

Adsorption Studies of Lead and Crystal Violet onto Modified Activated Carbon

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Abstract—Surface modification of activated carbon by synthesized dibenzotetraaza-macrocyclic complexes of Mn (II) and Co (II) has been carried out which showed the changes after modification with respect to functional groups. Cyclic voltammetric studies showed varied redox behavior of both the macrocyclic complexes after adsorption. New developed modified activated carbons further studied for the adsorption of heavy metal (lead) and basic dye (crystal violet). A comparison of the adsorption behavior of metal showed very slight changes. The amount adsorbed of metal on fresh and modified activated carbon is 182 mg/g for fresh Activated Carbon, 181 mg/g for MC-Mn(II) and 180.3 mg/g for MC-Co(II) while in case of dye significant decrease in the adsorption of basic dye that is 58.3 mg/g for MC-Mn (II) and 53.9 mg/g for MC-Co(II) from 104.5 mg/g for fresh Activated Carbon. These changes may be observed due to the changes in their characteristic behavior

Keyword: Activated carbon, macrocyclic complex, adsorption, differential pulse voltammetry.

1. INTRODUCTION

Adsorption on activated carbon has emerged as an effective and useful technique for water purification (1-2). Amongst other pollutants, dyes and metals, particularly heavy metals like lead have been found to contaminate water frequently. These pollutants cause a major problem in the present scenario; trace concentration of these pollutants is harmful in the water system (3-5). Heavy metals like Pb, Cd and Zn are the more carcinogenic pollutants which affect public health due to their high stability and bioaccumulation. Improving the water quality is of great interest and the removal of toxic metals from wastewater has become necessary (6-8). Amongst the various physicochemical methods of treatment, adsorption onto activated carbon has been found significant and reliable (3). Activated Carbon has peculiar characteristics like large surface area, microporous structures, surface active sites and high adsorption capacities, due to which activated carbon is used as adsorbent (9-10). Anodic stripping voltammetry has become also a powerful tool for the determination of trace metal ions, where mercury is commonly used as the working electrode because of excellent reproducibility and high sensitivity (11-12).

There is an increasing interest of surface modification of adsorbents specially activated carbon (13). In the adsorbent, surface functional groups play a vital role in the adsorption study (14-15). Oxidation of CNTs has been widely studied. The surface properties changed during oxidation of surface of carbon nanotubes due to the formation of new functional groups (16). Various substances have been used to study the surface modification of activated carbons such as coconut activated carbon surface modified by tetraoxalylethylenediamine melamine resin (17). In many studies modified activated carbon give better result for the adsorption of different kind of pollutants from the water bodies. (18-19)

Macrocyclic chemistry has expanded phenomenally to provide exciting and novel chemistry now-a-days. Macrocyclic ligand may contain various combinations of donor atoms like N, O, and S. Applications of macrocyclic complexes in medical field have been found as antiviral, anticarcinogenic, antibacterial, and antifungal and as MRI contrast agents (20). Surface modification of CNTs have also been achieved by dibenzotetraazaannulene complexes of nickel and copper (21). Catalytic applications of activated carbon supported porphyrin based macrocyclic complexes are known (22). Modification of glassy carbon electrode with similar macrocyclic complexes has been found effective for electroreduction of CO₂ (23).

In the present study, activated carbon has been modified by adsorption of macrocyclic complexes. The comparative adsorptions of lead and crystal violet onto fresh and modified activated carbons have been studied.

2. MATERIALS AND METHOD

All the chemicals used in this study were of analytical grade. Activated carbon and methanol purchased from Merck pvt.Ltd. Tetraazamacrocyclic complexes of Mn(II) and Co(II) used in the study, have been synthesized previously (24), the modified activated carbons have been referred as MC-Mn(II) and MC-Co(II) for Mn(II) and Co(II) macrocyclic complexes. Spectral studies carried out by UV/VIS spectrophotometer (Cary 60 Agilent) and FTIR (Shimadzu 8400S). The changes in initial concentration of lead metal after adsorption onto

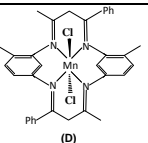
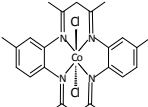
activated carbon were studied by the help of differential pulse voltammetry (DPV) (Metrohm Autolab 663 VA Stand).

3. MODIFICATION OF ACTIVATED CARBON

Adsorption of macrocyclic complexes over activated carbon has been carried out by using Mn (II) and Co (II) macrocyclic complex solution of a fixed concentration 6×10^{-4} M and 5×10^{-4} M in methanol respectively. 500 mg activated carbon and 500 ml solutions of macrocyclic complexes taken in 1000 ml volumetric flask and shake upto 1hr. and kept for overnight in water bath cum shaker at 27°C . The solutions filtered and dried in oven below 30°C . Macrocyclic loaded carbon is pronounced as modified activated carbons it is kept in air tight container.

4. ADSORPTION STUDY

The adsorption studies of Pb(II) and crystal violet on fresh and modified activated carbon were carried out to evaluate the adsorption efficiency. The unadsorbed Pb(II) in supernatant solution was characterized by differential pulse voltammetry (DPV) whereas unadsorbed crystal violet in supernatant solution was characterized by UV Vis spectroscopy. Differential pulse voltammetry is a system consisting three electrodes; hanging mercury drop electrode (HMDE) as working electrode, platinum (Pt) as auxiliary electrode and Ag/AgCl/KCl(3 mol/L) as reference electrode. For DPV, acetate buffer was prepared by taking 55.9 g potassium chloride (KCl) in a 500 ml volumetric flask and dissolved it in 100 ml of double distilled water, 25 ml 30% w/v NaOH and 14.2 ml glacial acetic acid were added and volume was made upto 500 ml. pH of solution was checked and adjusted to pH 4.62 by adding NaOH and acetic acid. Some physical properties has been listed in Table 1.

| Complexes | Molecular formula | Molecular weight | Structure |
|-----------------|---|------------------|---|
| Mn (II) complex | $\text{MnC}_{34}\text{H}_{32}\text{N}_4\text{Cl}_2$ | 622 |  |
| Co(II) Complex | $\text{CoC}_{24}\text{H}_{28}\text{N}_4\text{Cl}_2$ | 502 |  |

5. RESULTS AND DISCUSSION

The electronic spectra of Mn(II) and Co(II) macrocyclic complexes in methanol and supernatant liquids after adsorption of each complex on activated carbon (unadsorbed macrocyclic complexes) shown in fig.1. The spectrum of Mn(II) macrocyclic complex shows major absorption bands at 238, 280 and 355 nm whereas Co(II) macrocyclic complex shows bands at 243 and 278 nm. The spectra of unadsorbed macrocyclic complexes show same absorption bands with

decrease in absorbance due to adsorption of macrocyclic complexes on activated carbon. The amounts of adsorbed macrocyclic complexes were calculated by measuring absorbance ratio of the solutions before and after adsorption. The concentration of Mn(II) macrocyclic complex adsorption on activated carbon is found higher than the Co(II) macrocyclic complex. It is indicated that the adsorbent surface changed by the adsorbing tetraazamacrocyclic complexes.

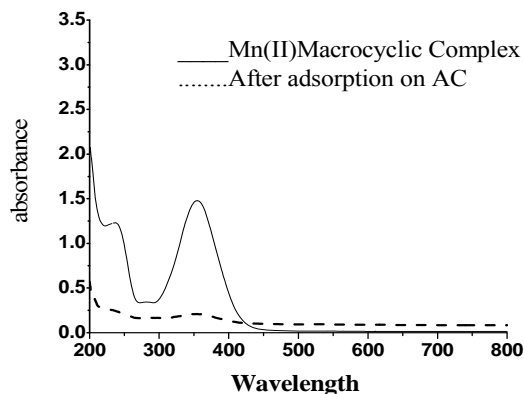


fig.1(a)

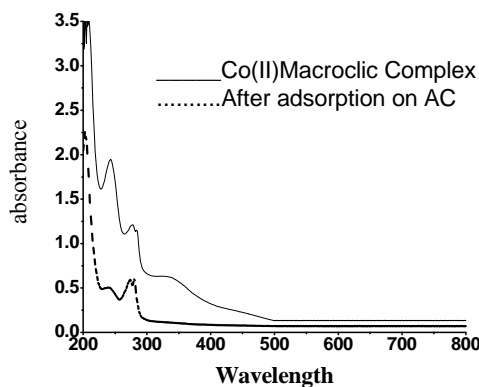


fig.1(b)

Fig. 1. (a) and (b) shows the electronic spectra of Mn (II) and Co (II) macrocyclic complex before and after adsorption on activated carbon

MC-Mn(II) and MC-Co(II) system are found stable in water as no λ_{max} has been obtained for supernatant liquid even after shaking modified carbons in water and keeping it overnight.

The IR of Activated Carbon before and after adsorption of Mn(II) and Co(II) complexes of recorded spectra shown in fig.2. Two new peaks observed in the IR spectrum of MC-Mn(II) at 1589 and 403cm^{-1} ; these peaks may be accounted for $>\text{C}=\text{N}$ stretching and M-N stretching respectively. In case of MC-Co(II), the corresponding peaks are observed at 1498 and 426cm^{-1} . These two peaks found absent in the IR spectrum of fresh activated carbon. The emergence of the two new

peaks clearly indicates binding between complexes and activated carbon (20,24).

The electrochemical studies of tetraazamacrocyclic complexes of Mn(II) and Co(II) before and after adsorption on activated carbon carried out by employing cyclic voltammetric technique in methanol solvent containing 0.1M tetraethyl ammonium perchlorate (TEAP) as supporting electrolyte by using Pt disc as working electrode at 100 mVs⁻¹ scan rate. Cyclic voltammograms of these tetraazamacrocyclic complexes before and after adsorption are shown in fig.3. The cyclic voltammogram of Mn (II) macrocyclic complex before adsorption show two main redox couples which found at Epa₁ -0.80 V, Epa₂ -0.10 V and a separated anodic peak Epa₃ also appear at +0.73 V. CVs of macrocyclic complexes after adsorption show the significant shifting of oxidation and reduction peaks in anodic and cathodic directions respectively. CV of Co(II) macrocyclic complex shows three anodic peaks at -0.82 V, -0.13 V and +0.87 V with corresponding two cathodic peaks at -0.50 V and +0.72 V but after adsorption it shows one anodic peak at +0.93 V and two cathodic peaks at -0.81 V and -0.21 V. The shifting of some redox couples clearly indicates the interaction of macrocyclic complexes with activated carbon. The interaction may be due to replacement of axial chloride ion by functional groups of activated carbon.

Fig. 2(a) and (b) represents Mn(II) and Co(II) macrocyclic complexes before and after adsorption on activated carbon

The cyclic voltammetric data of Mn(II) and Co(II) macrocyclic complexes (before adsorption) MC-Mn(II) and MC-Co(II)(after adsorption) listed in table 2.

Table 2: Cyclic voltammetric data of complexes, before and after adsorption.

| Complex | Epc1 (V) | Epc2 (V) | Epa1 (V) | Epa2 (V) | Epa3 (V) |
|------------|----------|----------|----------|----------|----------|
| Mn(II) | -0.52 | +0.91 | -0.80 | -0.1 | +0.73 |
| MC- Mn(II) | -0.79 | +0.93 | -0.89 | -0.89 | +0.17 |
| Co (II) | -0.5 | +0.72 | +0.8 | -0.13 | -0.82 |
| MC-Co(II) | -0.81 | -0.21 | +0.93 | - | - |

6. ADSORPTION OF METAL AND CRYSTAL VIOLET ONTO ACS

The adsorption capacity of lead and crystal violet on modified ACs has been studied by shaking 800 mg/L Pb(NO₃)₂ and 4 × 10⁻⁴M crystal violet aqueous solutions respectively with fresh and modified ACs. The solution were kept overnight in water bath cum shaker at 27°C. The supernatant solutions were characterized by DPV and electronic studies. Adsorption of lead metal can be easily studied by DPV. The voltammograms of equilibrium concentration of Pb (II) after adsorption on fresh and modified ACs shown in fig. 3a. The voltammograms show slight increase in the peak height and peak area. The amount adsorbed on adsorbent calculated by peak height and obtained 182 mg/g for fresh activated carbon and 181 mg/g for MC-Mn (II) and 180.3 mg/g for MC-Co(II).

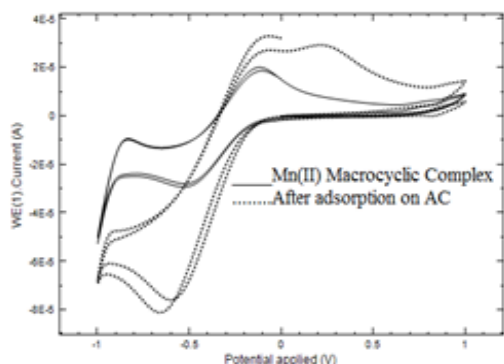


Fig.2(a)

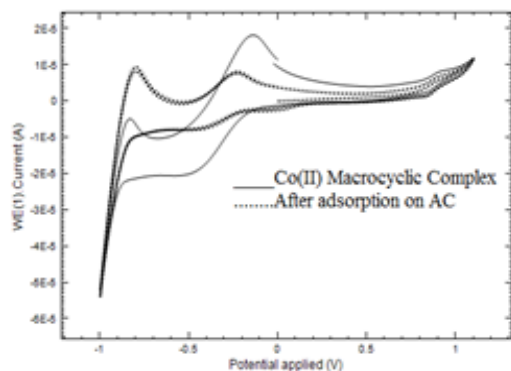
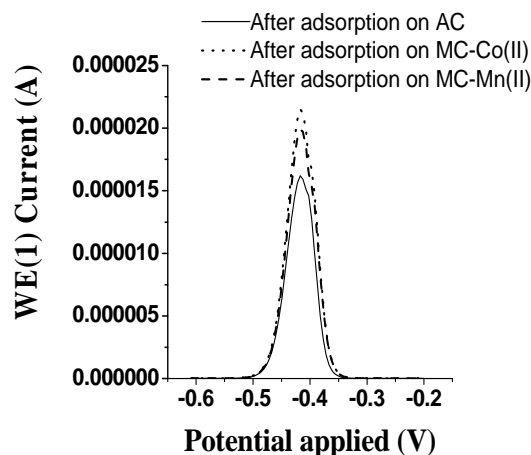


Fig.2(b)



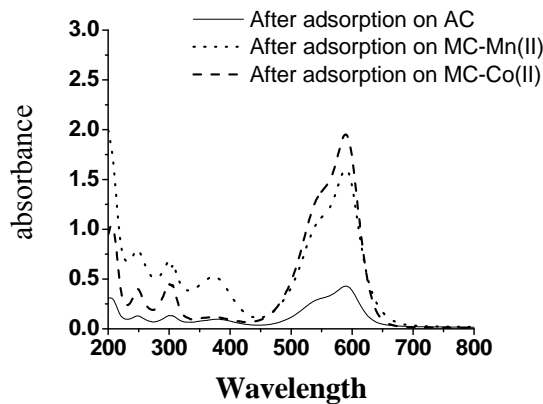


Fig. 3a: DPV voltammograms of Pb(II) Fig.3b: Electronic spectrum of crystal violet

Electronic spectra of crystal violet equilibrium concentrations after adsorption on fresh and modified activated carbon shown in fig.3b. The spectra of supernatants of both the modified ACs show increase in absorbance indicating the less adsorption capacity on modified carbons towards crystal violet. The amount adsorbed on adsorbent calculated by equilibrium concentration 104.5 mg/g for fresh activated carbon and 58.1 mg/g for MC-Mn(II) and 55.6 mg/g for MC-Co(II) it indicate the highly decreases amount of dye molecules. This highly decreases may due to steric hindrance shows in modified activated with crystal violet dye molecules. The small changes in case of metal ions may be attributed due to its smaller size than dye molecules.

7. CONCLUSION

Surface modification of activated carbon being used to solve the environmental pollution problem along with the study of redox behavior of modified ACs. new surface modified activated carbon has been prepared by using tetraazamacrocyclic complexes. Modified ACs were characterized by UV-Vis and IR spectral analysis. The cyclic voltammetric data also support the adsorption of macrocyclic complexes on AC. The adsorption studies show that macrocyclic complexes decrease the adsorption capacity of basic dye over modified ACs. The amount adsorbed on fresh and modified activated carbon is 104.5 mg/g for fresh activated carbon, 58.1 mg/g for MC-Mn(II) and 55.6 mg/g for MC-Co(II) is highly decreased amount of dye may due to steric hindrance shows in modified activated with crystal violet dye. But the effect is less for the adsorption of Pb, The amount adsorbed on fresh and modified activated carbon calculated by peak height and obtained 182 mg/g for fresh activated carbon, 181 mg/g for MC-Mn(II) and 180.3 mg/g for MC-Co(II). This may be attributed due to its smaller size than dye molecules.

8. ACKNOWLEDGMENT

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