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Adsorptive Removal of Cadmium (II) ion from Industrial Wastewater by Natural Adsorbent

S.R. Kuchekar[1]*, M.P. Patil[1], H.R. Aher[1], V.B. Gaikwad[2], S.H. Han[3]

[1*]*Principal, Women's College of Home Science & BCA, Loni (Kd), Tal. Rahata, Dist.Ahmednagar, MS, India, 413713*
[1]*Department of Chemistry, P. V. P. College, Pravaranagar, Dist. Ahmednagar, MS, India, 413713*
[2]*Department of Chemistry, KTHM College, Nashik, Dist. Nashik, MS, India, 422002*
[3]*Department of Chemistry, Hanyang University, Seoul, South Korea*

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shashi17@gmail.com ;
Phone: +919822522004;
Fax: +21329824945

Abstract

Heavy metal removal from Industrial effluent is important part of research. The current work focuses on paraphrasing the harmful effects of cadmium that is being released from industrial wastewater is highly toxic and has a serious health concern. In this current work, Adsorption technique using *Syzygium cumini* bark as a natural adsorbent which being cheap and locally abundant is adopted for the removal of cadmium (II) from industrial wastewater. The influence of adsorbent mass, contact time, pH, temperature, metal ion concentration on the removal of cadmium was investigated. The results showed 97.80 % removal efficiency at concentration 20 mg/L at 90 minutes. The FTIR spectral analysis showed the dominant mechanism of cadmium (II) adsorption onto the surface of *Syzygium cumini* was hydroxyl and amine groups.

1. Introduction

Water is the most essential substance for all life on earth [1-2]. Water pollution due to development in technology continues to be of great concern. The major pollutant includes toxic metals, the quantity of which permanently increases in the environment as the result of increased industrial activity [3-4]. Heavy metals in water resources are one of the most important environmental problem of countries, as heavy metals are natural components of the earth's crust, they cannot be destroyed and can easily enter our bodies through food chain, drinking water, air. Some heavy metals in trace are essential to maintain the metabolism of human body however if absorbed above the permissible labels, could lead to serious health disorders. The industrial sector releases severally toxic heavy metal ions in their wastewaters contaminating natural streams where in disposed, which is a major concern issue due to its toxicity to many life forms [5]. Industrial waste of many industries such as metal plating facilities, mining operations, battery industries, paper and pulp, pigment are the major sources of cadmium pollution in natural water, about 17000 tons of cadmium is used in industry annually of which only 5% is recovered. Cadmium is referred to as the 'dissipated element' with regards to the environment, as it is carcinogen and associated with the generation of a number of diseases, specifically bone, cardiovascular, nervous, kidney and blood diseases [6]. As per WHO's recommendation Cd (II) in drinking water is 0.003 mg/l [7]. In light of the facts, industrial effluent containing heavy metal treatment becomes quite necessary before being discharged into the environment. The researchers are therefore facing a tough task of cost-effective treatment of wastewater containing heavy metals. There are several conventional methods can be adopted for the removal of heavy metal from waste water like chemical precipitation, electroplating, ion-exchange, reverse osmosis, chemical coagulation and adsorption. These methods are highly costly, not very effective, require high energy input and non eco-friendly in nature [8-9]. Amongst these adsorption technique has gained importance due to its cost economy, high efficiency, harmless nature, ease handling for the removal of heavy metal from industrial wastewater [10]. Much attention has been made towards natural adsorbent material to be used in heavy metal removal. Most important task is selection of adsorbent efficiency, economies, avaibility and versatility of process depends on adsorbent [11].

Syzygium cumini (Indian blackberry) is an important underutilized tropical fruit crop of India possessing high nutraceutical value [12]. *Syzygium cumini* also called as Jamun, black berry, black plum and Java plum etc., belongs to Myrtaceae family. The Myrtaceae family is one of the world's leading commercial fruit tree families. Among the 121 genera belonging to this family *Syzygium* has constituted excellent nutritional values and being considered source of phytochemicals such as phenolic compounds, carotenoids and volatile compounds. Many of these phytochemicals have been linked to the prevention and management of several chronic and degenerative diseases including cancer, cardiovascular diseases, type 2 diabetes, mellitus, obesity, amnesia among these diseases [13]. Tradionally for myriad therapeutic purposes *Syzygium* (Myrtaceae) plant used as antibacterial, antifungal, antiprotozal, antidiabetes, antidiarrheal [14]. *Syzygium cumini* (L.) has much importance in medicine, as the tea from leaves are used by diabetics for lowering hyperglycaemia [15].The plant is identified as a rich in total ten phenolic compounds containing six phenolic acids (tannic acid, gallic acid, ellagic acid, caffic acid, ferulic acid, p-couramic acid) and four flavonoids (catechin, epicatechin, quercetin and myrcetin 3-O-rhamnoside) also glucoside [16-17]. *Syzygium cumini* as a natural reducing and stabilizing agent has gained importance also in the field of nanoscience and nanotechnology [18]. *Syzygium cumini* (L.) fruit contains large amount of phytochemicals, vitamins and minerals but are perishable, extension work is going on for the preservation of these valuable constituents [19]. The bark of *Syzygium cumini* contains tannins and carbohydrates accounting for its long-term use as an astringent.

Syzygium cumini possess various properties, by keeping this in mind in the present study an effort was made to explore the feasibility of utilizing *Syzygium cumini* bark powder as natural adsorbent for removal of Cd (II) ion from industrial wastewater. The main objective of this research is to understand the effects of various parameters as adsorbent dosage, contact time, pH, temperature and initial metal ion concentration on the adsorption efficiency of cadmium (II) ion on *Syzygium cumini* bark.

2. Material and Methods

2.1. Adsorbent Preparation

Syzygium cumini barks were collected locally. The collected barks were washed with deionized water severally to avoid dust and other soluble impurities. The washed *Syzygium cumini* barks were dried in sunlight for 5-6 days till became crisp and powdered finely in a mechanical grinder. The powder was sieved and the 240-320 mesh fractions were used directly as an adsorbent for cadmium adsorption without any pretreatment.

2.2. Stock Cd (II) Solution Preparation

A stock solution of Cadmium (II) concentration 1000 mg/L was prepared by dissolving 2.744 gm of $Cd(NO3)_2.4H_2O$ in 1000 ml distilled water. All chemicals used were of analytical grade. For working solutions it was further diluted to desired concentrations ranging as 20, 40, 60, 80, 100 mg/L by diluting the cadmium stock solution. The concentration of Cd (II) ion in the solution was determined complexometrically.

2.3. Adsorption Studies

Adsorption experiments were performed in rotary shaker at 150 rpm using 100 ml Erlenmeyer flasks containing 25 ml of different cadmium concentrations. After 90 minutes of contact with 2.5 gm of *Syzygium cumini* bark powder, equilibrium was reached. The reaction mixture was then filtered through Whatman no.41 for 5 minute. The metal content in the supernatant was determined complexometrically with $5x10^{-3}$ M EDTA solution. The percentage removal of cadmium was calculated using equation as:

$$R\% = [Ci\text{-}Cf / Ci] \times 100$$

Where R is the percentage removal of cadmium, Ci and Cf are the initial and final Cd (II) ion concentrations (mg/L) respectively. The effect of temperature ranging from 10 to 60^{o}C was studied at Cd (II) concentration of 20 mg/L and 2.5 gm adsorbent dose. The pH of solution was adjusted using 0.01N HCl and 0.01 N NaOH solutions.

2.4. Instrumental Characterization

Fourier Transform Infrared Spectroscopy (FTIR) was applied to analyze the various functional groups present on the surface of adsorbent before and after adsorption. Pellets of adsorbent were made with 1% KBR and 4000-600 cm^{-1} wavelength used on using Thermo-scientific instruments.

3. Results and discussion

The effect of different parameters as dose of adsorbent, contact time, pH, temperature and initial metal ion concentration on the removal of cadmium from wastewater were investigated in this study.

3.1. Effect of Adsorbent dose

Dosage of adsorbent is a key parameter that strongly affects the sorption capacity. The increase in adsorbent dosage from 0.5 to 2.5 gm resulted in an increase from 68.80 % to 94.48 %. The change in biosorption is so marginal when dosage is increased further, so 2.5 gm is fixed shown below (Figure 1). This behavior is due to the increase in number of binding sites resulting in increase in surface area of adsorbent for adsorption [20]

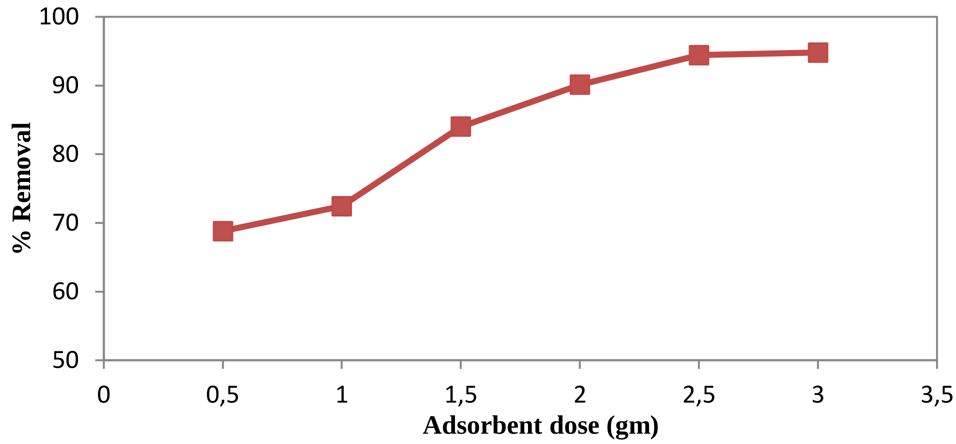

Figure 1: Effect of adsorbent dosage on percentage removal of cadmium

3.2. Effect of Contact Time

The contact time plays a crucial role in adsorbing the metal species onto the surface of the adsorbent. The graph of percentage adsorption removal versus adsorption time is shown (Figure 2). The percentage removal of cadmium is higher in the beginning time. This increase was due to the larger surface area of the adsorbent available for the adsorption of cadmium ion [21]. Result of the study, on the effect of contact time showed 96.55 % of cadmium removal at 90 minutes. Beyond 90 minutes, % biosorption is constant i.e. a plateau was observed.

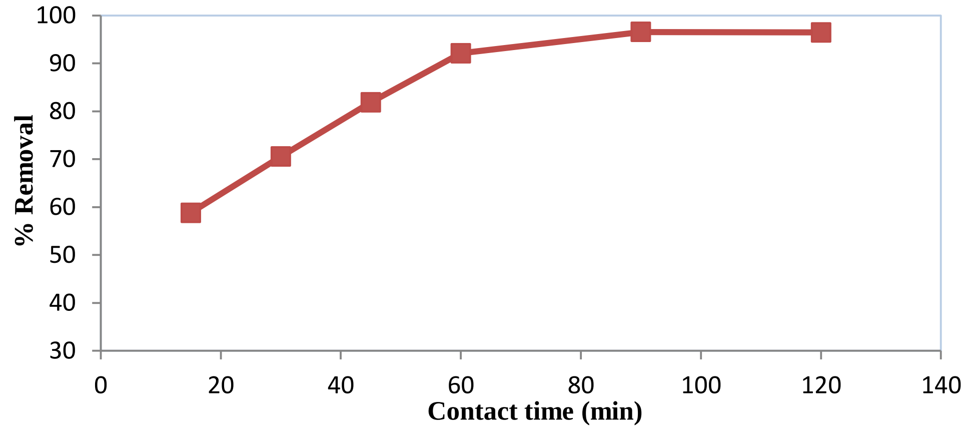

Figure 2: Effect of contact time on percentage removal of cadmium

3.3. Effect of pH

The pH is an important factor, which influences the surface charge of biosorbent, degree of ionization and controls the adsorption of cadmium from wastewater and aqueous solutions [22]. The percentage removal increased when pH increased from 3 to 8. In the present investigation maximum cadmium removal at pH 8 was found to be 95.50 % (Figure 3). Higher pH was not studied as precipitation was observed.

3.4. Effect of Temperature

Temperature plays a crucial role in adsorption reaction. Effect of temperature was studied by varying the temperature ranges from 10 to 60 ^{o}C, keeping other parameters constant (Figure 4). The cadmium (II) ion removal increased with the increase in temperature due to the endothermic nature of this process [23]. As the temperature rises, more surface area will be available for the adsorption by bond rupture of functional groups onto the surface of adsorbent [24-25]. The percentage biosorption of cadmium was found to be maximum 96.66 % at 60 ^{o}C.

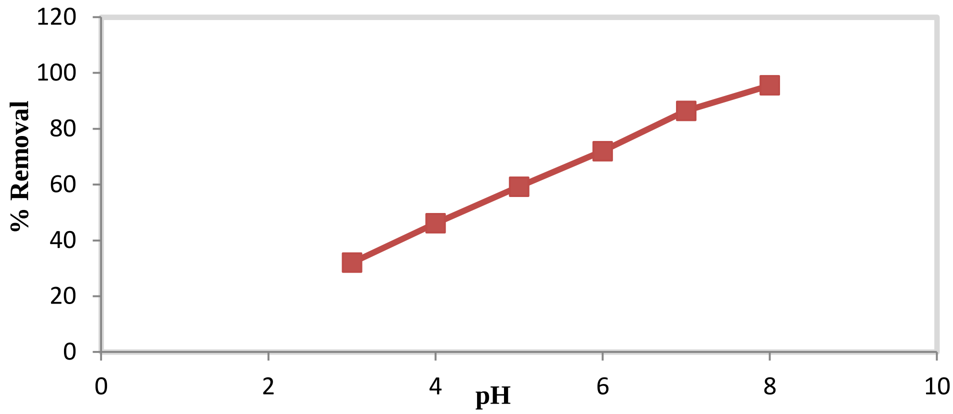

Figure 3: Effect of pH on percentage removal of cadmium

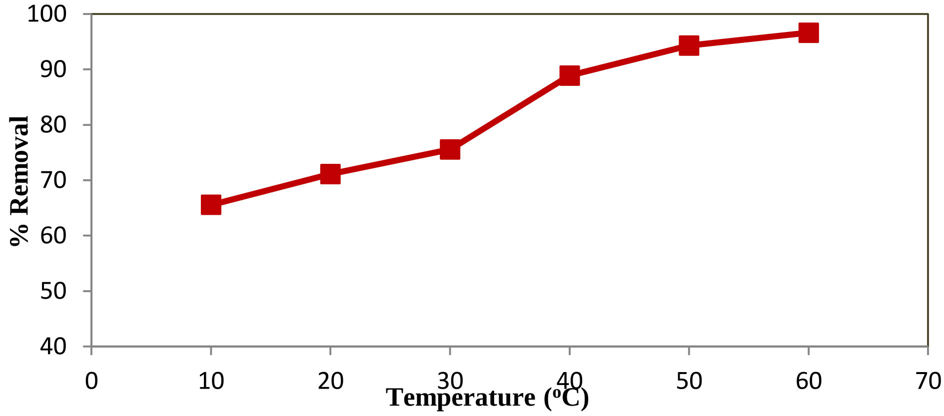

Figure 4: Effect of temperature on percentage removal of cadmium

3.5. Effect of Initial ion Concentration

The extent of adsorption depends on the mobility and charge of the ions present in the solution. In this study, concentrations in the range of 20 to 100 mg/L for the metal ion have been studied. Increases in the concentration, the percentage removal of the metal ion diffuse to the adsorbent surface by intra particle diffusion and the hydrolyzed ions diffuse at a slower rate, thus decreasing the percentage removal [26]. In this study, decreasing trend was seen with increasing initial metal ion concentration. The percentage biosorption of cadmium decreased from 97.80 % to 68.80 % (Figure 5).

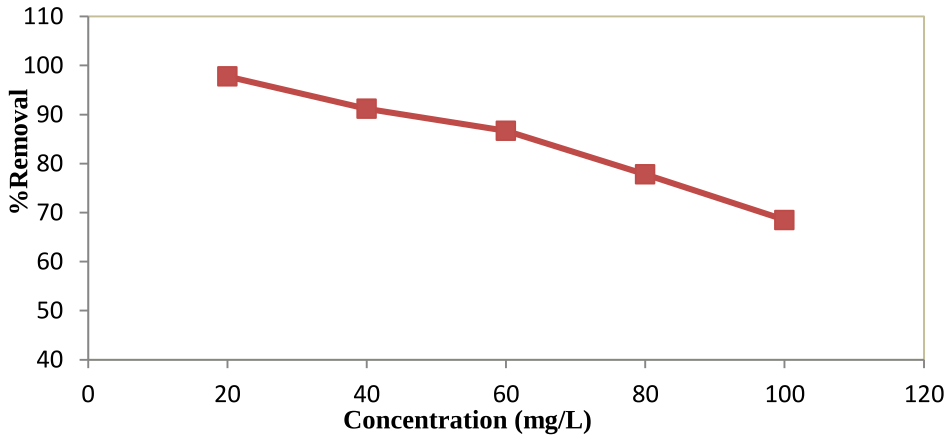

Figure 5: Effect of metal ion concentration on percentage removal of cadmium

3.6. FTIR Spectra of Syzygium cumini

The FTIR spectra of *Syzygium cumini* bark before and after cadmium adsorption is depicted in Figure 6 and 7. Peak at 3470.76 cm^{-1} assigned to the stretching of O-H group as alcohols, phenols, acids as in pectin, cellulose and lignin, the band at 1016.89 cm^{-1} maybe due to CN stretching vibrations of protein fraction, 1458.13 cm^{-1} correspond to ionic carboxylic group, 1540.84 cm^{-1} due to amide bond, 1671.29 cm^{-1} caused C=O chelat stretching, 2360.60 cm^{-1} is viberations of NH_2, 2916.65 cm^{-1} indicates C-H stretching. It is indicated from FTIR spectrum of *Syzygium cumini* that hydroxyl and carboxyl groups are present. The peaks observed after the adsorption of *Syzygium cumini* with Cd (II) ion had shifted slightly and higher at 1026.59 cm^{-1}, 1461.83 cm^{-1}, 1547.93 cm^{-1}, 2361 cm^{-1}, 2918.21 cm^{-1}, 3469.20 cm^{-1} wave numbers and new band at 3868.02 cm^{-1} is indicating presence of N-H viberations respectively. The changes in FTIR spectrum of *Syzygium cumini* after the adsorption of Cd (II) shows the involvement of OH of lignin structure and NH groups in the adsorption [27]. The presence of prominent functional group on *Syzygium cumini* surface suggests their participation in Cd (II) uptake from wastewater.

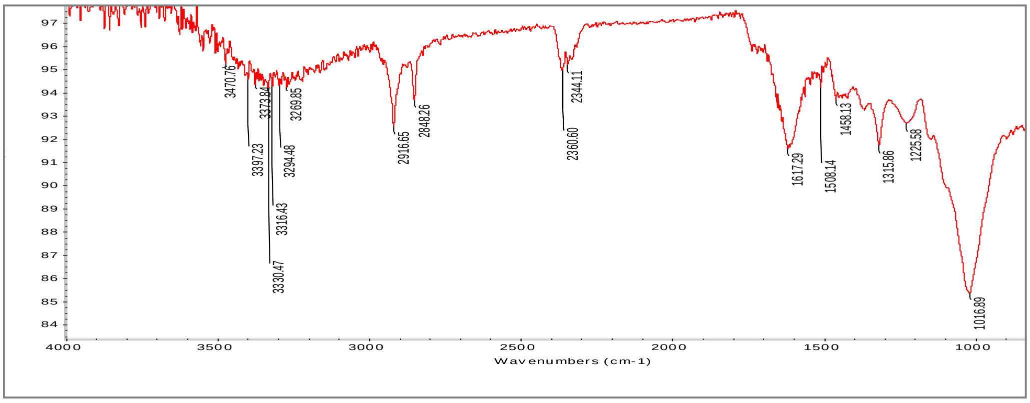

Figure 6: FTIR spectra of *Syzygium cumini* without Cd (II) adsorption

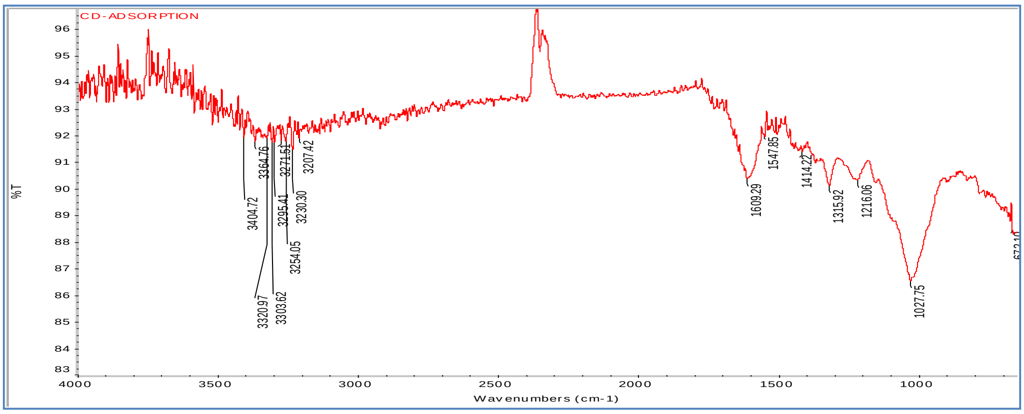

Figure 7: FTIR spectra of *Syzygium cumini* with Cd (II) adsorption

Conclusion

This study was undertaken to evaluate the adsorption of Cadmium on *Syzygium cumini* bark powder as a biosorbent. *Syzygium cumini* has shown the absorptive potential for removal of cadmium (II) ion. The uptake of cadmium ions by *Syzygium cumini* bark was increased by increasing adsorbent concentration i.e. 2.5 gm at pH 8 with contact 90 minutes. The biosorption capacity of *Syzygium cumini* was superior due to the higher content of hydroxyl and amine groups. The proposed method offers a very convenient, effective, eco-friendly alternative methodology for the adsorption of Cd (II) ion from industrial wastewater. This study can be fairly helpful in developing a wastewater treatment plant for the removal of metals from wastewater by using natural *Syzygium cumini* bark.

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