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CHEMISTRY

REMOVAL OF Zn(II) and Cu(II) IONS FROM AQUEOUS SOLUTION USING CHEMICALLY ACTIVATED CARBON DERIVED FROM PALMYRA SHELL

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ABSTRACT The ability of activated carbon prepared from palmyra shell (PAC) to remove Zn (II) and Cu (II) metal ions from synthetic effluent was investigated. The PAC was characterized using FTIR spectroscopy and SEM in order to ascertain the existence of functional groups and microspores responsible for adsorption of metal ions. The experiments were carried out in a batch system to optimize various experimental parameters like initial metal ion concentration, contact time, dose rate of adsorbent and pH. The adsorption data were well represented by Langmuir model. Kinetic studies showed that the adsorption rates were more accurately represented by a first order model. The obtained results confirmed the applicability of PAC as an efficient and economical adsorbent for the removal of heavy metal ions from waste water.

KEYWORDS : Palmyra shell Activated Carbon (PAC), Adsorbent

1. INTRODUCTION

Most of the heavy metals discharged into the waste water are found toxic and carcinogenic and cause a series threat to the human health[1]. Among the heavy metals copper causes lethargy, anorexia, damage to the gastrointestinal tract, epilepsy, melanoma, rheumatic arthritis, gastric ulcer, necrosis in the liver, kidney problems and loss of taste in humans[2-4] and zinc may cause stomach cramps, skin irritations, vomiting, nausea, anemia , diarrhea and sterility[5-7] Several methods and techniques have been proposed for zinc and copper ion removal including adsorptions[8], precipitation[9], bioremediation[10], membrane filtration[11], ion-exchange[12] and solvent extraction[13]. Among these techniques, adsorption was considered superior to its high efficient removal, easy operation, cost effectiveness and availability of efficient adsorbents[14]. In recent years, increasing cost and environmental consideration associated with the use of commercial adsorbents, have led to a significant body of research work aimed at developing new low cost adsorbents .

These studies include the use of coal[15], fly ash[16-20], bagasse pith[21], saw dust[22], rice husk[23], cotton seed shell[24], almond shell[25], coir[26], banana pith[27], jute[28] and palm-fruit bunch[29]. In this study, the use of chemically activated carbon derived from palmyra shell as a low cost adsorbent for the removal of Zn(II) and Cu(II) metal ions was investigated in order to arrive an alternate for high cost commercially activated carbon.

2. Materials and methods

2.1. Materials

Palmyra shell were collected and carbonized using muffle furnace by heating at 500°C for three hours. The carbonized palmyra shell was powered and sieved into 90 microns sized particles. The carbon was activated by digesting in 1:1 nitric acid solution for 120 minutes at 80°C.The supernatant solution was decanted. The carbon was washed with boiling de-ionised water several times to remove acid and the metal ions present in it then it was dried by keeping in air oven for 3 hours at 105°C. Stock solution of Zn(II) and Cu(II) were prepared by dissolving Analytical reagent grade $Zn(NO_3)_2.6H_2O$ and $CuSO_4.5H_2O$ in double-distilled water. The solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions.

2.2 Characterization method

The Zn(II) and Cu(II) metal ion concentration of the solutions before and after equilibrium was determined by using atomic absorption spectrometer-spectra AA 100/200-Varian-Australia.The pH of the solution was measured using Hanna pH meter using glass electrode.FT-IR analysis was carried out using Shimadzu Spectrophotometer with KBr pellets. The SEM images of the PAC and metal loaded PAC were analyzed using a electron probe micro analyzer model JEOL-J x A840 A made by Japan

2.3 Adsorption studies

Batch adsorption experiments were carried out by shaking the flasks using a horizontal bench shaker (Orbitek-Teqip-ACT/EQ/454) at 200 rpm. The experimental data obtained in batch studies were used to calculate the percentage removal of heavy metal ions and the adsorbed metal amount q_e (mg/g) was calculated by using mass balance equations 1 and 2 as follows.

$$\%Removal=100(C_o-C_e)/C_o \quad \ldots\ldots(1)$$

$$q_{e=}100(C_o-C_e)V/m \quad \ldots\ldots(2)$$

Where C_o and C_e are initial and equilibrium final concentrations (mg/L) of the metal solutions respectively and V is the volume of the solution (L); and m is the adsorbent mass (g).

3. Results and Discussions

3.1. Characterization of the PAC

FT-IR spectrum for the PAC before and after adsorption of Zn(II) and Cu(II) metal ions were recorded and reproduced in fig.1 and fig.2. The remarkable shifting and disappearance of stretching vibrations after adsorptions supported that the functional groups on PAC are participated in Zn(II) and Cu(II) metal ions removable process.

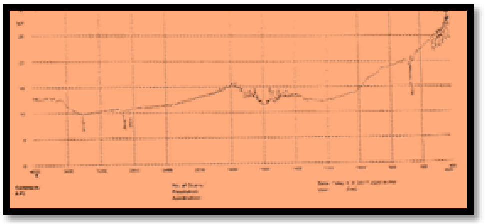

Fig.1.FT-IR spectrum of the PAC before adsorption.

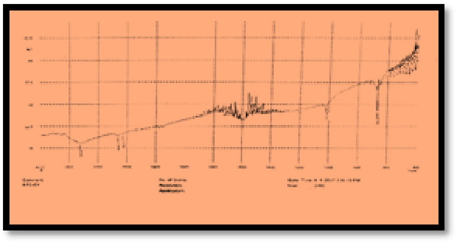

Fig.2.FT-IR spectrum of PAC after adsorption of Zn (II) ion

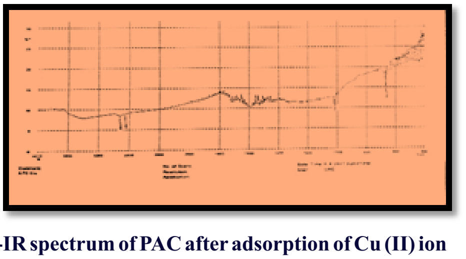

Fig.3.FT-IR spectrum of PAC after adsorption of Cu (II) ion

The SEM image of PAC before adsorption and after adsorption of Zn(II) and Cu(II) metal ions were recorded and reproduced in fig.4, 5 and 6. removable process.

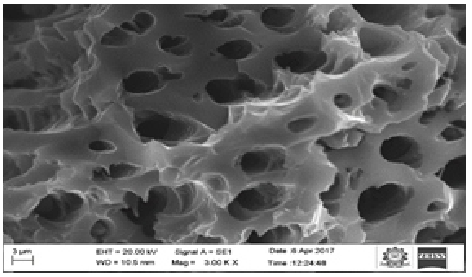

Fig.4.SEM image of PAC before adsorption.

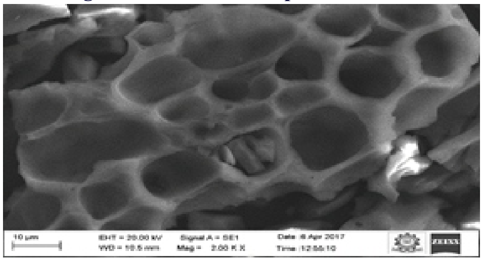

Fig.5.SEM image of PAC after adsorption of Zn(II) ion.

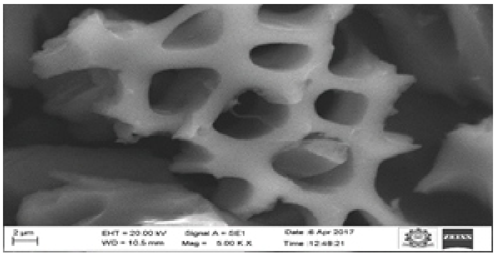

Fig.6.SEM image of PAC after adsorption of Cu(II) ion.

The SEM image of PAC before adsorption indicate that the existence of micro and meso pores which are responsible for the removal of metal ions from waste water. The fading of porous nature of adsorbent after adsorption in the SEM image of PAC supported that the Zn(II) and Cu(II) metal ions are incorporated in to the pores of the adsorbent.

3.2. Optimum conditions for maximum removal

The parameters which influence the mechanism of the adsorption and the efficiency of the removal of metal ions by adsorption on PAC are initial concentration of the metal ions, dose of the adsorbent, contact time and pH of the solutions. The optimum conditions for the maximum removal of Zn(II) and Cu(II) metal ions were determined on varying all parameters by keeping any one of the parameter as constant. The effect of initial concentration on the adsorption of Zn(II) and Cu(II) metal ions by adsorption on PAC adsorbent is shown in Fig.7.

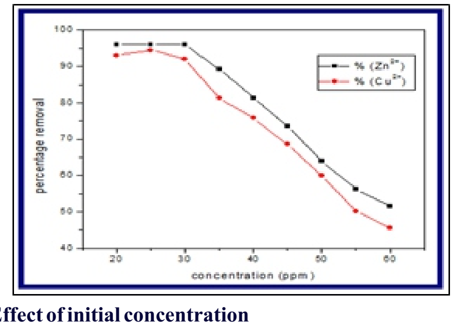

Fig.7.Effect of initial concentration

The percentage removal of metal ions found to decrease with increase of initial concentration of the metal ions. It is due to that, after the formation of monolayer of the respective metal ions at the surface of PAC, the formation of second layer of metal ions is highly hindered at higher initial concentration, due to the repulsive interaction between adsorbed and un adsorbed metal ions present on solid surface and in solution, respectively. The optimum concentration for maximum percentage removal of Zn(II) and Cu(II) metal ions by adsorption on PAC was found to be 30ppm and 25ppm respectively.

The effect of contact time on the removal of Zn(II) and Cu(II) metal ions by adsorption on PAC is shown in Fig.8.

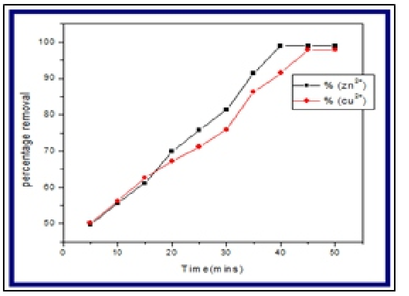

Fig.8.Effect of Contact time

It is observed that the percentage removal of the metal ions increases as the contact time increases and reaches a maximum value. Similar results have been reported by many researchers[30-32]. The optimum contact time for maximum percentage removal of Zn(II) and Cu(II) metal ions by adsorption on PAC was found to be 40 minutes and 45 minutes respectively.

The effect of dose rate on the removal of Zn(II) and Cu(II) metal ions by adsorption on PAC is shown in Fig.9

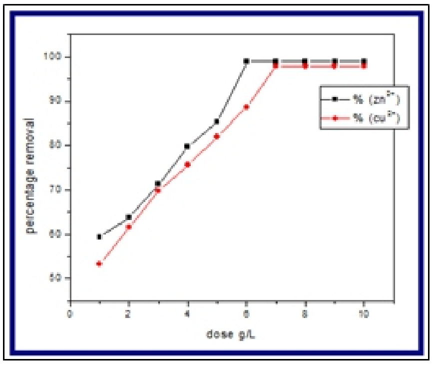

Fig.9.Effect of Dose rate

It is noted that the percentage removal of metal ions increases with increase in adsorbent dose rate. This is due to the increase in number of active sites of adsorbent with increase in dose of the adsorbent[33-35].This results has been supported by various researchers. . The optimum dose rate for maximum percentage removal of Zn(II) and Cu(II) metal ions by adsorption on PAC was found to be 6gL^{-1} and 7gL^{-1} respectively.

The effect of pH on the removal of Zn(II) and Cu(II) metal ions by adsorption on PAC is shown in Fig.10.

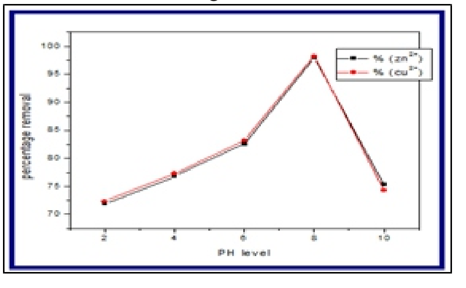

Fig.10.Effect of pH

It is observed that the percentage removal of the metal ions increases as the pH increases and reaches maximum then decreases when there is further increase in pH. It is due to that, at lower pH the PAC surface will be positively charged, creating electrostatic repulsion between the positively charged surface of the PAC and the Zn(II) and Cu(II) ions. At higher pH the number of positively charged sites are reduced and raised the number of negatively charged sites, which increases the electrostatic attractions between Zn(II) and Cu(II) ions and PAC surface. The similar phenomenon has been supported by various researchers[36-37]. . The optimum pH for maximum percentage removal of Zn(II) and Cu(II) metal ions by adsorption on PAC was found to be 8 respectively. The percentage removal decreases on further increase in pH after the optimum level. This is due to that the formation of metal hydroxides precipitate when the pH above the optimum level.

3.3. Isotherm and Kinetics of adsorption

The equilibrium data for the removal of Zn(II) and Cu(II) ions were modelled with Langmuir isotherm given in equation 3.

$(C_e / q_e) = (1 / Q_o b) + (C_e / Q_o)$ ………. (3)

$R = 1 / 1+bC_o$ ………. (4)

Where Q_o and b are Langmuir constants related to adsorption capacity (mg g^{-1}) and energy (L mg^{-1}). The Langmuir isotherm plots are shown in Fig.11.

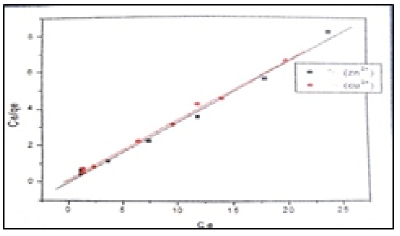

Fig.11.Langmuir isotherm for removal of Zn(II) and Cu(II) ions by adsorption on PAC

The separation factor (R=0.1351) calculated as per the equation 4 falls in between 0 to 1 indicates that the feasibility of adsorption of Zn(II) and Cu(II) ions on PAC.

The kinetics of adsorption was studied by Natarajan and Khalaf equation given in equation 5.

$k = (2.303/t) \log (C_o / C_t)$ ……….. (5)

The plot of $\log (C_o / C_t)$ Vs. time is shown in fig.12.

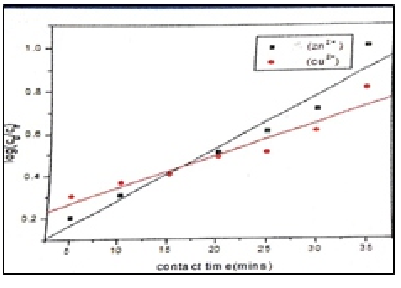

Fig.12.Kinetics of adsorption of Zn(II) and Cu(II) ions by PAC.

The straight line plots for the above equation shows that the adsorption follows first order kinetics. The rate constant of the adsorption of metal ions were calibrated and it is found that the rate constant is higher in the case of Zn(II) ion ($0.307 \times 10^{-2} min^{-1}$) than Cu(II) ion ($0.253 \times 10^{-2} min^{-1}$).

4. Conclusion

The present studies shows that palmyra shell activated carbon is a multifunctional, micro porous and meso porous material which is used as an effective adsorbent for removing Zn(II) and Cu(II) metal ions from contaminated water sources. The adsorption of Zn(II) and Cu(II) ions were strongly dependent on the pH, and the maximum removal was attained at pH 8.0 . The adsorption of Zn(II) and Cu(II) metal ions increases with increase in contact time and adsorbent dose. The adsorption efficiency of Zn(II) and Cu(II) ions on PAC decreased with increase initial concentrations of Zn(II) and Cu(II) metal ions. The equilibrium data was described well with Langmuir isotherm. Kinetics study demonstrated that the adsorption mechanism of Zn(II) and Cu(II) ions followed the first order kinetics. Hence the low cost palmyra shell activated carbon is the best alternate for high cost commercial activated carbon for the waste water treatment.

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