Adsorption Kinetics And Equilibrium Of Crystal Violet Dye Onto Hooves Keratin-Stabilized Silver Nanoparticles

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Abstract

Crystal Violet (CV) is a hydrosoluble, highly hazardous, stubborn dye extensively use in textile industries while posing serious life-threatening health and environmental pollution challenges. In this study, we explored the efficiency of synthesized silver nanoparticles (AgNPs) stabilized by keratin extracted from sheep hooves for adsorptive removal of CV dye. FTIR characterization of AgNps revealed existence of alkyl, nitrile amide I- III and carbonyl functional groups. Batch experimental results showed that removal of CV dye strongly dependent on the initial CV concentrations, dosage, sorption time and temperature. The adsorption equilibrium was attained within three hours and sorption efficacy of up to 97.9% dye removal achieved. The optimum adsorbent dosage was found 8 mg at optimum pH range of 3.0 - 5.0. Modelling of the kinetic data revealed that pseudo-second order had a perfect fit, inferring that chemisorption process best explained the adsorption of CV onto AgNps with maximum equilibrium adsorption capacity of 24.69 mg/g. The biogenically prepared AgNps were found to be highly effective in CV dye sorption and could go a long way in valorization of abundant keratinous waste such as sheep hooves which are currently an environmental menace

Key Word: *Adsorption; Silver nanoparticles; Kinetics; Crystal violet dye; Keratin*

I.   Introduction

Wastewaters contaminated with organic dyes from industries like textile, plastic, automotive, cosmetic, printing inks, leather tanning and paper pose a dire life-threatening risks and environmental pollution complications. For instance, textile industry alone consume about 7.5×10^5 tons of organic dye annually and discharge over $1.5 \times 10^5 M^3$ of contaminated wastewaters containing about 10-15% of unutilized dye [1–3]. There is a vital demand for an efficient treatment and disposal techniques of wastewaters containing dyes because dyes are cancerous, mutagenic, toxic and unsafe. In addition, colored wastewaters negatively affect photosynthesis of hydrophytic plants, reduce oxygen amounts in water and in extreme circumstances, leads to asphyxiation of aquatic life [4].

Different chemical, physical and biological approaches including crystallization, solvent extraction, membrane filtration, reverse osmosis, coagulation/flocculation, ion exchange, microbial degradation, sedimentation, evaporation, oxidation/reduction, bio-catalytic degradation and electrocoagulation have been employed in wastewater treatment with varied degree of success [5–8]. However, these approaches have drawback issues like costly, long operation time, generation of toxic sludge that require further treatment and inefficiency at lower concentration [9]. Adsorption has attracted a special attention as the most effective technique for wastewater treatment because it faster, easily applicable for large volume, allows for regeneration and recycling of solid adsorbents and dye molecules. High adsorption capacity of the sorbent is highly affected by the available surface area on the solid. Activated carbon is the broadly used owing to high efficacy, but its high exorbitant cost and requirement for an expensive recovery/regeneration make it uneconomically. This has pushed researchers to explore for a cheap and cost-efficient complementary materials such as copper-keratin nanoparticles [10], chitosan/acid-treated biomass[11], apricot seed shell [12], cellulose-based hydrogel[13] and metal oxide-clay nanocomposites [14]. In persistent effort to search for cost effective adsorbent, attention has been drawn to nanoparticles which provides a higher adsorption capacity and due larger surface area [15]. Nanoparticles are actual very small particles of size ranging from 1-100 nm [16]. Different nanoparticles such starch-based nanocomposites[17], chitosan-modified clays [18], oxide-clay nanocomposites [14] as have been

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prepared and applied for dyes removal with varied degree of efficacy. However, the potential and application of silver nanoparticles stabilized by keratin extracted from sheep hooves is largely limited in the literature.

Kenya just like other Eastern African countries are leading livestock producers for animals such as cattle, donkey, goats, Sheep, pig deer camel, bison etc that provide beef, hides/skins, organic fertilizer and foreign exchange. However, the non-edible keratinous parts of these animals such as hair, hooves, and horns etc. form substantial quantities of solid waste that pose severe environment pollution. Keratin has abundant cross linking of disulfide bonds that prevent its digestibility by humans and animal enzyme. The keratin solid wastes are currently managed by disposing them off in landfill, incineration burning in open field and burial which cause more health problems [19]. In addition, accumulation of these keratinous wastes at slaughter houses and landfill is blamed for providing auspicious habitat conditions for breeding of snails, rodent, mosquitoes, snakes and disease pathogens. In effort to alleviate environmental pollution and exploit the potential value of animal hooves this study affords the opportunity to synthesize silver nanoparticles stabilized by keratin extracted from sheep hooves for effective adsorption of CV dye. Crystal Violet dye ($C_{25}H_{30}ClN_3$) is a cationic triphenylmethane dye extensively in printing ink, textile, athletes feet antiseptic, as anti-freezers, fertilizers, paper and leather industries [20,21]. Even though the dye is extensively used to yield a strong violet color, it is known to be recalcitrant toxic, genotoxic and carcinogenic posing health risks [1]. This research offers opportunity to develop an alternate approach for utilizing abundant keratinous materials in solving pollution problems in our continued struggles to triumph affordable, high performing and effective adsorbent for adsorption of dyes and other pollutants from wastewaters.

II. Material And Methods

Keratin extraction

All chemicals and reagents deployed in this work were procured from Sigma-Aldrich Nairobi, were of the highest analytical grade and used without extra purification. Waste sheep hooves were sourced from a slaughter house, Kericho town, Kenya. They were washed severally with clean hot water to remove soil, foreign particles and dirt. The hooves were dried in the sun for one week to remove moisture, pulverized and stored in a zip lock bag. 50 g of the hoof powder was transferred to a clean 600 mL Pyrex glass, 200 mL of 2.5 % NaOH added and placed on a water path set at 80 ℃ for 2 h. The resultant mixture was filtered to get rid of proteins with lower molecular mass. Filtrate solution pH was reduced to pH 3.8 using HCl to get keratin precipitate.

Synthesis and Characterization of AgNps

0.1 g of keratin powder was added to 50.0 mL of 0.01 mol/L $AgNO_3$ in a 250 mL Erlenmeyer flask and covered with aluminium foil. The mixtures were placed on an orbital shaker (GS-20 AKMLab) set at 140 rpm for 10 minutes before adding 15 mL of 2.0 M NaOH with constant agitation for 30 min. The solution mixture were heated on a water path set at 80 ℃ for 90 min. The solution was let to settle for 24 hrs for effective formation of AgNps. The AgNps obtained were filtered using Whatman filter paper (No.1), rinsed severally with double distilled water and 70% ethanol before drying at 25 °C [22]. The optical properties of AgNps were determined using a UV-Vis spectrophotometer (U-2810 Hitachi High-Technologies Co) while Fourier-transform infrared spectroscopy (FTIR) instrument (IRAffinity-1S FTIR-Shimadzu model) was used to probe main functional groups interacting between AgNps formed and keratin.

Adsorption studies

A stock solution of 1.0 g/l CV dye was made by dissolving proper weight of the CV dye powder in double distilled water and subjected to sorption experimentations. All batch adsorption experimentations were done in duplicate and the average value presented. The working volume for batch adsorption experiments were made from the stock solution by suitable dilution. A set of experiment were performed in 50 mL conical flasks containing 10 mL of 10ppm of CV dye solution. Impact of pH was scrutinized at a pH range of pH 2.0-pH 10.0 using 8.0 mg of AgNps. Effect of AgNps dosage was determined usingadsobent mass ranging from 2 mg to 12 mg while dye concentration influence was determined using CV dye solution ranging from 0.625 ppm to 20ppm. Effect of temperature was investigated at 303k, 313k, 323k and 333k. Aliquots of 3.0 mL were withdrawn at an interval of 20 min and evaluated for the remaining CV dye using UV-Vis spectrometer before returning to the flasks to maintain the initial dye solution volume. The total amount of the CV dye removed per a unit mass of AgNps were determined using equ 1.

$$q_e = \frac{V(C_\circ - C_e)}{W}$$ (1)

Where C_o and C_e are the preliminary and equilibrium dye concentration (mg^{-1}), V is the volume of CV dye solution (L) and W is the quantity of AgNps used (g). Percent dye removed was estimated by equ 2.

$$\% \text{ of dye removed} = \frac{C_\circ - C_e}{C_\circ}$$ (2)

Kinetics of CV dye adsorption was studied using varied dye concentrations at room temperature. 8.0 mg of AgNps was added to 10 mL CV dye solution in a 50 mL conical flask and placed on a shaker set at 140 rpm. 3.0 mL of dye solution were withdrawn from the flask at an interval of 20 minutes to determine dye concentration and then returned to the flask to reinstate the original volume.

III. Results And Discussion

Preparation of keratin stabilized AgNps

Silver nanoparticles were synthesized by reacting keratin extracted from sheep hooves with silver nitrate ($AgNO_3$). The formation of AgNps was observed by the emergence of brown color with intense absorption peak at λ_{max}410 nm. Results shows that yield of silver nanoparticles improved with escalation of time up to 90 min before declining (Fig.1). During the synthesis process, more silver ions were reduced to AgNps, hence the quantity of nanoparticles increased with increase in time till saturation point (90 mins). After the 90th minute, the Amount of AgNps declined with further upsurge of time owing to aggregation of small particles [23].
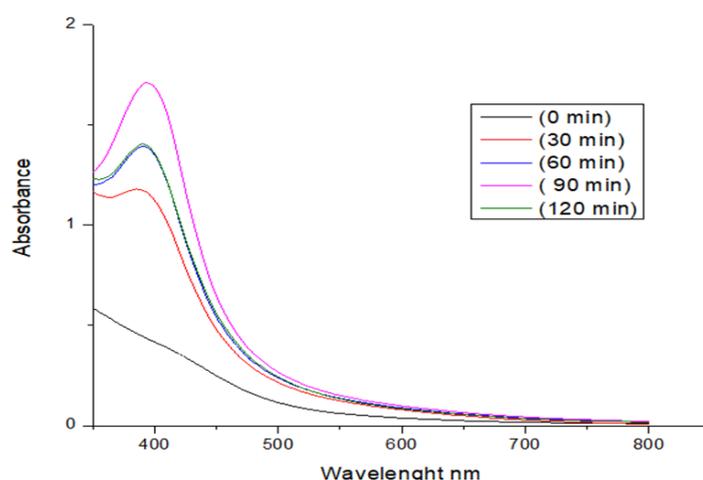

Fig. 1. UV–Vis spectra of AgNPs yield at different time

Characterization of keratin stabilized AgNps

FTIR characterization was done to qualitatively establish the probable interactions between keratin and silver in AgNps. A comparison between the extracted keratin alone and AgNps revealed (Fig.2.) revealed the involvement of keratin bio molecules in formation of silver nanoparticles. The characteristic amide III band at wavenumber 1217 cm^{-1} indicates $C - O$ stretching [24]; characteristic peak at 1369 cm^{-1} is linked to $C - H$ bending in keratin bio molecules; amide II band at 1533 cm^{-1} is assignable to $C - N$ stretching coupled with $N - H$ bending [25] and amide I band at wavenumber 1739 cm^{-1} indicated $C = O$ stretching in the carboxyl group [26,27]. The result further reveals that all the bands in AgNPs experienced red-shift to a lower frequency verifying that keratin protein formed a shell coat over the AgNPs sequentially stabilizing the nanoparticles. Similar findings have been observed in silver nanoparticles stabilized by wool keratin [28]
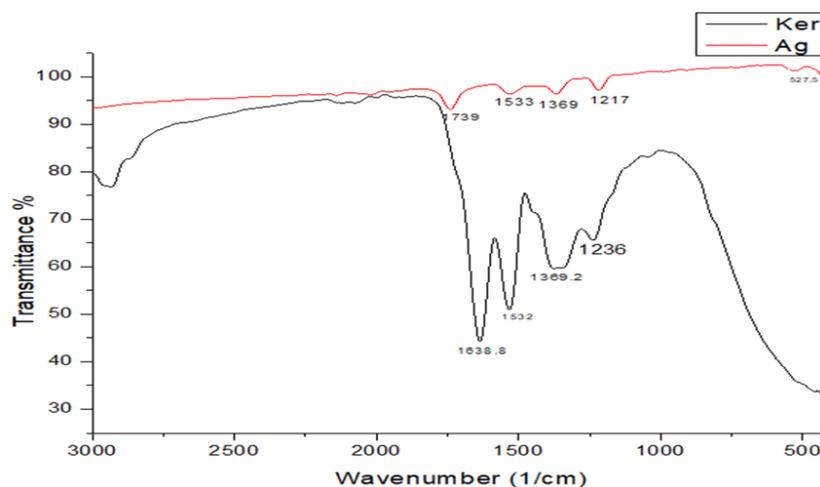

Fig. 2. FT-IR Spectrum for keratin (Ke) and silver nanoparticles (Ag)

Adsorption experiment
Effect contact time

The period taken for a successful adsorption cycle is critical when designing large scale wastewater treatment plant, managing daily overlaying operational cost and determining process efficacy. Fig. 3 displays the influence of contact time on sorption of CV dye by silver nanoparticles. The results reveal that sorption process attained equilibrium after 160 minutes and the ratio of dye removed surged with rise in time. AgNps speedily removed over 55% of the dye in the first 40 min after which percent dye removal became fairly steady till equilibrium where 97.9 % dye removal achieved. This could be attributed to their large surface area accessible for interaction with the CV dye [29]. High dye removal at the outset could be ascribed to the huge amount of vacant surface existing for dye uptake. However, as time progressed, active sites on AgNps gradually became exhausted up to a point where the small number of remaining active sites could not be filled owing to the strong repellant forces between the CV dye molecules on the solid and solution phases. Comparable outcome have been reported earlier in adsorption of CV dye utilizing silver nanoparticles immobilized on the activated carbon[29].
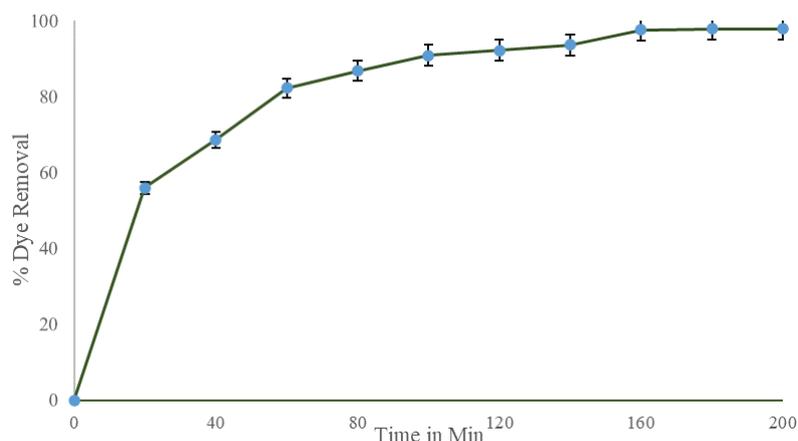

Fig. 3. Effect of contact time on adsorption of crystal violet by AgNPs: (Silver nanoparticles 8 mg/10 mL at 25 ° C)

Initial dye concentration effect

Initial CV dye concentrations effect on adsorption of CV was studied at varied concentrations and outcomes presented in Fig.4. The amount of dye removed increased with rise of CV concentration. For instance, when dye concentration was increased from 0.625 ppm to 20 ppm, the amount of dye adsorbed improved from 0.6867 to 23.50 mg/g. Increasing CV dye concentration increases concentration slope bring about enhanced driving force necessary to overpower mass transfer resistances of the dye molecules between the bulk solution and solid phases thereby pushing more CV molecules to diffuse into AgNps pores [30]. These findings are comparable with outcome in sorption of CV dye by coffee shells [1,30].
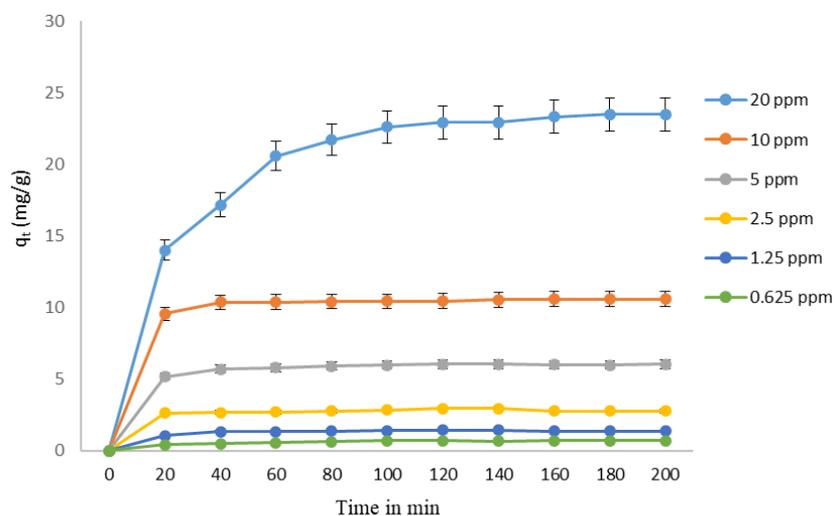

Fig. 4. Effect of dye concentration on adsorption of CV dye by AgNps (Silver nanoparticles 8 mg/10mL at 25 ° C)

Effect of AgNps dosage

The amount of adsorbent utilized in the removal of pollutants is essential since it determines the adsorbent–sorbate proportion and cost-effectiveness of the adsorption scheme [2,6]. The impact of AgNp dosage on CV dye sorption was investigated by altering the quantity of AgNps used and results revealed in Fig 5. It is clear that the quantity of CV dye removed improved with rise in the amount of AgNps upto 8 mg before a slight decrease. The increase in the quantity of AgNps avails more surface providing additional adsorption sites resulting in rise in amount of dye removed [3]. The small decline in the amount of dye removed when AgNps increased beyond 8 mg could be linked to particle aggregation resulting in overlying of available active adsorption sites weakening dye removal [31].
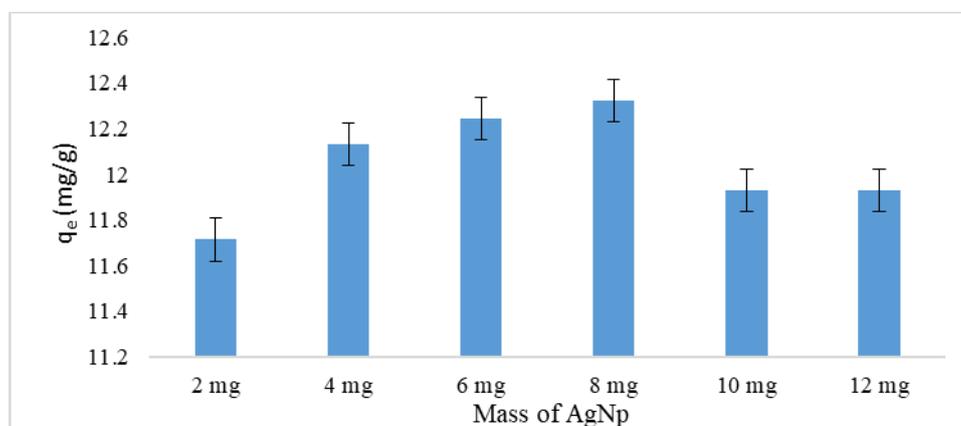

Fig. 5: Effect of adsorbent dose on CV dye adsorption by AgNps (Crystal Violet: 10 ppm; Temperature 25 °C; Time: 160 min)

Effect of pH on dye adsorption

pH performs a crucial function in altering the magnitude electrostatic charges on the adsorbent surface and the scale of adsorbate dissociation [32]. The impact of pH on CV dye sorption by AgNps was evaluated by varying CV dye solution pH from pH 3 to pH 10 and findings given in Fig. 6. Though pH is recognized to exert impact on dye uptake by adsorbents, we witnessed from the results that CV dye removal by AgNps remained relatively constant at a pH range of pH 3 to pH 8 before a slight declining beyond pH 8. In the acidic and neutral region, it was visible that pH had no impact on CV dye adsorption while in basic media, an increase in pH witnessed a decline in adsorption. Similar outcomes have been recounted on sorption of CV dye onto multi walled carbon nanotubes [31].
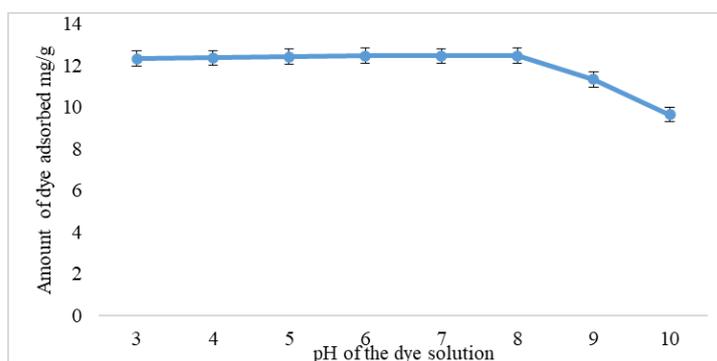

Fig 6: Effect of pH on adsorption of CV dye by AgNps (Crystal Violet: 8.0 ppm; dosage: 8gm; 25 °C; Time: 160 min).

Effect of Temperature

Solution temperature have an impact on kinesis, density and viscidness of the solution and in some cases alter the coagulation of adsorbent particles which have a bearing on rate diffusion of dye molecules into adsorbent pores [33]**.** Temperature influence on CV dye removal using silver nanoparticles was probed at different temperatures ranging from 25 °C to 60 °C and results displayed in Fig 7. The results revealed a small increase in amount of CV adsorbed from 12.02 to 12.10 mgg^{-1} when temperature improved from 25 °C to 40 °C. However, as the temperature further increased, dye sorption capacity begun to fall due to decline in the intensity of binding forces leading to some CV dye molecules detached from AgNps [1].
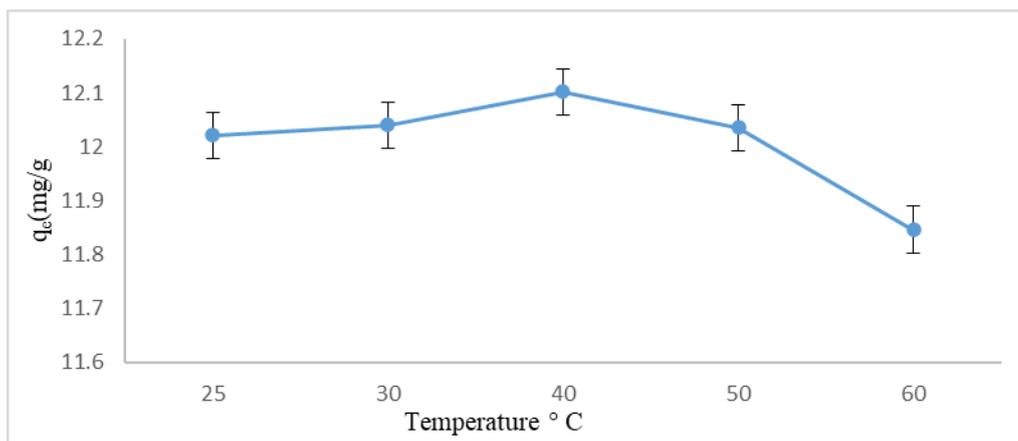
Fig. 7: Effect of temperature on adsorption of CV Dye by AgNps (Crystal Violet: 10.0 ppm; Time: 160 min, dosage: 8gm; pH: 8)

Adsorption Kinetics

The speed and efficacy of dye removal by an adsorbent is of great significance with regards to potential upscaling of the treatment systems. The data obtained in the sorption of CV dye onto AgNps was fitted on pseudo first and second order kinetic model to determine the rate dye sorption [31]. Pseudo first order kinetic model in integral form is given by equ 3.

$$\log (q_e - q_t)= \log q_e - \frac{tk_1}{2.303} \tag{3}$$

Where k_1 denotes rate constant for adsorption in the pseudo 1st order model. q_e and q_t represents the quantity of CV dye adsorbed by AgNps at equilibrium and time t. The rate constants, estimated equilibrium removal and equivalent coefficient of correlation for the analyzed concentrations were computed and displayed in Table 1. Pseudo-first order kinetic model did not provide a good fitting to the test data with a lower R^2 values. Similarly, experimental and theoretical sorption capacities varied widely portraying insufficiency of the model in depicting sorption of CV dye on AgNps. The pseudo 2nd order model is given by equ 4:

$$\frac{t}{q_t}= \frac{1}{k_2} \cdot \frac{1}{q_e^2} + \frac{t}{q_e} \tag{4}$$

Where k_2 is the rate constant of dye sorption (g/mg min), q_e and q_t are the amount of CV dye adsorbed on AgNps surface at equilibrium and time t(mg/g) respectively. The quantities of q_e and k_2 are computed from gradient and intercepts of t/qe vs t respectively. Fig. 8 shows a graph of pseudo-second order kinetics for sorption of CV dye on silver nanoparticles. Values of k_2, q_e and R^2 were determined and displayed in Table 1. The results show higher value of correlation efficient ($R^2 > 0.99$) and the experimental data had a better fit on pseudo 2nd order model signifying that removal of CV dye by silver nanoparticles can be exemplified by pseudo 2nd order kinetics model. The outcomes show that sorption process is highly predetermined by the amount of AgNps and the number of vacant sorption sites on the adsorbent [33]. Maximum quantity of dye adsorbed was found to be 24.69 g/mg at 20ppm. Similar kinetic modelling have been observed in the adsorption of CV dye by coffee husks [1], adsorption of CV onto carbon nanotubes [31] and sorption of MB dye by pomegranate fruit peel [34].

Table 1. Kinetics data for adsorption of CV dye by Silver Nanoparticles

	Pseudo First order models parameters				Pseudo second order models parameters		
CV (ppm)	$q_{e (exp)}$(g^{1}mg)	$q_{e\ calc}$(g^{1}mg)	k_1 (gmg^{-1}min^{-1})	R^2	$q_{e\ calc}$(mg/g)	k_2(g mg^{-1}min^{-1})	R^2
0.625	0.687	0.5678	0.0242	0.9515	0.7277	0.11207	0.9912
1.25	1.417	0.8041	0.0334	0.8809	1.398	0.3109	0.9983
2.5	2.935	1.263	0.0281	0.5550	2.813	0.79937	0.9976
5.0	6.028	3.391	0.0426	0.9307	6.083	0.07947	0.9998
10.0	10.60	2.428	0.0286	0.8006	10.65	0.06710	0.9999
20.0	23.50	12.69	0.0274	0.9792	24.69	0.00388	0.9957

Comparison of adsorption capacity of nanoparticle adsorbents obtained from other agricultural wastes for the removal of CV dye are summarized in (Table 2) and demonstrate that prepared AgNps are relatively effective adsorbent.

Table 2. Comparison of adsorption capacity of Crystal Violet dye onto nanoparticle with literature

Adsorbents	Dye	Adsorption capacity (mg/g)	References
Magnetized orange peel (MOP	Crystal Violet	46.93	[35]
mesoporous guar gum/NiWO4 nanocomposite	Crystal Violet	170.42	[36]

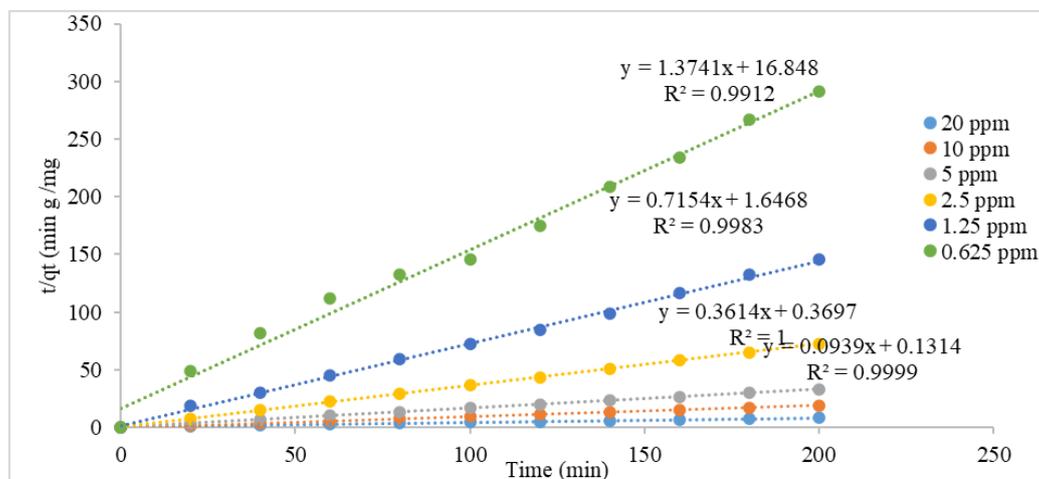| L-Ascorbic Acid-g-Polyaniline Mesoporous Silica Nanocomposite	Crystal Violet	88.42	[37]
Magnetic Chitosan-Glutaraldehyde/Zinc Oxide/Fe₃O₄ Nanocomposite	Crystal Violet	176.6	[38]
Rice Husk Biochar-Based Magnetic Nanocomposite	Crystal Violet	185.6	[39]
Spirulina Based Iron Oxide Nanoparticles	Crystal Violet	55.62	[40]

Fig. 8: Plots for Pseudo Second order model in adsorption of CV by AgNPs

Adsorption Isotherms

Freundlich and Langmuir isotherms were applied to envisage the sorption capacity of AgNps for crystal violet dye. Langmuir isotherm assumes monomolecular layer sorption on homogeneous adsorbent surface where the binding sites are actively analogous and identical. The nonlinearly and the linear models of Langmuir isotherm equations are depicted in equ 5 and 6 respectively.

$$q_e = \frac{q_{mx} b C_e}{1 + b C_e} \qquad (5)$$

$$\frac{1}{q_e} = \frac{1}{q_{mx} b C_e} + \frac{1}{q_0} \qquad (6)$$

Where q_e (g/mg) is the amount of the CV dye removed at equilibrium, C_e is the equilibrium concentration of the CV dye in solution phase. q_{mx} (g/mg) denotes the maximum coverage capacity for the mono-layer on surface of AgNps ; b (mg/L) is a Langmuir constant that describes binding sites affinity. From the graph of $\frac{1}{q_e}$ vs $\frac{1}{C_e}$ (Fig 9a) the values of q_{mx} and b are gotten from the gradient and $\frac{1}{q_e}$ intercept respectively. Further evaluation was carried out to determine separation factor R_L used to illustrate the favorability of sorption process was evaluated using equ 7:

$$R_L = \frac{1}{b C_o + 1} \qquad (7)$$

Where C_o is the initial CV dye concentration. The R_L value ascertains if the isotherm is non reversible ($R_L = 0$), satisfactory ($R_L > 0 < 1$), non- satisfactory ($R_L > 1$) or rectilinear ($R_L = 1$) [41]. The value of R_L attained in the removal of CV by AgNps were less than 1, signifying a satisfactory process. The value of R_L , b and q_{mx} were work out and portrayed in Table 2. The high value of R^2 indicates that the data obtained fitted well to Langmuir isotherm indicating that it suitable isotherm for illustrating sorption of CV dye on AgNps. Freundlich isotherm denote multilayer sorption process appropriate for describing adsorption on heterogeneous surfaces. The linearized form of Freundlich isotherm is donated by equ 8:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (8)$$

Where K_F (mg/g)(L/mg) denotes Freundlich isotherm constants. $\frac{1}{n}$ stand for adsorption intensity. Values for K_F, and $\frac{1}{n}$ can be realized from antilog of the log q_e intercept and the gradient respectively. The scale of the exponent, 1/n, gives a suggestion of the favorability of sorption. Values of n > 1 denote favorable sorption conditions. Fig. 9(b) displays a graph of log q_e verses log C_e for the sorption of CV on AgNps and the corresponding Freundlich isotherm coefficients were calculated and tabulated in Table 3. The lower value of coefficients of correlation ($R^2 = 0.9245$) point out that Freundlich isotherm was not suitable for describing sorption of CV on AgNps.
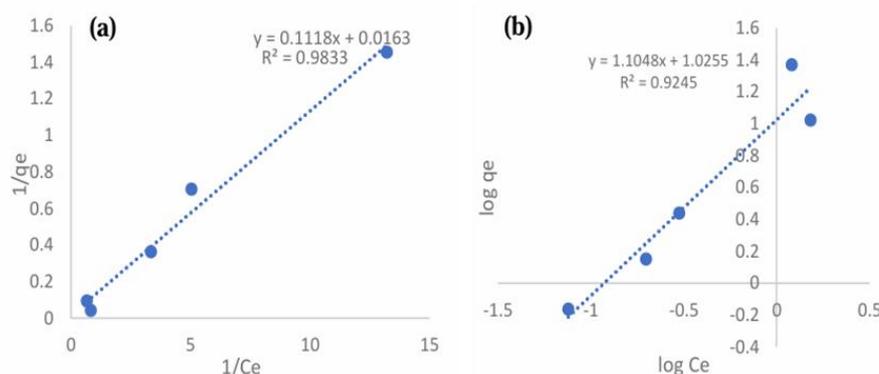
Fig 9: (a) Langmuir (b) Freundlich Isotherms for removal of CV dye by AgNps

Table 3: Langmuir and Freundlich isotherm constants for adsorption of CV dye on AgNPs

Langmuir adsorption isotherm				Freundlich adsorption isotherm		
q_{max}	b	R^2	R_L	K_F	n	R^2
2.313	61.35	0.9833	0.2554	10.60	0.9051	0.9245

IV. Conclusions

In this study, we investigated the efficiency of synthesized AgNPs stabilized by keratin extracted from sheep hooves for adsorptive removal of CV dye. FTIR characterization of AgNps revealed existence of alkyl, nitrile amide I- III and carbonyl functional groups. In addition, FTIR showed a red-shift to a lower frequency verifying that keratin protein formed a shell coat over the AgNPs subsequently stabilizing the nanoparticles. The synthesized AgNp were effective in adsorptive removal of CV dye. Experimental results established that removal of CV dye strongly dependent on the initial CV concentrations, dosage, sorption time and temperature. The optimum conditions for the batch adsorption to attain equilibrium was found to be 180 minutes with sorption efficacy of 97.9%. A pH range of 5-6 and temperature of 40 °C were found suitable for optimum CV dye adsorption. Adsorption of CV followed pseudo second order kinetic model while adsorption isotherm fitted to Langmuir isotherm model demonstrating a monolayer adsorption. The findings demonstrates that sheep hooves currently an environmental menace can be utilized as a cheap source of keratin for stabilizing AgNp for subsequent used in removal of organic pollutants such as dyes from aqueous environments. This could go a long way in valorization of abundant keratinous waste for sustainable development, safe environmental and good health**.**

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