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SYNTHESIS OF STARCH SILVER NANOPARTICLES AND ITS SYNERGISM WITH HONEY FOR ENHANCED INHIBITION OF MILD STEEL CORROSION IN ACID MEDIUM

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ABSTRACT

In this research, the corrosion of mild steel was studied in acidic medium and the inhibitory effect as well as the synergism of starch silver-nanoparticles (AgNPs) in combination with honey was evaluated. Synthesized starch-AgNPs- was used to explore the reticence of mild steel in acidic medium. The inhibition efficiency (% IE) for starch-AgNPs alone showed a maximum efficiency of 63.136% at 30˚C (200 mg/L) and a minimum efficiency of 19.9% at 70˚C (1 mg/L). However, the addition of honey improved the %IE as a maximum efficiency of 67.608% at 30˚C (200 mg/L) and a minimum efficiency of 29.914% at 70˚C (1 mg/L) were recorded. This supports the claim that starch-AgNPs show promising inhibitory properties and starch-AgNPs with honey are synergistic. Also, from the gravimetric data, it was observed that corrosion was aggravated at elevated temperature but a decrease was recorded at reduced temperature, with maximum and minimum corrosion rates of 52.467 at 70˚C and 4.248 at 30˚C respectively, which is in contrast to the %IE which decreased with increase in temperature. The experimental values do support the claims that starch-AgNPs is a good inhibitor for the corrosion of mild steel.

Keywords: Corrosion, inhibition, mild steel, nanoparticles, synergism, synthesis

INTRODUCTION

Nanotechnology is the manipulation of matter on an atomic, molecular and super molecular scale [1]. Nanoscience has been established recently as a new interdisciplinary science. It can be defined as a whole knowledge on fundamental properties of nano-size objects [2, 3]. Nanotechnology is very diverse, ranging from extension of conventional device physics to completely new approaches based upon molecular self-assembly from developing new materials with dimension on the nanoscale to direct control of matter on the atomic scale. In the United States, more than 4 x 10^6 tons of silver were consumed in 2000. Colloid silver is of particular interest because of distinctive properties such as good conductivity, chemical stability, catalytic and antibacterial activity [4].

Nanoparticles involve particles that are within the scale of nanometer [5]. Nanotechnology may be able to create many new materials and devices with a vast range of application, such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as any new technology, including concerns about toxicity and environmental impact of nanomaterials [5]. Additional applications include molecular diagnostics and photonic devices, which take advantage of the novel optical properties of these nanomaterials. An increasingly common application is the use of silver nanoparticles for antimicrobial coatings, and many textiles, keyboards, wound dressings, and biomedical devices now contain silver nanoparticles that continuously release a low level of silver ions to provide protection against bacteria [6].

The use of corrosion inhibitors is one of the most practical methods for the protection of metals against corrosion, especially in acid media. The corrosion inhibitors are generally used to protect metals against the attack of the acid solutions, which are widely used in acid pickling, industrial cleaning, acid descaling, oil well acidizing, etc. [7].

Starch is a natural polymer, available in abundance at low cost, renewable, and biodegradable. The packaging of amylose and amylopectin within the granules has been reported to vary among the starches from different species. The activity of the enzymes involved in starch biosynthesis may be responsible for the variation in amylose content among the various starches [8]. Chemically, it is a polysaccharide carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. Starch is produced by all green plants as an energy store. It is known to exhibit a very good performance as inhibitors for steel corrosion [9].

Honey is a sweet food made from bees using nectars from flowers. Honey bees, transforms nectars into honey by a process of regurgitation, and stores it as a primary food source in wax honey combs inside the beehive. Honey gets its sweetness from the monosaccharides, fructose and glucose, and has approximately the same sweetness as that of granulated sugar [10]. Honey belongs to the carbohydrate group of foods (sugars and starches), and is mainly a watery solution of two invent sugars: dextrose (glucose or grape sugar) and levulose (sucrose and fruit sugar), in nearly equal proportions [11].

This research aims to synthesize starch silver nanoparticles and synergise it with honey for the inhibition of mild steel corrosion in acid medium.

The aim will be accomplished by fulfilling the following research objectives:

1. Synthesis of silver nanoparticles using starch
2. Study of the corrosion rate of mild steel in acid medium
3. Study of the inhibition efficiency of starch AgNPs on mild steel using weight loss method
4. Evaluation of the synergistic effect of starch AgNPs and honey
5. Characterization of silver nanoparticles (AgNPs) with UV-Vis Spectrophotometer.

EXPERIMENTAL

Reagents

Silver Nitrate ($AgNO_3$), Hydrochloric Acid (HCl), Ethanol, Acetone, Starch, honey, Deionized water.

Materials

$AgNO_3$, HCl, acetone and pure starch of analytical grade were purchased from Sigma Aldrich. The sheet of mild steel was obtained from Engineering Department, Ahmadu Bello University Zaria. The starch selected for the investigation is soluble pure having solubility of 100g/L (30°C), bulk density 300 kgcm^{-3} and the pH value 7.5 (20 g/L H_2O, 27° C).The concentrations of starch prepared and used for the study varied at 1, 5, 10, 50, 100, 200, and 500 mg/L respectively [9].

Preparation of the Mild Steel

The sheet of mild steel were mechanically press-cut into coupons of length 49 mm and diameter 10 mm using Center Lathe Machine (Sp214-II, China) with the aid of HSS turning tool and sand paper to aid a thorough polishing so as to obtain a shiny surface which was then degreased with ethanol and dried with acetone [12].The coupons had purity 99.25% Fe, with chemical composition of 0.645% Mn, 0.12% C and 0.10% Si using Thermo Scientific Niton Metal Analyzer (XL2 XRF, Germany). All prepared steel sample were preserved in a desiccator [12].

Reagent Preparation

The solution of 0.5 M HCl was prepared in 250 cm^{3}volumetric flask using deionized water. Similarly, an aqueous solution of 0.1 M $AgNO_3$ was prepared using deionized water in a 200 cm^3 volumetric flask. The starch selected for the investigation is soluble pure having solubility of 100g/L (30ºC), bulk density 300 kgcm^{-3} and the pH value 7.5 (20 g/L H_2O, 27º C). The concentration of starch prepared and used for the study were varied at 1, 5, 10, 50, 100, 200 and 500(mg/L) [13].

Preparation of the Composite

The prepared 0.1M of aqueous solution of $AgNO_3$ was used for the synthesis of silver nanoparticles. The preparation was done in three phases. Firstly, different concentrations (1 mg/L, 5 mg/L, 10 mg/L, 50 mg/L, 100 mg/L, 200 mg/L and 500 mg/L) of aqueous solution of the starch was prepared on a hot plate. Secondly, the respective concentration of the starch solution was used to prepare the AgNPs from the already prepared aqueous solution of 0.1 M $AgNO_3$. Thirdly, to every 100 cm^3 of the respective composite, 5 cm^3 of natural honey which served as capping agents was added [14].

5cm^3 of starch was added to 95cm^3 of 0.1M aqueous solution of $AgNO_3$ in 250cm^3 Erlenmeyer flask, and mixed thoroughly by manual shaking and exposed to sunlight for 15 minutes for complete reduction [13].

Weight Loss Measurement

The weight loss experiment was performed for duration of 8h [12]. The pre-weighed cleaned mild steel coupons was suspended in 200cm^3 beakers containing 150cm^3 of the various test solutions maintained at 30ºC, 40ºC, 50ºC, 60ºC and 70ºC in a thermostatic bath with the aid of hooks. That is the blank solution, the starch AgNPs at varied concentration and the solution containing the respective mixture of various concentration of starch AgNPs in the presence of 5 cm^3 of honey. The expected weight loss taken was the difference between the weight at a given time and the original weight of the coupons. The measurements were carried out for the uninhibited solution (blank), solutions containing the respective concentration of the starch AgNPs, and finally the solution containing the mixture of the respective concentration of starch AgNPs and 5 cm^3 honey [9,14].

The corrosion rates were determined using the equation:

$$\text{Corrosion rate (mpy)} = \frac{534W}{pAt} \qquad (1)$$

Where: W is weight loss in mg, p is the density of specimen in g/cm^3, A is the area of specimen in square inch and t is exposure time in hours.

The %IE of the test solutions was evaluated using the following equation:

$$\%IE = \frac{CRo - CRi}{CRo} X\ 100 \qquad (2)$$

Where: CR_o is the corrosion rate of mild steel in absence of inhibitor and CRi is corrosion rate of mild steel in presence of inhibitor [15].

Synergism Evaluation

The synergistic effect of the various concentrations (1mg/L, 5mg/L, 10mg/L, 50mg/L, 100mg/L, 200mg/L, and 500 mg/L) of starch AgNPs in addition of 5 cm^3honey for mild steel in 0.5 M HCl at different temperature was considered.

The synergism parameters S_1, was evaluated using the relationship:

$$S1 = \frac{1 - I1{+}2}{1 - I'1{+}2}$$

Where, $I_{1+2} = (I_1 + I_2)$; I_1 is %IE of starch AgNPs and I_2 is %IE of honey, and I'_{1+2} is %IE of starch AgNPs in combination with honey.

The values of the synergism parameters for the various concentrations of starch studied were calculated from the gravimetric data at 30^{o}C, 40^{o}C, 50^{o}C, 60^{o}C and 70^{o}C [9].

Standard buffer solution: one buffer tablet each of pH 4.0, 7.0 and 9.2 was dissolved in distilled water separately and made up to 100 cm^3. Exactly 10 g of the air-dried and sieved (0.125 mm) starch was weighed into a glass container and 10 cm^3 of distilled water was added. The mixture was allowed to stand for 1 hour. The pH meter was turned on and allowed to warm for 15 minutes. The glass electrode was standardized using a standard buffer of pH 7.0 and thereafter, calibrated with the buffer pH = 4. The glass electrode of the pH meter was immersed in the mixture and the pH values to the nearest 0.1 unit were taken. The glass electrodes were standardized after every ten determinations [16].

UV-Visible Analysis

UV-Visible spectroscopy is one of the most widely used techniques for the structural characterization of silver nanoparticles [17]. The bio reduced sample was spectroscopically confirmed by UV-Visible spectrophotometer (CARY 630 UV Agilent Technology, United State). The obtained AgNPs was purified through repeated centrifugation for 20 min and washed with distilled water [18]. The sample was analyzed by preparing dilute solution made in deionized water. The reduction of Ag^+ ions was monitored from 300 – 800nm with deionized water serving as blank.

RESULTS AND DISCUSSION

Silver nanoparticles exhibits yellowish brown colour in aqueous solution due to excitation of surface plasma vibration in silver nanoparticles [17]. As the starch was mixed in aqueous solution of silver ion complex, a change in colour from colourless to yellowish brown due to reduction of silver nanoparticles was observed [18] as shown inplate 1. Formation of AgNPs from 0.1 M solution of $AgNO_3$ produced by reduction using starch is represented in this study. Depending on the concentration of the starch used, the samples were denoted as SAg1, SAg5, SAg10, SAg50, SAg100, SAg200 and SAg500 for 1, 5, 10, 50, 100, 200 and 500 g/L, respectively.

Plate 1: Biosynthesized composite of AgNPs using starch visible observation

Corrosion inhibition of mild steel using starch silver nanoparticles and honey in 5 M HCl was investigated in this study using weight loss technique. The plots represented in (Figure 1 and 2), show that the corrosion rate decreased in the presence of inhibitor (Starch-AgNPs) in contrast to that of the blank solution (acid), at each of the temperatures. Also the corrosion rate increased with increase in temperature at all concentrations. This corresponds to reports in previous literatures [9]. The results from the gravimetric data revealed that the steel was more corroded as the surface was rougher in blank medium than in the inhibited medium. The results further suggest that the presence of inhibitor reduced the extent of corrosion, the surface became smoother compared to the sample in the uninhibited solution. This reveals the performance of inhibitor by protective layer formation, which separates the interaction between the metal and corrosive medium. Similar behavior was observed in previous literature [19].

The plots of IE for starch-AgNPs and starch-AgNPs in combination with honey at varied temperatures as represented in figure 1 and 2 respectively also reveal that IE increases with increase in starch concentration showing a maximum efficiency of 63.136% at 30^{o}C in presence of AgNPs concentration of 200 mg/L. Further addition of starch does not significantly influence the IE. A decrease in IE with increasing temperature suggests possible desorption of some of the adsorbed starch molecules from the metal surface at higher temperatures. This behavior shows that the starch was physically adsorbed on the metal surface [20].As the temperature increases, the quantity of equilibrium of adsorption decreases and as a result, the plot of higher temperatures is below the lower ones. The data derived from the weight loss measurement suggests that it is an adsorption inhibitor and the adsorption inhibition process occurs physically on the metal surface since the inhibition efficiency of starch AgNPs for mild steel corrosion decreases with increase in temperature [9].

The increased IE with increasing starch concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film [21].In addition, the binding interactions between starch and silver nanoparticle are weak and can be reversible at higher temperatures, allowing separation of the synthesized particles [18].

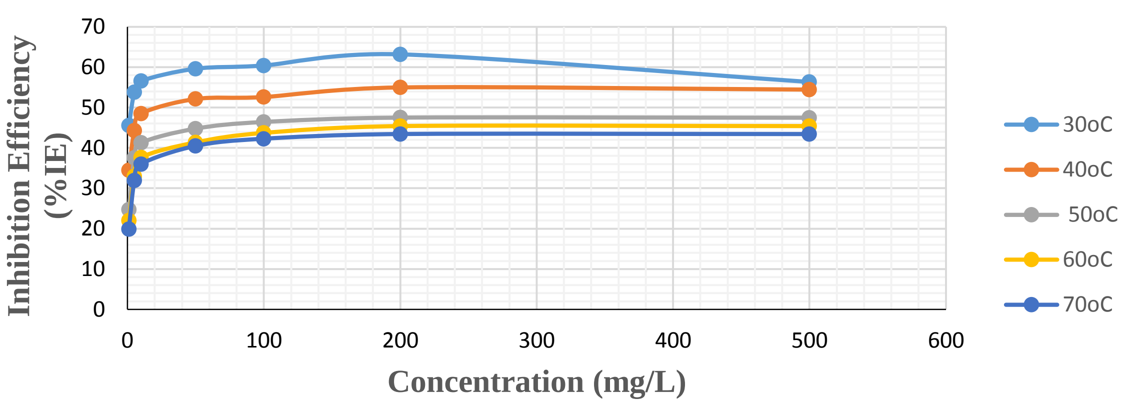

Figure 1: Plot of Inhibition Efficiency (%IE) for Mild Steel in 0.5 M HCl in the Presence of Varying Concentration of starch AgNPs at (30ºC, 40ºC, 50ºC, 60ºC and 70ºC) from Weight Loss Measurement

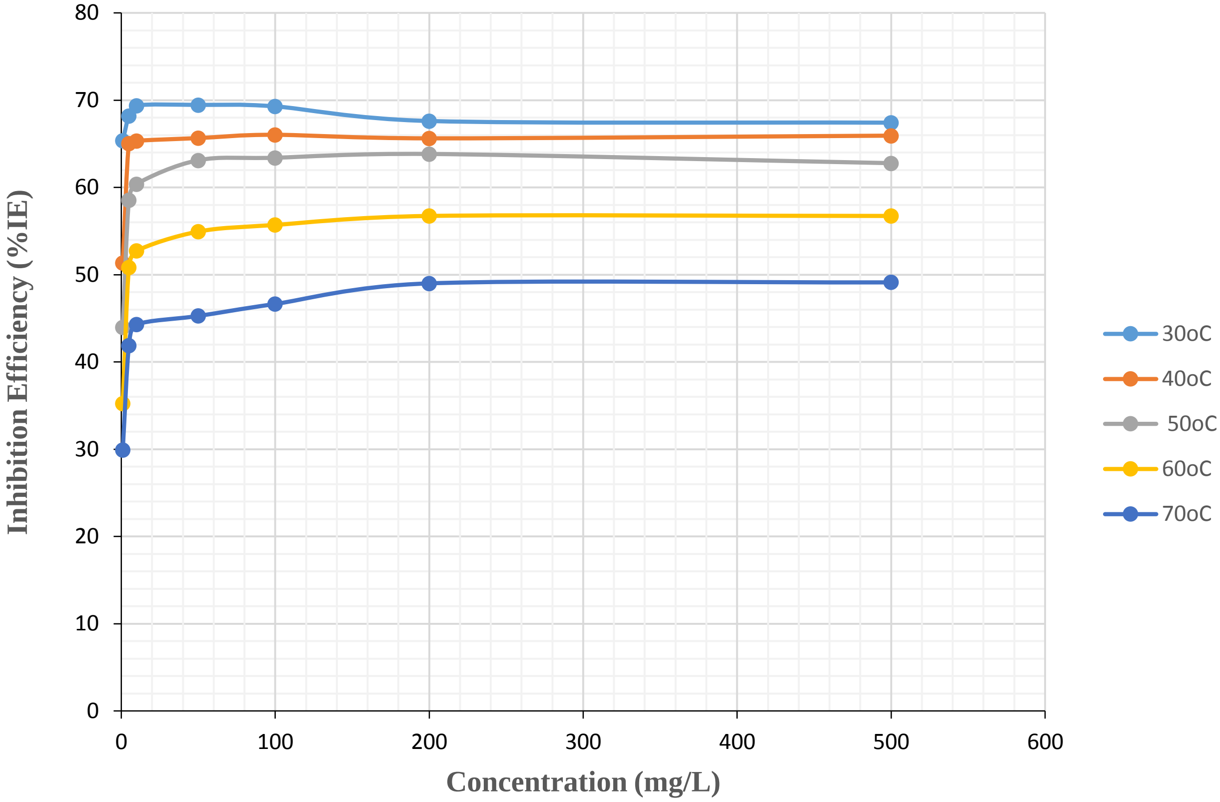

Figure 2: Plot of Inhibition Efficiency (%IE) for Mild Steel in 0.5 M HCl in the Presence of Varying Concentration of starch AgNPs with 5 cm^3 honey at (30ºC, 40ºC, 50ºC, 60ºC and 70ºC) from Weight Loss Measurement

To observe the effect of honey on the corrosion inhibition behavior of starch-AgNPs, the corrosion of mild steel in 0.5 M HCl in absence and presence ofvarying concentration of the starch-AgNPs in combination with honey (5 cm^3) was separately studied in the temperature ranges of 30ºC, 40ºC, 50ºC, 60ºC and 70ºC by weight loss technique. The results from the gravimetric data are shown in Table 1. From the results, it can be observed that the corrosion rates of mild steel in 0.5 M HCl in presence of starch-AgNPs in combination with honey are further reduced in comparison to the AgNPs alone. Figure 3 reveals the plot of synergism parameter (S_1), for mild steel in 0.5 M HCl in the absence and presence of varying concentration of starch-AgNPs with 5 cm^3 honey at (30ºc, 40ºc, 50ºc, 60ºc and 70ºc) from weight loss measurement. S_1 Approaches 1 when no interaction between inhibitor (AgNPs) and the honey exist, whereas $S_1>1$ indicate a synergistic effect. In the case of $S_1<1$, antagonistic behavior prevails which may be attributed to competitive adsorption [9].

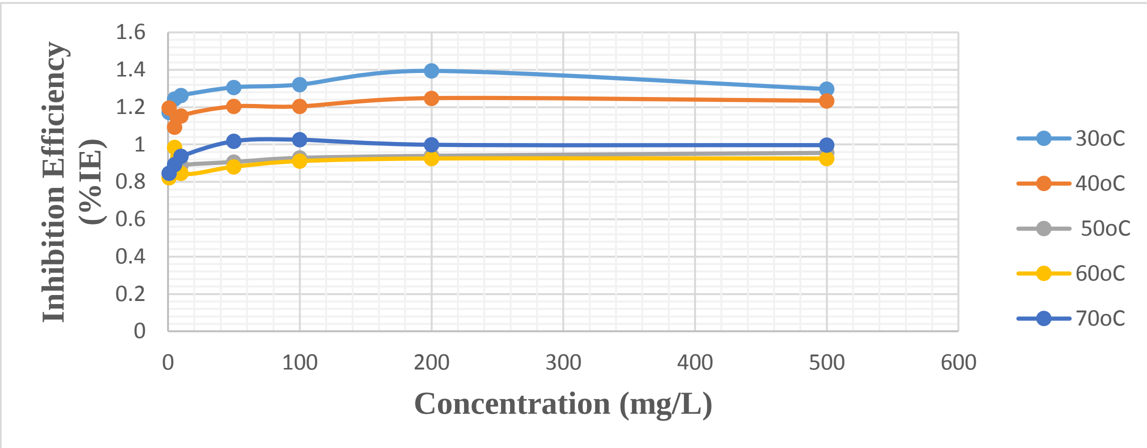

Figure 3: Plot of Synergism Parameter (S_1), for Mild Steel in 0.5 M HCl in the Absence and Presence of Varying Concentration of Starch AgNPs with 5 cm^3 Honey at (30°C, 40°C, 50°C, 60°C and 70°C) from Weight Loss Measurement

Table 1: Synergism Parameter (S_1), for Mild Steel in 0.5 M HCl in the Absence and Presence of Varying Concentration of Starch AgNPs with Honey at (30°C, 40°C, 50°C, 60°C and 70°C) from Weight Loss Measurement

Starch AgNPs Conc. (mg/L)	**Honey (cm^3)**	**Synergism Parameter (Si)**				
		30°C	**40°C**	**50°C**	**60°C**	**70°C**
Black	**Black**	–	–	–	–	–
–	**5**	–	–	–	–	–
1	**5**	1.172	1.196	0.844	0.822	0.846
5	**5**	1.244	1.094	0.853	0.985	0.893

10	**5**	1.263	1.154	0.889	0.846	0.937
50	**5**	1.306	1.204	0.907	0.881	1.018
100	**5**	1.321	1.204	0.929	0.911	1.026
200	**5**	1.395	1.248	0.940	0.925	0.999
500	**5**	1.297	1.234	0.956	0.925	0.997

Figure 4 shows UV-Vis spectra recorded from the composite AgNPs. Corresponding with what was recorded in previous literature. All the solutions exhibited characteristic silver surface plasmon resonance (SPR) typically located in between 415-425 nm. The absorbance peak was recorded at 415 nm which corresponds to that of AgNPs; 410 – 430 nm [18].

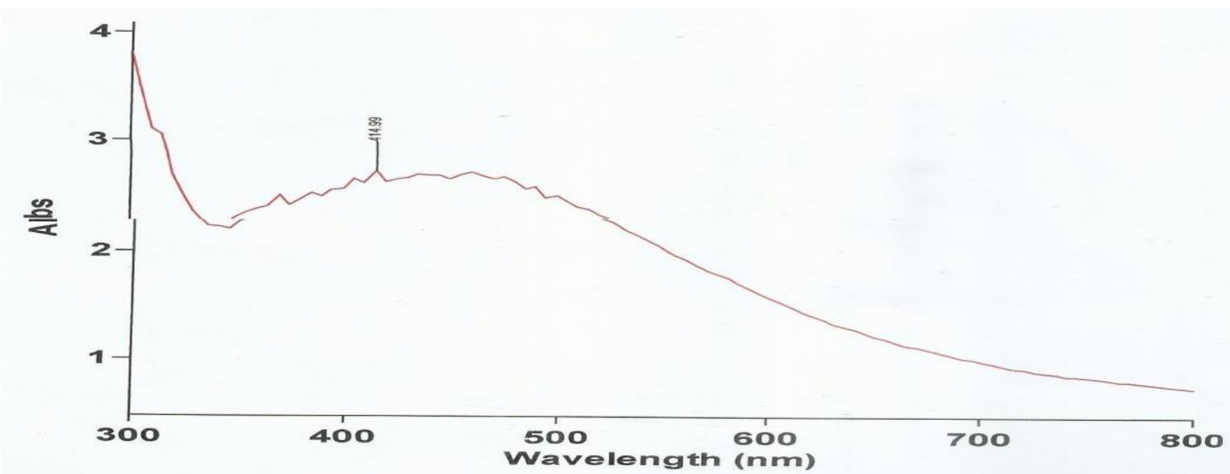

Figure 4:UV-Vis Spectra of AgNPs Synthesized by Starch

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