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Employment of Surface Modified Biomaterial in Sequestering Divalent Metal Ion

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Abstract

The study is designed to investigate the potential applicability of Nano sized Treated Goat Teeth (NTGT) as adsorbent for Ni(II) removal from metal laden solutions. The desized novel nanomaterial (NTGT) is characterized by AFM and TGA- DTA techniques. Batch Equilibration study is carried out for Ni(II)- NTGT system under varied influential parameters viz., dosage, agitation time intervals, optimized initial metal ion concentration (250 mg/L), pH (5.5) and temperature (303K). The results of the experiment registered a two fold increase in the removal of Ni(II) from aqueous media with one half amount of required dose and agitation time interval in comparison with that of the counterpart TGT. High performance of NTGT in trapping Ni(II) ions is extended to field trials by treating electroplating effluent samples collected from Coimbatore industrial belt, the results suggesting the derived NTGT as an efficient biosequestrant

Keywords: Nickel ions; Characterization; Batch studies; Sorption

1. Introduction

The directory of “Agency for Toxic Substances and Disease Registry Priority List of Hazardous Substances” offer top 10 positions for heavy metal ions due to its toxicity and potential exposure from a wide range of sources (Daneshfozouna *et al.*, 2017). Indiscriminate disposal of toxic metal ions are still continuing and even increasing in developing countries. Coimbatore city is well known for small and medium scale electroplating industries. Nickel plating is the most common process in the studied area and high concentrated effluent in huge volume is discharged per day, even at small units. Nickel is considered a moderately toxic element (< 0.5 mg/L) comparing with other transition metals.

Exposure to nickel is associated with respiratory cancer, dermatitis, gastrointestinal distress, chronic bronchitis, cardiovascular, kidney diseases and a skin disorder known as nickel-eczema (Li *et al.*, 2018). Thence, efficient removal of Ni(II) ions from industrial wastewaters are the prime need for concern. Adsorption is among the most common methods employed for heavy metal ion trapping due to its simplicity, feasibility and effectiveness. Biosorbents ensures maximum sorption capacity and the best alternative for non-degradable activated carbons. In the present work, Goat Teeth (GT) has been chosen as the biosorbent. GT is a shear litter, causing solid waste disposal problem, other than being helpful to determine the age of a goat.

Herein, chemically modified and nano-sized GT are prepared, characterized and equilibrium parameters are experimentally investigated. To the best of our knowledge, Ni(II) ion removal employing goat teeth have not been explored so far.

2. Experimental Section

2.1 Materials and Modification

Goat Teeth were collected from local butcher shop, detached from jaw bones, washed well with running water to eliminate colloidal impurities, later sun-dried for removal of moisture content. Goat Teeth consist of high percentage of mineral contents, especially exchangeable Ca^{2+} ions and organic/bio-chemical materials such as collagen, proteoglycan (chondroitin sulfate, keratin sulfate), lipids. Therefore, the washed GT were subjected to chemical treatment by soaking in 0.1N HCl after pulverization into 0.18 mm particle size. The treated goat teeth (TGT) was washed and air dried (Anuradha *et al.*, 2017).

2.2 Preparation of Nano- biosorbent

40 grams of Treated Goat Teeth TGT was weighed and desized to nano level by a top-down approach. This was carried out in a Planetary Ball Mill (Model- VBCC/PM/24-13/14) equipped with Tungsten Carbide bowl and 2 mm balls. The above procedure was followed by milling for 15 hours at 260 rpm. The resulted powder agglomerates was stored in an airtight container and referred as NTGT.

A stock solution of 1000 mg/L Nickel nitrate was prepared, from which aliquots of varying concentrations were derived.

2.3 Characterization

2.3.1 Atomic Force Microscopic (AFM) Analysis

AFM analysis offers visualization in three dimensions and surface roughness. Individual particles and groups of particles can be resolved finer, compared to other microscopic techniques. The top and 3-dimensional view (20μm x 20μm x 300 nm) of the nanoparticles is depicted in figures 1, 2 respectively. The thickness of the nanoparticle is measured using the data obtained from line profiles on the interfacial region and the size was found to be in the range of 50–90 nm. The attainment of nano particles' size was confirmed by the Atomic Force Microscope histograms (fig c) and the appearance of a clear peak around 60.75 nm in confirms the existence of a maximum number of the nanoparticle.

2.3.2 TG- DTA Technique

Thermo Gravimetric /Differential Thermal Analysis (TG/DTA) measurements were obtained using Simultaneous DTA- TGA Apparatus, (DTG- 60, Shimatzu- Japan). The small amount ~ 1 wt% of TGT was placed in the platinum thermo balance crucible for analysis. The samples were heated from room temperature to 900°C, at a heating rate of 20°C/min; the measures were carried out in a constant Air atmosphere.

2.4 Batch Studies- Aqueous Solutions and Industrial Effluents

Batch equilibration experiments were verified for the operating factors viz., doses of TGT/ NTGT (50-200 mg : 50 mg), agitation time intervals (5- 20 min: 5 min) at optimized initial metal ion concentration (250 mg/L), pH 5.5 and temperature (303K). The efficiencies of the nano particles were also tested with effluent sample [Ni(II)- 220 mg/L, pH 5] collected from electroplating industry at Coimbatore. After the contact period, the supernatant was filtered and the initial and residual Ni(II) ion concentrations were recorded using Atomic Absorption Spectrophotometer (Shimadzu AA 6200) at a wavelength of 232 nm.

The percentage values and the amounts of metal ion adsorbed from aqueous solutions were calculated using the equation,

$$\%\ adsorption = \frac{(C_i - C_e)}{C_i} \times 100$$

$$q = \frac{V(C_i - C_e)}{W}$$

V - volume of the solution (L)
m - mass of the adsorbent (g)
C_i / C_e - initial / equilibrium metal concentrations (mg/L)

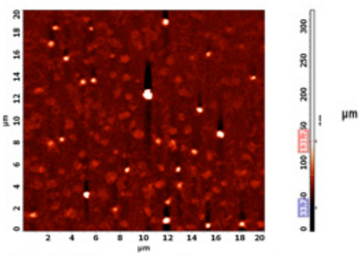
3. Results and Discussion

AFM provides us microscopic information on the surface structure and plots the surface topography of the adsorbent. Fig 1(a), 1(b) shows 2D/3D AFM images from sorbent surface and fig 1(c) clear-cut the size of the nano material. NTGT tended to aggregate, thus contributing to some bright areas in AFM height images. According to fig 1(c), the grain size of the crushed sample is 60.75 nm. The color range shows the morphological changes of the surface, which indicate the adsorption sites on the surface of nano TGT (Khorzughy *et al.*, 2015).

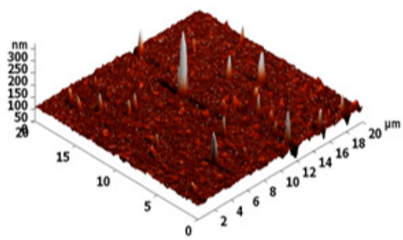
Thermo Gravimetric- Differential Thermal Analyses for NTGT was studied to evaluate the effect of functionalization on their thermal degradation behavior under air atmosphere. Fig 2(a) indicative of TG curve pertaining to thermal stability of NTGT, shows a deflection point at 100°C corresponding to the removal of water. A typical degradation behavior of NTGT envisaged at 270°C, [Thermal Decomposition Point (T_d)] confirmed the derived sample from TGT through HCl treatment (Rana *et al.*, 2017). Again, a dip in the curve at 500°C refers to the deterioration of organic matter (listed under Materials and Modification). This fact is supported by the absence of significant weight loss occurring between 600°C - 800°C, emphasizing the total removal of organic matter.

An endothermic peak in the DTA curve [fig 2(b)], at 66.3°C infer the moisture loss followed by an exothermic counterpart at 154.8°C corresponding to the thermal decomposition / pyrolysis of organic content (Teaford *et al.*, 2007).

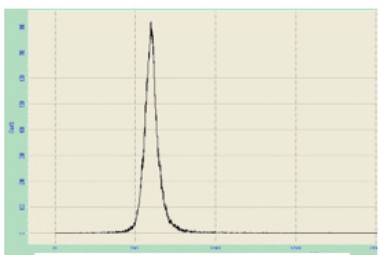
Experimentally verified graphical representation for pH influence is depicted in fig 3. A peak height at pH 5.5, imply the maximum amounts of Ni(II) ions being adsorbed, that too, enhanced in the case of NTGT. In view of this, pH 5.5 was fixed as the optimum pH for the sorption systems. Fig 4 and 5 refer to the effect of dosage at different



(a) 2D Surface Topography



(b) 3D Surface Topography



(c) Histogram (60.75 nm)

Figure 1. AFM Images - NTGT

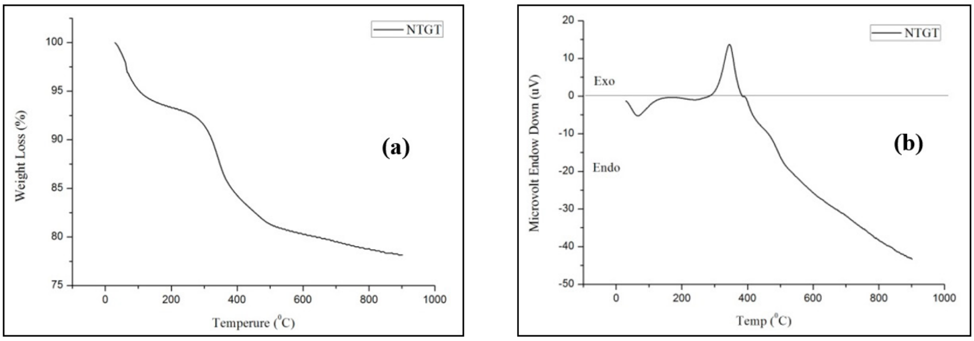


Figure 2. TG- DTA Analyses

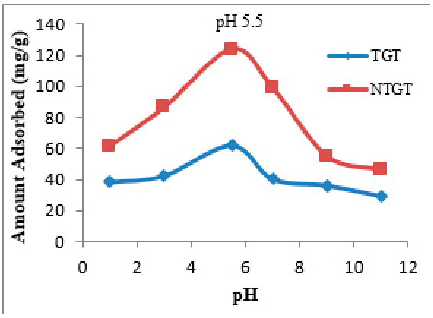


Figure 3. Effect of pH

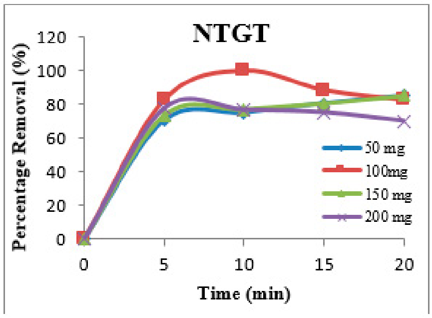


Figure 4. Effect of Dosage: Ni(II)- NTGT

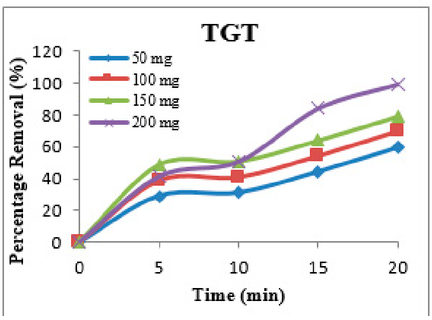


Figure 5. Effect of Dosage: Ni(II)- TGT

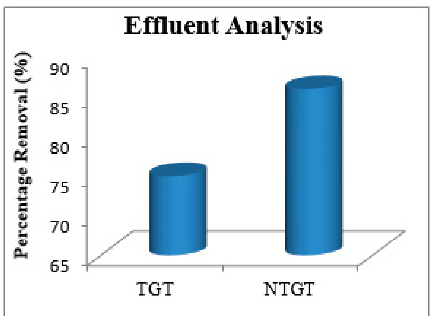


Figure 6. Nickel Plating Effluent

time periods and percentage removal of Ni(II) ions. Results pronounced the enhanced sorptive ability of nano particle against their modified counterpart in case of both aqueous solution and plating effluent.

An agitation time/adsorbent dose of only 10 min/100 mg NTGT was sufficient against 20 min/200 mg TGT, to trap 99.8 % and 86 % Ni(II) ions from both aqueous / effluent samples (Fig 6). A decrease in adsorption rate was registered at higher time period and dosages, invariably in all cases which may be due to the very rapid initial uptake rate and overlapping /aggregation of adsorption sites as a result of overcrowding of sorbent particles after equilibrium state.

Maximum adsorption capacity of 123.68 mg/g at 10 min time interval, 100 mg dosage of NTGT was registered, which was twofold time maximized value than the chemically modified counterpart (62.09 mg/g).

The percentage removal of the metal ions from effluent sample was observed in fig 6, to be less than the corresponding aqueous solutions, which shall be due to the presence of interfering ions in the case of former.

4. Conclusion

Experiments pertaining to the adsorption of Ni(II) ions from wastewaters onto the modifications/ size reduction of chosen slaughterhouse waste were designed. Almost 100% removal of divalent ion was achieved under specified laboratory environment using low-cost adsorbents' viz., 250 mg/L initial metal ion concentration, pH 5.5 and different dosage/ contact time [TGT- 200 mg, 20 min; NTGT-100 mg, 10 min]. The results of the present investigations would be useful for the fabrication and designing of wastewater treatment plants, utilizing such novel bio/ nano materials in an effective manner. Our future study aims at the establishment of performance oriented approach of TGT/ NTGT for other toxic heavy metal ions. This can be accomplished by developing suitable modification procedures in the sorbents viz. encapsulation and immobilization, thereby ensuring the safe disposal of the metal loaded sorbents, which in turn does not pose a great threat to the environment.

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