The Use of Starch Silver Nanoparticles for the Inhibition of Mild Steel Corrosion Using Weight Loss Technique

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ABSTRACT

In this research, the corrosion of mild steel was studied in acidic media and the inhibitory effect of starch silver-nanoparticles (AgNPs) was evaluated. Synthesized starch AgNPs was used to explore the reticence of mild steel in acidic medium. The inhibition efficiency showed a maximum efficiency of 93.168% at 30°C and a minimum efficiency of 82.806% at 70°C. This supports the claim that starch nanoparticles show promising inhibitory properties. Also, it was observed that the corrosion rate increased as temperature increased, with maximum and minimum corrosion rates of 0.788 at 70°C and 0.022 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, Synthesis.

INTRODUCTION

The field of nanotechnology is one of the most active areas of research in material science. Nanotechnology has achieved status as one of the critical research endeavours in the 21st century as scientist harness the unique properties of atomic and molecular assemblage built at the nanometerscale. Nanotechnology is the manipulation of matter on an atomic, molecular and super molecular scale [1].

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. 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 [2].

In the United States, more than 4×10^6 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. For example, silver colloids are useful substrate for surface enhanced spectroscopy (SERS), since it partly requires an electrical conducting surface. Chemical reduction is the most frequently applied method for the preparation of silver nanoparticles (AgNPs) as stable colloidal dispersions in water or organic solvents [3] Silver nanoparticles have unique optical, electrical, and thermal properties and are being incorporated into products that range from photovoltaics to biological and chemical sensors [4]. Examples include conductive inks, pastes and fillers which utilize silver nanoparticles for their high electrical conductivity, stability, and low sintering temperatures. 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 [5].

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 and many more [6].

Natural inhibitors substances are more attractive than synthesized organic inhibitors because they are environmental friendly, nontoxic, cheap and readily available source of materials. In a "green" synthetic strategy, it is important to use nontoxic chemicals, environmentally benign solvents, and renewable materials [7].

Starch is a natural polymer, available in abundance at low cost, renewable, and biodegradable. 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. It inhibits the corrosion rate of mild steel to a considerable aspect and is used as protecting agent because it is renewable and it can form dispersion in water [8].

Mild steel is popular in the construction of different structures like pipelines, thermal chemical reactor and cooling system, since it is excellent in performance, highly recyclable, high life span, and strength as well as more ductile. The corrosion of materials is one of the main problems facing industrial processes, generating huge financial losses. Metallic industrial structures such as mild steel are often exposed to conditions that facilitate corrosive processes.

MATERIALS AND METHODS

Reagents

Silver Nitrate (AgNO₃), Hydrochloric Acid (HCl), Ethanol, Acetone, Starch, 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 H₂O, 27° C). The concentration of starch prepared and used for the study at all level was 50 mg/L.

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 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 [9].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 Analyzer (XL2 XRF Model). All prepared steel sample were preserved in a desiccator [9].

Reagent Preparation

The solution of 0.5 M HCl was prepared in 250 cm³ volumetric flask using deionized water. Similarly, an aqueous solution of 0.1 M AgNO₃ was prepared using deionized water in a 200 cm³ volumetric flask [10].

Synthesis of Silver Nanoparticles (AgNP)

The prepared 0.1 M of aqueous solution of $AgNO_3$ was used for the synthesis of silver nanoparticles. 5 cm³ of starch was added to 95 cm³ of 0.1 M aqueous solution of $AgNO_3$ in 250cm³ Erlenmeyer flask, was mixed thoroughly by manual shaking and exposed to sunlight for 15 minutes for the rapid reduction of silver nanoparticles. The colour change (reddish brown) signaled the formation of the composite [11].

Weight Loss Measurement

The weight loss experiment was performed for duration of 8 hours [12]. The cleaned mild steel coupons were suspended in five 200 cm³ beakers containing 150 cm³ of test solutions (i.e the acid blank and the respective inhibitor solutions) maintained at 30°C, 40°C, 50°C, 60°C and 70°C in a thermostated bath with the aid of hooks. The concentration of inhibitor (starch) in HCl was kept at 50 g/L. The 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) and solutions containing starch silver nanoparticles [7].

The corrosion rates (CR) were determined using the equation:

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

Where: W is weight loss in mg; p is the density of specimen (mild steel) in g/cm³; A is the area of specimen in sq. inch and t is exposure time in hours. The inhibition efficiency (%IE) of starch silver nanoparticles was evaluated using the following equation:

$$\% IE = \frac{CRo - CRi}{CRo} X \ 100 \tag{2}$$

Where: CR_0 is the corrosion rate of mild steel in absence of inhibitor and CRi is corrosion rate of mild steel in presence of inhibitor [10].

RESULTS AND DISCUSSION

Test for starch solubility: The solubility of the starch in water was determined by adding 2.5 cm³ of water into a 5 cm³ test tube. To the water, starch was gradually added in portions starting from 100 mg. The addition was done till the point when the solution became saturated. The total amount of starch added in g/L is the solubility of the starch.

Test for bulk density: The bulk density in kg/cm³ which is the weight per unit volume of the starch was ascertained by taking the weight of the starch powder and dividing it by the volume i.e: d = m/v.

Test for pH: The use of pH meter which was used to probe the hydrogen ion activity of the starch was preceded by a litmus test using a litmus paper to ascertain if the starch was basic or acidic. The no colour change in the litmus paper indicates neutrality [13].



Biosynthesized composite of AgNPs using starch visible observation

The results of corrosion study using mild steel as sample in 0.5 M HCl in the presence and absence of the inhibitor (starch AgNPs) using weight loss technique at specific temperature (30°C, 40°C, 50°C, 60°C and 70°C) is shown in Table 1. It can be seen from the table that at each of the temperatures, the corrosion rate decreased in the presence of inhibitor (AgNPs) in contrast to that of the blank solution. The result also revealed that at higher temperature, the %IE is reduced showing a maximum efficiency of 93.168% at 30°C. 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 [14]. The inhibition of mild steel corrosion in the presence of starch could be attributed to the adsorption of the compound on to mild steel surface, which blocks the metal and thus do not permit the corrosion process to take place [7].

The decrease in %IE with increasing temperature may be due to the fact that most of the effects at elevated temperatures are adverse to corrosion inhibition by increasing the corrosion rate and decreasing the tendency of the starch to be adsorbed on the steel surface [7]. In addition, the binding interactions between starch and silver nanoparticles are weak and can be reversible at higher temperatures, allowing separation of the synthesized particles [15].

Temperature (°C)	C.R (mpy) in blank	C.R (mpy) in inhibitor	% I.E
	After 8 hours	After 8 hours	
30	0.322	0.022	93.168
40	1.504	0.147	90.210
50	3.580	0.394	88.994
60	4.296	0.644	85.009
70	4.583	0.788	82.806

Table 1: Calculated values for corrosion rate (in blank and inhibitor) and inhibition efficiency

UV-VISIBLE ANALYSIS

The bio reduced sample was confirmed by UV-Visible analysis and the spectra reported in figure 2 for visible observation. The obtained AgNPs was purified through repeated centrifugation for 20 minutes and washed with distilled water. The sample was analyzed by preparing dilute solution made in deionized water. The reduction of silver nanoparticles was monitored from 300 – 800 nm with deionized water serving as blank. The absorption peak was recorded at 115 nm which corresponds to that of AgNPs; 110 – 130 nm reported in previous studies [13].

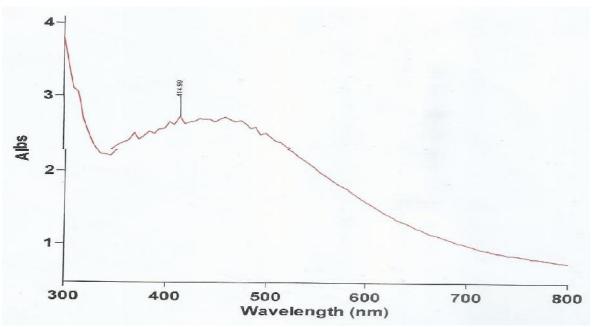
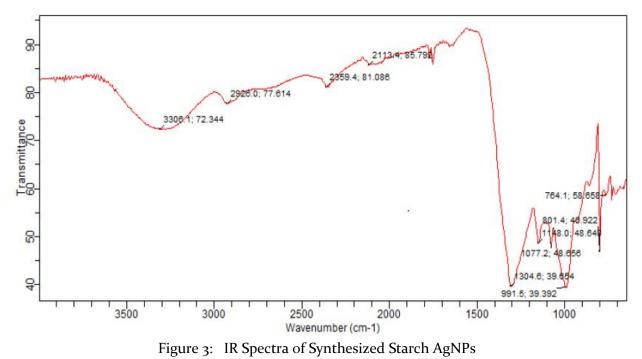


Figure 2: UV-Vis Spectra of AgNPs Synthesized by Starch

Fourier Transform Infrared Spectroscopy (FTIR) Spectra of the Composite AgNPs

Fourier Transform Infrared Spectroscopy (FTIR) measures the molecular vibration, determines the functional group present and the molecular structure of the compound [16] [17]. The FTIR Spectra of the composite was carried out in the range 200 – 4000 cm⁻¹ using CARY 630 FTIR Agilent Technology to determine the functional group present on the composite AgNPs. The FTIR spectra of the AgNPs are shown in figure 3. The functional group observed from the spectra explicates the successful redox reaction. From the spectra in figure 3, the sharp peak espied at 1304.6

cm⁻¹ wave number is indicative of -C-O Carboxylic stretching. Also, at wave number 1725.3 cm⁻¹, -C=O carboxylic stretch can be observed. Finally, the broad stretch observed at wave number 3306.1 cm⁻¹ is a characteristic feature of carboxylic -OH. This further justifies the oxidation of aldehyde in starch to carboxylic.



CONCLUSION

This study shows that starch AgNPs acts as a good capping agent and inhibitor of mild steel in acidic medium. The results do support the claim; Starch AgNPs is a good inhibitor for the corrosion of mild steel. 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. It was also seen that the binding interactions between starch and AgNPs are weak and as such dissociates at higher temperature, allowing the separation of the synthesized particles.

ACKNOWLEDGEMENTS

My profound gratitude goes to my supervisors and my colleagues for their immersed contribution to the success of this work. Not forgetting my Mom for her financial support through the course of my research.

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