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Experimental Investigations on Treatment of wastewater using Dehydrated Carbon from Date Palm Leaves

Anna Jesil, A.M. Saravanan*, Eman Mohammed

Department of Mechanical and Industrial Engineering, Caledonian College of Engineering, Seeb, Oman

*Corresponding author email: amslogin@gmail.com

ABSTRACT

Research in the area of wastewater treatment due to increasing shortage of water becomes more intensive in the world. Although, there are many technologies for treatment of waste water such as physical and chemical technology for removal of heavy metals from wastewater including electro-coagulation, membrane filtration, precipitation, flotation and decontamination, they are very expensive. In this research work, a methodology based on adsorption has been developed. Dehydrated carbon material has been synthesized from date palm leaves via sulfuric acid. Acid will cause dehydration via the removal of water. The dehydrated carbon in amounts ranging from 0.1 to 0.7 grams was tested for Zn^{+2} removals from synthetic waste water prepared from standard solutions and analyzed by Atomic Absorption Spectrophotometry. The parameters varied were dehydrated carbon dosage, stirring time, stirring speed, initial concentration and pH. Optimum values of initial concentration, stirring time and pH was observed to be 10 ppm, 60 minutes and 3 for Zn^{+2} removal.

Keywords - Dehydrated carbon, Heavy metal, Atomic absorption spectrophotometry, Pollution.

1. INTRODUCTION

Since last few years the problem of pollution has increased and this has posed a major concern because of the adverse impacts to nature. Though there are several physicochemical methods available for removal of heavy metal ions concentration in industrial wastewater, including chemical precipitation, ion exchange, reverse osmosis, filtration, solvent extraction and electro deposition, their applicability is limited for dilute solutions as well as for a wide range of pollutants (Tong et al 2011).Adsorption is an efficient method for removal of heavy metals and bio recalcitrant compounds. Recent investigations have been focused on identifying low cost adsorbents that can be used to remove heavy metals from aqueous solutions.

The potential for the application of low cost adsorbents for the removal of bio recalcitrant compounds has increased tremendously. Rafatullah and researchers have organized the information on a wide range of potentially low cost adsorbents for Methylene Blue removal (Rafatullah et al 2010). Biomass and agricultural products such as date pits, olive stones, ground nut shell, rice husk, straw, coconut fiber, wheat bran and oil palm shell have been investigated for their adsorption capabilities. As methylene blue is a cationic dye, the authors have speculated the possibility of ion exchange mechanism in the adsorption of Methylene Blue. On modification of the adsorbent by treatment with $CaCl_2$ or using basic medium, the ion exchange sites on the surface of the adsorbent are converted to cationic form and the cations are exchanged as Methylene Blue is a cationic dye. Low pH resulted in low adsorption for Methylene Blue making the conditions unfavorable for adsorption. The adsorption capacity is affected by various factors like source of raw materials used, pyrolysis temperature, activation time, surface chemistry, surface charge and pore structure (Kannan et al 2001).

There are two common methods adopted by researchers (Gupta et al 2009) for the preparation of activated carbon, one of the oldest known adsorbents as shown schematically in Fig. 1. Physical activation is carried out in two stages namely calcination of the raw materials in an inert atmosphere at temperature from 600ºC - 900ºC which is then followed by gasification with CO2, air and steam at temperatures from 600ºC to 1200ºC (Banat et al 2003).There are advantages and disadvantages for the two methods. The physical activation method requires high temperature conditions. The chemical activation method requires thorough washing of the prepared activated carbon to remove the resident chemicals.

Demirbas (2009) has evaluated a number of low cost adsorbents derived from agricultural wastes and its capability for dyes removal from waste water making it as a viable alternative to activated carbon for treatment of contaminated water. The author postulates that the adsorption capacity depends on initial dye concentration, contact time, sorbent dosage and pH.

Experimental studies using date leaves as adsorbent was carried by Gouamid and researchers (Gouamid et al 2013) for removal of Methylene dye removal of methylene dye removal from aqueous solutions. The parameters varied were pH, contact time, adsorbent dose, temperature and dye concentration. Surface morphology was performed using a field emission scanning electron microscope. Composition of the date leaves comprises cellulose (38%), hemicellulose (23%), lignin (12%) and ash (8%). Temkin isotherm was demonstrated to provide the best fit for the experimental data.

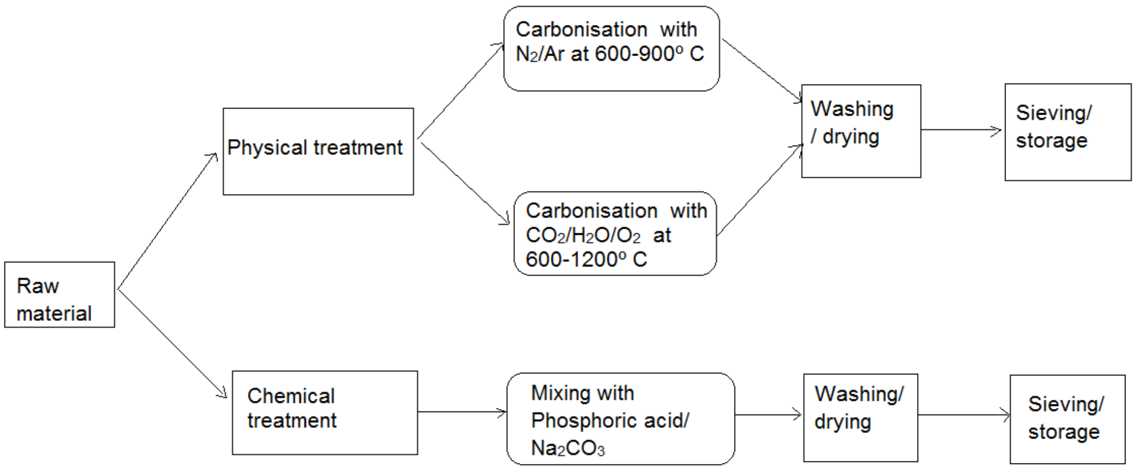

Fig. 1 Schematic for the preparation of activated carbon by the two routes.

Recovery of Au (III) ions from aqueous solution by adsorption technique was investigated by Al-Saidi (2013). Raw date pits was the adsorbent and its characteristics namely surface morphology, specific surface area and functional groups was analyzed using scanning electron microscopy, methylene blue adsorption method and FT-IR spectroscopy. 90% removal of gold was obtained in an acidic medium. The author has postulated the mechanism to be adsorption coupled with reduction, which includes adsorption of Au (III) ions to the surface of the adsorbent followed by reduction of Au^{3+} to Au.

Longan seed which has a content of C, O and H is abundantly available and has been used for the synthesis of activated carbon. Activated carbon from longan seed was prepared by chemical activation using NaOH and evaluated for removal of Cr (VI) from aqueous solution. Influence of operating parameters like shaking speed, adsorbent dosage, initial pH, temperature were studied by performing batch experiments. The surface area determined by BET isotherm was found to be 1511.8 m^2/g and the total pore volume found to be 0.742 cm^3/g. External diffusion did not affect adsorption efficiency when minimum speed was maintained at 170 rpm. Experimental data fitted better to the Langmuir isotherm equation. Evaluation of thermodynamic parameters showed the process to be spontaneous and endothermic.

In the work of Isabel and co-researchers (Villaescusa et al 2004) potential of grape stalk wastes as a low cost adsorbent has been experimented for its adsorption potential for removal of Copper and Nickel from aqueous solutions. Parameters investigated were pH, ionic strength and initial metal concentration. The optimum pH was found to be between 5-6 for both metals. The cations released from the grape stalks were analyzed using ICP –AES by treatment with 0.14 M HCl after 3 or 4 washings. The total ionic content may be considered as a measure of the cation exchange capacity of the grape stalk. The observed decrease in absorption of Cu, Ni in the presence of NaCl can be attributed to formation of Copper and nickel chloro complexes.

Modified as well as unmodified cassava waste for the removal of Cadmium, Copper and Zinc was investigated as low cost adsorbents by Abia and co-researchers (Abia et al 2003). Increase in adsorbivity of the adsorbent was noted when the adsorbent was modified by thiolation.

2. METHODOLOGY, DESIGN AND EXPERIMENTATION

2.1. Materials

Date palm leaves were collected from a local farm in Muscat and were washed with distilled water several times to remove dirt, dust and surface impurities and cut to approximately 2-3 cm. 80 ml sulfuric acid (13 M) was used as solvent for date palm leaves. Beaker, flask, filter paper, deionized water was used for all experiments. 0.01N of HCl and NaOH were used for pH adjustment.A stock zinc sulphate solution as synthetic wastewater was prepared by dissolving 4.39 g of zinc sulphate in 1000 ml deionized water.

2.2. Preparation of carbon adsorbent

Dry palm leaves were collected from a local farm in Muscat and were washed with distilled water to remove dirt, dust and surface impurities. The cleaned leaves were put in plastic trays and left to dry at room temperature around 1 hour. The leaves were cut them into small pieces 2-3 cm by scissors. Approximately 25 g of date palm leaves were chemically-carbonized by mixing clean air-dried palm leaves with 250 of distilled water, and 80 ml of Sulfuric acid (13 M).The mixture was heated around 170 ± 2 ºC for 20 min with occasional stirring and was kept in that temperature range for 25 min for complete carbonization. The mixture was then dried in the oven at around 180º C at 8 hours. The resulting black mixture was allowed to cool to room temperature and the spent sulphuric acid was washed in a gooch crucible with distilled water to remove residual acid until the wash water did not show a change in methyl orange color. The sample was then subjected to a cycle of washing and filtration with distilled water till acid free and left under suction for 30 min to remove water among the particles. Sample was then dried at 120ºC in the oven for 4 hours. The carbon was characterized in terms of surface area as granules or powder as presented in (Fig 2).

Fig. 2 Dehydrated carbon adsorbent

2.3. Adsorption experiments

For kinetic studies, dehydrated carbon for waste water (zinc) experiments was performed as follows: A sample of 0.1 g dry carbon was mixed with 50 ppm of zinc solution at initial pH 3. At different time intervals, an aliquot of supernatant was withdrawn for analysis. Batch experiments were carried out by mixing 0.3 g of the adsorbent with 50 ml of solution of different concentration in the range from 10 to 50 ppm at different stirring times in the range from (15 - 120) minutes . In most cases, experiments were performed at room temperature and at the same pH 3 and speed of shaker was maintained at 100rpm until equilibrium was reached. The effect of pH was studied by adding the appropriate amount of HCl / NaOH solution for both real and simulated sample. After filtration, the samples were stored in 100 ml plastic bottles and labeled as concentration (10, 20….50) ppm and time (15, 30……..120) minutes for further analysis in AAS & UV instrument. Standard solutions were prepared in the range from 0.01 to 0.08 ppm to be used in AAS instrument at a wavelength of 273 nm.

3. RESULTS AND ANALYSIS

Cellulose, hemicelluloses and lignin are the main constituents of the agricultural waste of date palm leaves. Concentrated sulphuric acid acts as an extremely strong dehydrated agent, carbonizing the cellulose and hemicelluloses via the removal of water (El-Shafey et al., 2012). Moreover, it acts as a strong oxidizing agent because of its affinity to lose at atom of oxygen to form sulphurous acid that readily decomposes to sulfur dioxide and water.

3.1 Effect of pH

pH has an important influence in the uptake of heavy metals from wastewater. The uptake and the removal percentage of zinc from the solution is effected by the pH as is illustrated by Fig 3. The effect of pH was studied by varying the pH from 3 to 5. In the experiment, 0.3 g of dehydrated carbon was added to the sample of initial concentration 10 ppm. The stirring time was fixed at 60 minutes at 100 rpm/min stirring speed. As can be seen, the maximum reduction in concentration was observed at pH 3. As the pH increased further, the reduction efficiency decreased. The possible reason could be that at very low pH, the concentration of positive H+ ions will be more reducing the attraction between the adsorbent and the zinc cation. As the pH increases the concentration of H+ ions decrease and the adsorption of zinc is more efficient. However, when the pH increased further, the removal efficiency of zinc decreased and this may be due to metal complex precipitation at high pH.

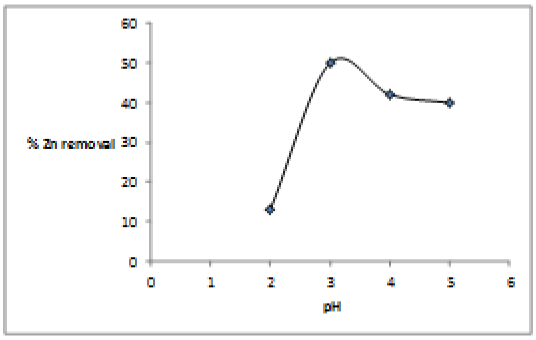

Fig. 3 Effect of pH

3.2 Effect of stirring time

The effect of stirring time was studied by varying the stirring time between 30 and 120 mints. The adsorption rate increased for the first 60 minutes as evident by the removal percentage of zinc and then remained constant (Fig 4). The amount of dehydrated carbon was fixed at the optimized dosage of 0.3 g and the pH was maintained at 3. The stirring speed was maintained at 100 rpm. As the percentage removal was maximum for the initial concentration of 10 ppm zinc at 60 minutes, this was selected as the optimized time. As the stirring time is increased, contact between the adsorbent and metal is increased and hence the maximum degradation of around 48 could be observed. The reason for this trend observed is that the adsorption sites are saturated after 60 minutes and equilibrium condition has been attained.

3.3 Effect of dehydrated carbon dosage

The amount of dehydrated carbon used also influences the uptake of metals in waste water. The effect of pH was studied by varying the amount of dehydrated carbon from 0.1 to 0.7 g. In the experiment, 5 beakers in which 50 ml of 10 ppm zinc solution was taken and the dehydrated carbon amount was varied in each of these beakers in the range from 0.1 to 0.7 g. The pH was maintained at 3 and the stirring time was fixed at 60 minutes at 100 rpm stirring speed. The effect has been shown in (Fig 5). Initially as the amount of adsorbent increased the removal efficiency increases. This is because of the availability of the number of large of number of adsorption sites that increases proportionally. However; as the adsorbent amount is increased further, the removal efficiency decreases. This is due to the overlapping of the adsorption sites and causing a screening effect at high dosage.

3.4 Effect of initial concentration

Fig. 6. shows the trend observed when the initial concentration was increased from 10 ppm to 50 ppm at the optimized conditions of pH 3, dehydrated carbon dosage 0.3 g, stirring speed 100 rpm and stirring time of 60 minutes. This can be explained due to the limited adsorption sites available when the concentration of zinc is increased.

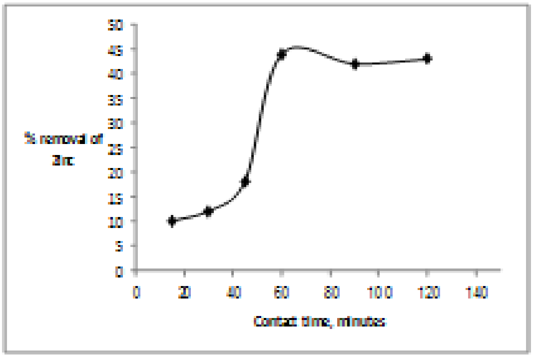

Fig. 4 Effect of contact time

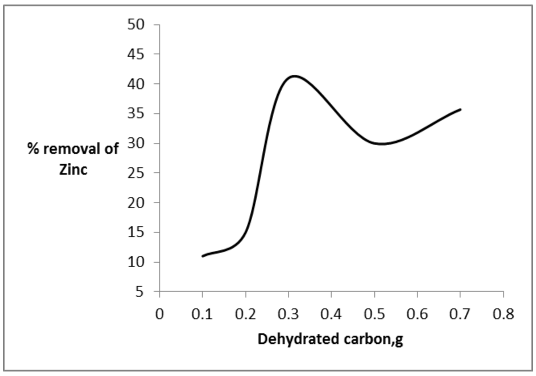

Fig. 5 Effect of Dosage

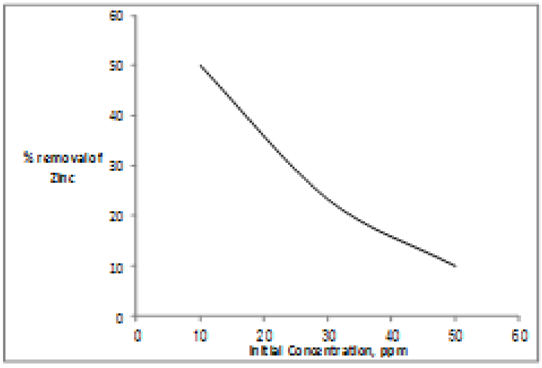

Fig. 6. Effect of initial concentration

3.5 Evaluation of adsorption isotherm

Adsorption isotherms will be helpful to determine the efficiency of the dehydrated carbon and the economic viability. Hence, at the optimized conditions of dehydrated carbon dosage of 0.3 g, pH of 3, stirring time of 60 minutes and stirring speed of 100 rpm the percentage removal of Zinc at different initial concentrations was measured (Table 1) and is illustrated in Fig 7. This data can be used to find out which model namely Langmuir or Freundlich will be suitable to describe this system.

Table 1. Effect of stirring time on different initial concentration when the dehydrated carbon amount is 0.3 g and solution maintained at pH=3

Dehydrated carbon	0.3g				
pH	3				
Stirring Time, mins	0	15	30	45	60
Concentration, ppm	Percentage decrease				
10	0	13	26	45	52
20	0	11	23	32	43
30	0	10	18	31	25
40	0	6	16	25	26
50	0	5	15	23	36

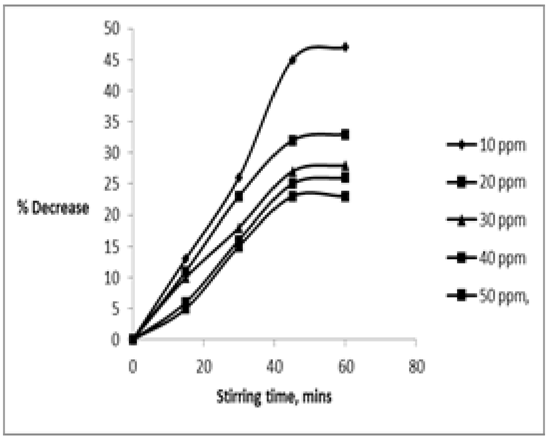

Fig. 7. Percentage decrease in Initial concentration on adsorption with dehydrated carbon at pH 3, dehydrated carbon 0.3 g.

4. CONCLUSION

Dehydrated carbon is cheap and efficient for zinc removal in wastewater. Experiments show the adsorption increased with time as well as with decrease in pH and concentration. % reduction increased when pH was 3 and the adsorption of zinc is more efficient. With regard to contact time, the adsorption increased for the first 60 minute and then remained constant at which a maximum degradation of 48 % was observed for 10 ppm initial concentration. The optimized conditions were pH 3, dehydrated carbon dosage 0.3 g, stirring speed 100 rpm and stirring time of 60 minutes for initial concentration of 10 ppm. Thus, it was shown that dehydrated carbon is an efficient method for zinc removal though filtration is required for separation of dehydrated carbon. This has been corroborated by other works of other researchers (El-Shafey , 2013) in Fig 8.

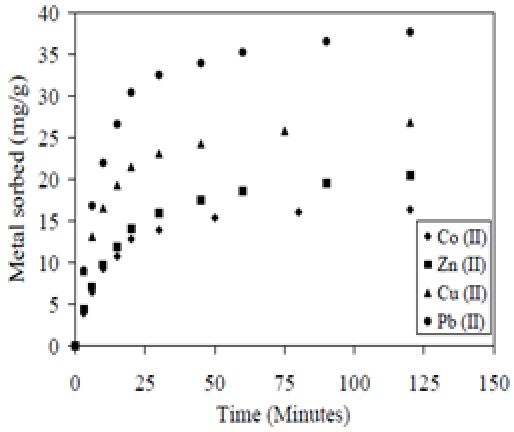

Fig. 8. Sorption kinetics of Pb^{2+} Cu^{2+}, Zn^{2+}, Co^{2+} on dehydrated carbon at 25°C. (El-Shafey, 2013)

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