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Characterization and cation exchange capacity of seeds of *Ziziphus spina-christi*

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Abstract: There are several naturally existing materials have ability to utilize as ion-exchangers. Most of these materials are by-products of waste material from industry or agriculture. Agriculture ion exchange materials include: lemon orange, grapefruit, apple, peas, broad bean, and meddler peels, kernel core, and grape skins. This research deals with the utilization of agriculture waste biomass of napak seed as natural cation exchanger for removal of cationic pollutant from aqueous solution. Methylene blue dye method was used to determine the cation exchange capacity of the stone and it was characterized by IR and TGA methods. The results showed that the highest dye sorption capacity was found at pH 7, the equilibrium time was 60 min, sorbent dose = 0.1g, particle size 177µm and methylene blue concentration range 10-50 ppm. The equilibrium sorption data were analyzed by Langmuir and Freundlich isotherm models.

Keywords: cation exchange capacity; *Ziziphus spina christi*; seeds; methylene blue dye

I. Introduction

Ion exchange materials are classified into synthetic and natural ion exchange materials. Synthetic ion-exchange resins are the main materials used and prepared from organic polymers. The most common examples of these organic polymers include cross-linked polystyrene attached to certain ionizable groups. Natural materials such as clays and zeolites have ion-exchange capability. There is also several other naturally existing materials have been studied by various researchers to determine their ability to utilize as ion-exchangers. Most of these materials are by-products of waste material from industry or agriculture. Agriculture ion exchange materials include: lemon orange, grapefruit, apple, peas, broad bean, and meddler peels, and kernel core [1], coconut shell powder [3] and coconut copra meal [4] and olive stones [5]. Agriculture wastes have been investigated as eco-friendly, low cost and renewable adsorbents for waste water treatment [6]. Agricultural by-products have unique chemical compositions that cause them to be more efficient and feasible option for pollutant removal. These by-products are mainly composed of lignocellulosic materials that consist of three main structural components, which are lignin, cellulose, and hemicelluloses [7]. Also Agriculture wastes, contains lipids, proteins, simple sugars, water, hydrocarbons, and starch [8]. Other polar

functional groups of lignin may be also included, such as alcohols, aldehydes, ketones, carboxylic, phenolic, and other groups [4]. Sidr plant (*Zizyphus spina-christi*, family Rhamnaceae) is a plant that grows in Saudi Arabia since it prefer coastal, desert, and semi-desert areas. The fruit of this tree is called Nabak. The seeds of *Zizyphus spina-christi* contains 4.46 % of Moisture, 1.55 % Ash , 7.18 % protein, and 31.8 % fiber, as it contains also a small percentage of fat around 4.25 % and moderate amount of carbohydrates 54.86 % include sucrose, fructose and glucose [9].

The aim of this work is to study the surface characterization of nabak seed (NS) and feasibility of using as natural cation exchange resin. Cation exchange capacity (CEC) is used to described the capacity of a sorbent to exchange cations where negative charge of material is balanced with an index - cation. Then CEC can be determined by measuring the difference between the initial and the remaining content of the index-cation [10]. Cation exchange capacity can be determined by several methods. These method include exchange of the cations by using different types of cations such as methylene blue, K(I), Na(I), Ba(II), ammonium cation, Co(III) hexamine complex, Ag(I) thiourea complex and Cu(II) ethylenediamine complex. Also there is indirect way to determine the cation exchange capacity of the exchanger by exchange with organic cations such as alkyl ammonium [11]. Methylene blue dye is a cationic dye that becomes popular for determining cation exchange capacity due to its easily application, no need special equipment, and it gives accurate results [12].

II. Experimental Section

II.1 Apparatus:

A grinding machine, pH meter (eco Testr pH), a shaker device (GFL), UV-VIS Double Beam Spectrophotometer (GBC cintra 6), TGA device (SDT 600), IR spectrometer (FTIR-84005 SHIMADZU), sensitive balance (Mettler Toledo), centrifuge device (heraeus sepatech labofuge 200).

II.2. Materials:

Methylene Blue (MB) was purchased from BDH chemicals Ltd pool England. The chemical formula and molecular weights for MB 41 are $C_{16}H_{18}N_3S$ Cl, 319.85 g/mol and the chemical structure of MB is shown in Fig 1.

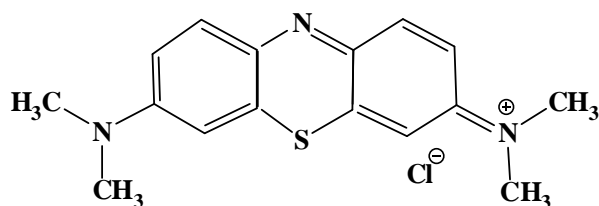


Figure 1: Chemical structure of Methylene Blue

The maximum wave length λ_{max} of methylene blue dye is 665. Stock solutions MB dye, NaOH and HCl were prepared by dissolving appropriate weight in distilled water and the experimental solutions of the desired concentration were obtained by dilution. The pH of solutions was adjusted with diluted NaOH and HCl using pH meter.

II.3. Preparation of Napak Seeds:

Napak seeds (NS) were collected from Al Madinah Al Monawarah and washed by distilled water to remove dust, water soluble material and other impurities. They were washed and dried for 2 day in the air then grinded by domestic grinder and sieved to obtain particle size 177, 250, 841, 2000 microns then stored in glass bottle in a desiccator for further use.

II.4. Batch sorption experiments

The pH of basic dyes (MB) solutions was adjusted from 4 to 9 by using 0.05 M HCl or NaOH solution. 50 ml of MB dye solution of 20 mg.L^{-1} were shaken with 0.1 g of sorbent (NS) for equilibrium time then the adsorption mixture was centrifuged to separate the seeds from the solutions and the filtrates are analyzed for determine the remain concentration of dyes by UV-Visible In order to characterize the other optimum sorption conditions, experiments were performed varying the following experimental parameters: biosorbent dosage (01- 0.5 g), particle size (177, 250, 841 and 2000 microns), initial dye concentration ($10\text{--}50 \text{ mg L}^{-1}$) and time range (15 –180 min).

III. Results and Discussion

III.1. Surface Characterization

III.1.1. IR analysis

IR analysis of NS was done to predict the functional groups that found in it. FTIR spectra for sorbent (Figure 2) show a number of absorption peaks, suggesting complex properties of the NS. The dominant peak at 3360 cm^{-1} in NS is attributed to O–H or N–H stretching vibrations [13-15]. O–H group may be due to alcohol, phenol and carboxyl of lignin and cellulose and N–H group may be due to amide groups. The peak at 1738 cm^{-1} is assigned to carbonyl C=O. The carbonyl groups present in protein and the acetyl ester groups of hemicelluloses [14, 16, 17]. The peaks at 1506 cm^{-1} and 1419 cm^{-1} , may be ascribed to C=C stretching of aromatic skeletal mode [26]. These peaks may also attribute to $\text{C}=\text{O}$ of amide group [10]. The peak at 1371 cm^{-1} are due to C–H bending vibrations. The band at 1234 cm^{-1} is due to the bending modes of O–C–H, C–C–H and C–O–H [14]. The peaks in the region $1200\text{--}950 \text{ cm}^{-1}$ may represent C–O stretching vibrations. The absorption at 897 cm^{-1} for sidr stones are related to C–H rocking vibrations of cellulose. Consequently, the FTIR results indicate that the NS have different functional groups such as hydroxyl, carboxyl and carbonyl, and amid which may be potential biosorption sites for MB dye [14].

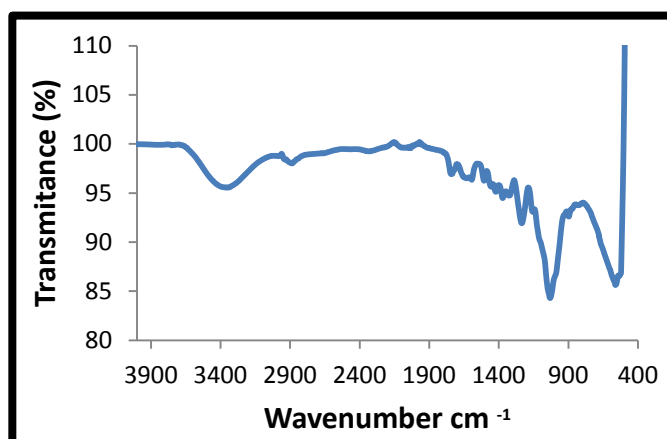


Figure 2: IR analysis of raw Napak Seeds

III.1.2. Thermogravimetric analysis of Napak Seeds

Figure 3 shows the TGA and derivative thermogravimetric analysis (DTG) curves of NS. The experiments are performed under nitrogen atmosphere and heating rate of $10 \text{ }^{\circ}\text{C.min}^{-1}$. NS sample exhibited three mass losses. The first one of 5% was related to the loss of water molecules in the range of RT to $100 \text{ }^{\circ}\text{C}$. The second mass loss in the range of 200 to $370 \text{ }^{\circ}\text{C}$, was associated to the release of chemical bonded water, lignocellulosic materials (hemicellulose, cellulose) and proteins, and it reached about 60 %. The third mass loss of 35 % occurred at higher temperatures above 400°C , and associated to the decomposition of remaining cellulose and the lignin. Lignin peak is

broad and low intensity. The mass loss which occurred in three steps, at temperature range from 200°C to 370°C, shows a maximum at 317 °C [16-19].

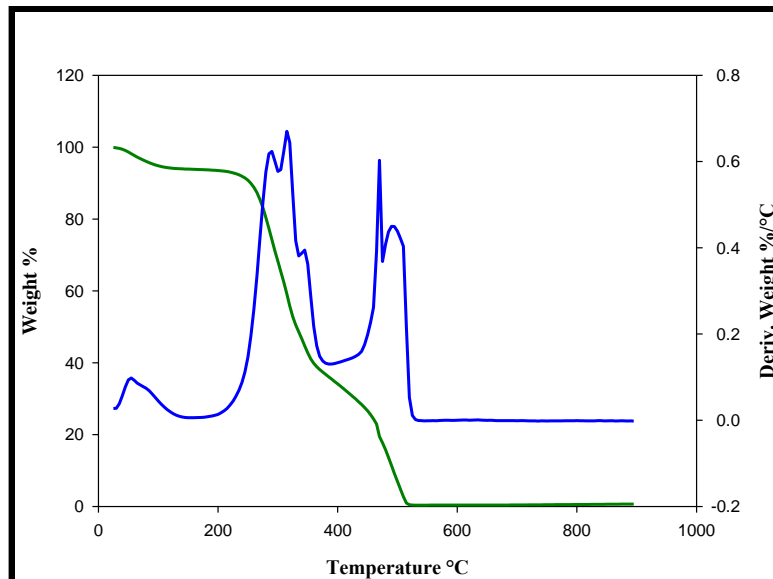


Figure 3: Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) curves of Napak Seeds.

III.2. Cationic Dyes Uptake Capacities:

A batch mode study was carried out to evaluate the uptake capacity of a cationic dye (Methylene Blue MB) from aqueous solution. Factors that affect the biosorption process such as operating parameters such as pH, sorbent dosage, sorbent size, time and initial dyes concentration were evaluated. The uptake capacity at equilibrium (q_e , mg/g) was measured as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

C_0 , C_e and m are the initial concentration, equilibrium concentration and mass of NS, respectively

III.2.1. Effect of pH on uptake capacity of MB by NS.

The pH factor is very important parameter on dye uptake by biosorbent. The pH influences on the surface charge of the sorbent, the dissociation of functional groups on the binding sites, the degree of ionization of the different pollutants and the structure of the dye molecule. The method of sorbate - sorbent interaction depends on the pH of an aqueous medium by two ways:

1. The organic functional groups and unsaturated bonds of dyes alter their ionization potentials at different pH.
2. There are various functional groups on biosorbent surface, so the net charge on biosorbent is also pH dependent [20, 21].

In this study, the initial concentration (20 ppm) of MB was shaken with certain amount of sidr stones (0.1g) size 250 microns at different pH value (4 – 9) for one hour. The results were depicted in Figure 4.

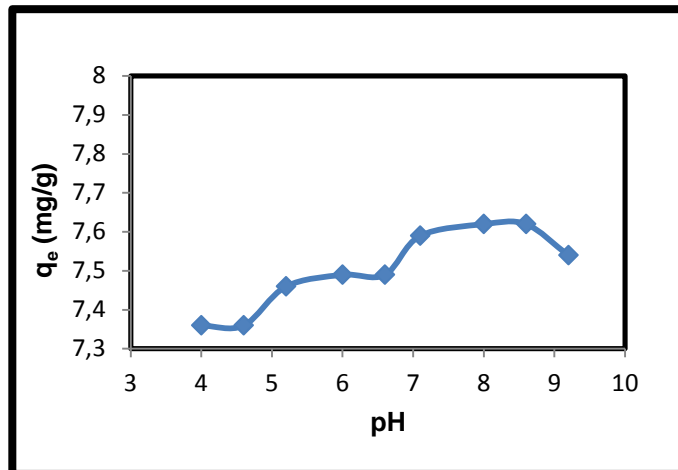


Figure 4: Effect of pH on uptake capacity of MB by Napak Seeds

It was shown that uptake capacity of MB on sidr stones increased slightly with increasing pH and reached a maximum level at the pH of 7.0, and uptake capacity did not change significantly up to pH 9. At low solution pH, the functional groups, on sidr stones are protonated so, the sorbents became more positively charged and the excess of H⁺ ions would compete with cationic dye molecules for the sorption sites. The sorption capacity of the sidr stones decreased slightly at low solution pH and the deprotonated negatively charged surface of sorbents attract more cationic dye molecules. Therefore, the sorption capacity of the sorbents increased at higher pH value [21, 22].

III.2.2 Effect of contact time on sorption capacity of Napak Seeds

Batch tests were done at different contact time and initial concentration with fixed pH (pH =7) and (0.1g) sorbent dose. The results of sorption capacity are given in Figure 5.

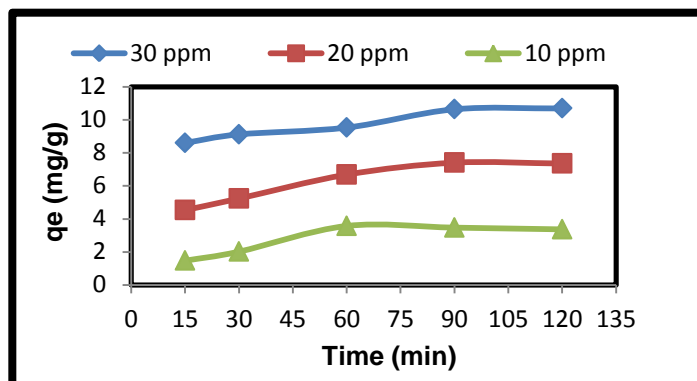


Figure 5: Effect of contact time uptake capacity of MB by Napak Seeds

From the results, the sorption capacity of dye increases with increase of contact time. The capacity was found to be rapid at the initial period and then becomes slow with increase in contact time. At low concentration of MB dye (10 ppm) the equilibrium time is 60 min and at high concentration (20 – 30 ppm) the equilibrium time is 90 min (Figure 5). The equilibrium time increases with increasing concentration of dye because at lower dye concentrations, the available sites in biosorbent are high thus, the dye species can easily find biosorbent sites. Reversibly at higher concentrations the available sites of biosorbent become fewer so it takes more time [23].

III.2.3. Effect of particle size of Napak Seeds:

Influence of particle size on dye sorption was investigated in this study by using four different sizes: 2000, 841, 250 and 177 μm . The initial dye concentration (10 ppm) was shaken with 0.1g of each size from Napak Seeds until the equilibrium time. The results are shown in Figure 6.

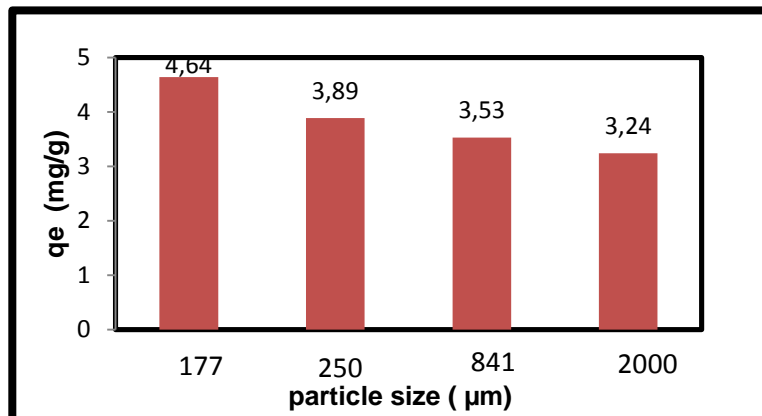


Figure 6: Effect of particle size of Napak Seeds on uptake capacity of MB dye

From the previous figure 6, the MB dye uptake capacity increase with decreasing particle size of Napak Seeds. This result is due to the surface activity and the surface area of the sorbent. The small particles have large surface area and move faster in solution than large particles so in large particles the diffusion resistance to mass transport is higher and most of the internal surface isn't used for sorption thus lead to decrease capacity [21, 24].

III.2.4. Effect of Sorbent Dose on the sorption capacity

The biosorption of Methylene Blue onto NS was studied by varying the sorbent quantity (0.1, 0.2, 0.3, 0.5 g) in the test solution while keep the initial concentration, pH, contact time constant. Figure 7 shows the plot of sorption capacity (mg/g) against sorbent dose (g). As we observed in Figure 7, the dye uptake capacity decreases with increase of the sorption dose. Thus, the smallest quantity of biosorbent (0.1 g) provided optimum sorption capacities, this may be due to overlapping of sorption sites as a result of overcrowding of sorbent particles [25, 26]. Moreover the sorption capacity (the amount of adsorbed per unit mass) decreases due to the splitting effect of flux (concentration gradient) between adsorbates that lead to a decrease in amount of dye adsorbed onto unit weight of biomass [27].

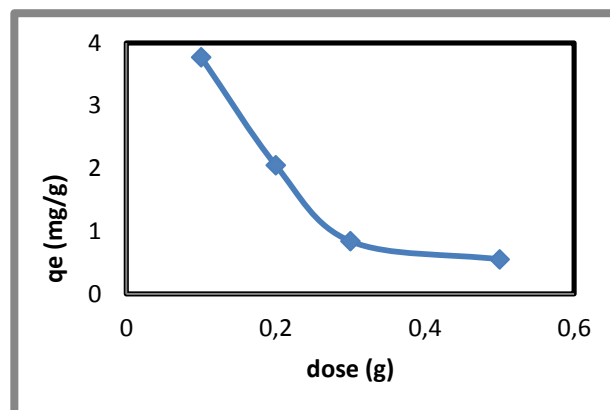


Figure 7: Effect of particle dose on uptake capacity of MB dye by NS

III.2.5. Effect of Initial Concentration and Sorption Isotherms

The sorption was carried out by taking various concentrations of dyes (5-50ppm) and constant amount of NS (0.1 g) and shaken for the equilibrium time. Sorption isotherms provide fundamental physicochemical data for evaluating the applicability of sorption process. Langmuir and Freundlich isotherms are used to analyze the experimental data. Langmuir’s model is based on the monolayer coverage of the adsorbate at specific homogeneous sites of the outer surface of adsorbent [28]. The Langmuir isotherm can be represented by:

$$q_e = \frac{qm KL Ce}{1+KL Ce} \tag{2}$$

The linear form of Langmuir equation is

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{qm KL} \tag{3}$$

The Freundlich isotherm gives information about the heterogeneity of the surface, distribution of the sites and their energies as well as multilayer sorption. Freundlich equation and linear form of Freundlich equation are given by the following equations:

$$q_e = K F C_e^{1/n} \tag{4}$$

$$\ln q_e = \ln KF + \frac{1}{n} \ln C_e \tag{5}$$

Where the value of n can be used also to describe the adsorption. So if the n=1, the adsorption is linear while if n <1, it implies that the adsorption process is favoured by chemisorption and if n >1, the adsorption process is favoured by physisorption [27].

Langmuir isotherm is obtained by plotting the relationship between C_e against Ce/q_e. While Freundlich isotherm is given from the relation between lnC_e against ln q_e in Figure 8. The data from these relationships is used to calculate maximum sorption capacity q_m, R² for Langmuir isotherm and k_f, n and R² for Freundlich these data are shown in table 1.

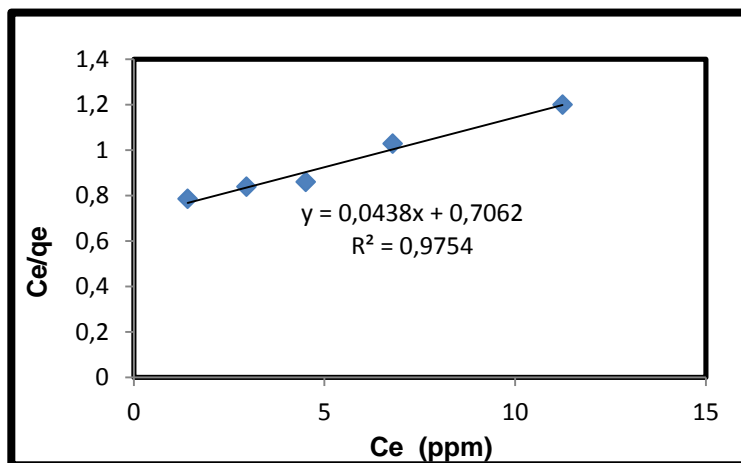


Figure 8: Langmuir isotherm for sorption of MB onto NS.

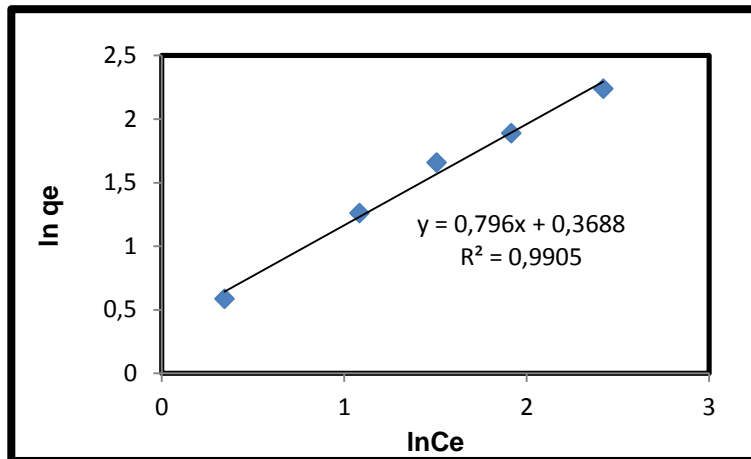


Figure 9: Freundlich isotherm for sorption of MB onto NS

Table 1: Isotherm constants for the sorption MB onto NS

Langmuir parameters				Freundlich parameters		
q _m (mg/g)	K _L	R ²	K _f	n	1/n	R ²
23.25	0.06	0.975	1.4	1.2	0.8	0.99

From the previous isotherms all R² values for Langmuir and Freundlich were great than 0.95 indicating almost equal applicability of the two types of sorption isotherm. The maximum MB dye sorption capacity of NS was found 23.25 mg/g. In addition, it can be seen that the numerical value of n is 1.2, it indicates MB is favorably by physisorption onto NS [30].

IV. Conclusion

This study shows that Nabak stone, an agricultural waste, can be used as natural cation exchanger for removal of cationic pollutant. Sorption capacity MB by NS is affected from several parameters like pH, sorbent dose, sorbent grain size, and initial dye concentration. Both Langmuir and Freundlich isotherm are applicable.

It is therefore recommended in the future to use these stones in the removal of positive ions from aqueous solutions.

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