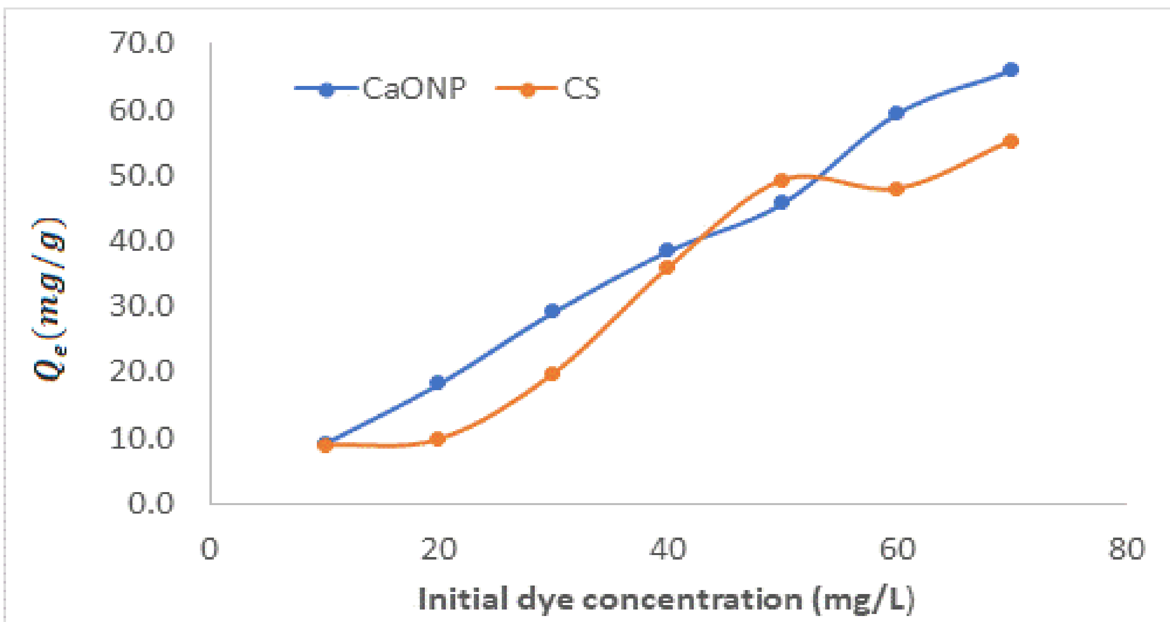

Fig. 2: Variolization of equilibrium amount of dye adsorbed with the initial concentration of dye

The results presented in Fig.2 also reveal that the CaONP exhibited better adsorption properties than CS which can be attributed to an increase in surface area and other properties associated with its nano dimension (Odiongenyi and Afangide, (2019).

3.2 Adsorption isotherm

Adsorption isotherms can provide information on the behaviour of the adsorbate and adsorbent such as existing interactions, mode of adsorption, mechanism of adsorption and other properties. The basic adsorption isotherms are the Langmuir and Freundlich isotherms.

The Langmuir isotherm is mostly applicable to ideal monolayer adsorption on a homogeneous surface (Eddy and Ekop, 2010). On the other hand, the Freundlich isotherm applies to nonideal adsorption on heterogeneous surfaces based on the assumption that a large number and many different types of available sites act simultaneously with the different free energy of sorption (Odoemelam *et al*. (2018).

The Langmuir adsorption isotherm can be written according to equation 5 (Uchechukwu *et al*., 2018)

$$\frac{1}{Q_e} = \frac{1}{Q_{max} b} \times \frac{1}{C_e} + \frac{1}{Q_{max}} \quad (5)$$

where Q_e is the equilibrium amount of dye adsorbed, Q_{max} and b are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively. Based on equation 4.1, the plots of $1/ Q_e$ versus $1/ C_e$ were linear for both CaONP and CS with R^2 values of 0.9994 and 0.8238 respectively, which confirmed that the adsorption of crystal violet dye onto CaONP and CS followed monolayer adsorption to a good extent as shown in Fig. 3. Calculated Q_{max} for CaONP (1111.11 mg/g) was higher than that of CS (181.81 mg/g), which also confirms that the CaONP displayed better adsorption capacity than the CS due to nano configuration. A similar observation has been reported by Odiongenyi and Afangide (2019) for nano alumina and alumina.

The Freundlich model can be written according to equation 6 (Eddy, 2009)

$$lnQ_e = lnk_F + \frac{1}{n} lnC_e \quad (6)$$

From equation 5, a plot of lnQ_e versus lnC_e were linear for the adsorption of crystal violet dye on the surfaces of CaONP and CS. The measured degrees of linearity were 0.9983 and 0.9128 for CaONP and CS respectively which indicates that the adsorption of crystal violet dye by CaONP fitted the Freundlich model more than the adsorption by CS, Estimated values of 1/n were 1.0188 and 1.081 which gave n values of 0.9815 and 0.9251 for CaONP and CS respectively. Literature reveals that the variation in the slope between 0 and 1 is consistent with chemisorption mechanism which could not be upheld in this study because the slopes are greater than unity, which points towards cooperative adsorption

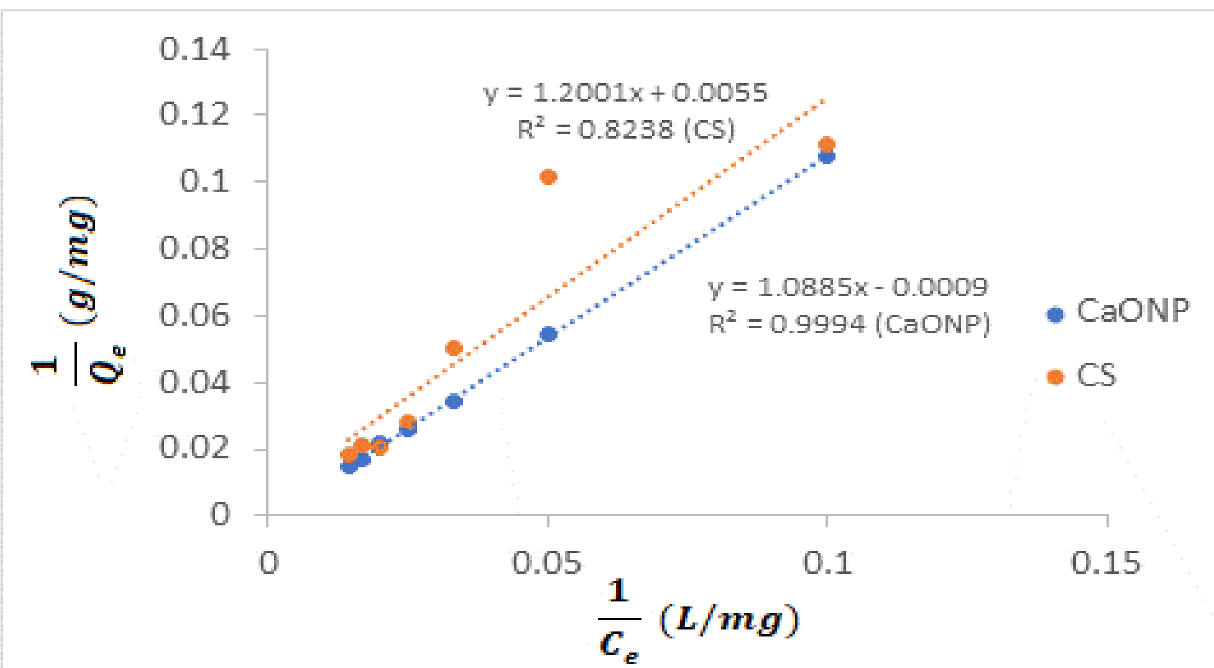

Fig. 3: Langmuir isotherm for the adsorption of crystal violet dye on CaONP and CS

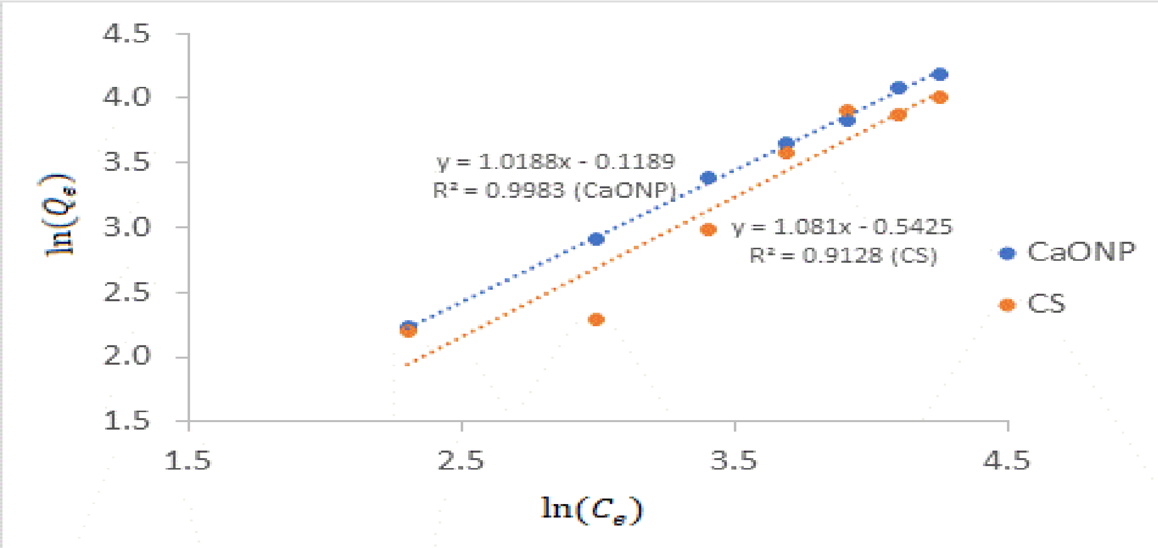

Fig. 4: Freundlich isotherm for the adsorption of crystal violet dye on CaONP and CS

4.0 Conclusion

The present study reveals the following findings,

(i) CaONP and CS are good adsorbents for the removal of crystal dye from an aqueous solution

(ii) CaONP is a better adsorbent than CS because of improved surface area and other properties associated with its nano dimension

(iii) The adsorption of crystal violet on CaONP and CS obeyed the Langmuir and Freundlich adsorption isotherm with CaONP showing a better degree of linearity

(iv) The adsorption of crystal violet on both CaONP and CS occurs through a cooperative adsorption process

(v) The mechanism of physical adsorption couldn't be sustained for the adsorption of crystal violet on CaONP and CS since the present study did not consider thermodynamic models

Given the outstanding information that is needed to firmly establish the excellent nature of these adsorbents, it is recommended that feature work should be conducted on the following,

(i)

(ii) Effect of contact time, temperature, adsorbent dosage, pH, ionic activity and spinning on the adsorption of crystal violet by CaONP and CS

(iii) Investigation into the morphology of both adsorbent and identification of functional groups associated with the adsorption

(iv) Identification of the actual composition of the crab shell and the CaONP as well as their indentation

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