



## REMOVAL OF CADMIUM IONS FROM WASTE WATER USING RAW AND TREATED COALS AS ADSORBENTS

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### ABSTRACT

Studies on the adsorption of cadmium (II) ions from waste water on two raw coals viz. North Tisra and South Tisra collieries, along with their eight chemically treated coal samples (which were used as adsorbents) were carried out. The chemical treatments adopted were (a) alkali treatment, refluxing – 72 BS mesh size coal with 25% w/v NaOH solution for 6 hrs., (b) acid treatment, refluxing – 72 BS mesh size coal with 50% v/v HCl for 6 hrs, (c) alkali-acid treatment, refluxing alkali treated coal with 50% v/v HCl for 6 hrs. and (d) acid-alkali treatment, refluxing acid treated coal with 25% w/v NaOH solution for 6 hrs. These treatments have shown changes in the moisture, ash volatile matter and fixed carbon values. FTIR & SEM spectra of treated coals were compared with the corresponding spectra of raw coals indicating structural and morphological changes in coal after the treatment. Adsorption studies reveal that acid treatment reduced the adsorption capacity of coal whereas alkali treatment improved it. Alkali-acid treatment, which gave the highest ash reduction, also did not improve the adsorption capacity substantially. The best results, as far as the improvement in adsorption capacity is concerned, were obtained from acid-alkali treated coals. This clearly indicates that it is not the reduction in the mineral matter content of coal by acid, which is important for the improvement in the adsorption capacity, but it is the alkali treatment, which changes the chemical character of both; the organic and mineral matter part of coal, which ultimately results in improvement in its ion exchange capacity.

**Key words:** Cadmium, Coals, Removal, Waste water.

### INTRODUCTION

Pollution from industrial waste water is enhancing day by day and is creating major health hazards. Considerable work has been carried out on the treatment of wastes from

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industries through conventional treatment methods such as precipitation<sup>1</sup>, coagulation<sup>2</sup>, chemical oxidation<sup>3</sup>, biological techniques<sup>4</sup> and adsorption<sup>5</sup>. However, many of these technologies generally lack the broad scope of treatment efficiency required to reduce all the diverse pollutants present in the waste water. Among the methods, adsorption is very attractive because it is a well established and powerful technique for treating domestic and industrial effluents. Also adsorption method has an edge over the other methods due to its low cost, simple design, easy handling and sludge free operation. It is particularly useful for the removal of metal ions, colour, odour etc. from waste water. There is a possibility of recovery of sorbed metals and the reuse of sorbent, which make this process economical. It is generally employed as a final step after precipitation or as an independent unit process, when the initial metal concentrations are low. Due to the high degree of purification that can be achieved, this process is often used at the end of a treatment process. The application of adsorption technology for pollution control usually deals with the control of organic compounds and trace metals. Activated carbon, the most popular adsorbent, has been traditionally used for the removal of metal ions, colour, odour etc. from waste waters. High adsorptive capacity and versatility of activated carbon has expanded its application in the treatment of numerous industrial effluents. Despite this advantage, it suffers from a number of drawbacks. Activated carbon is quite expensive and regeneration is also not very economical.

This led many researchers to look for cost effective non-conventional adsorbents like industrial and agricultural waste products/by products/ores/metal oxides, minerals etc. The removal of toxic heavy metal contaminants from waste waters is one of the most important environmental and economic issues today. Greater awareness of the ecological and biological effects of toxic metals and their biomagnification through food chains as well as highly publicized episodes of disasters due to heavy metal pollution such as Mina mata, has prompted increased demands for their removal from aqueous streams. The main objectives for the removal of metals from aqueous system are (i) Removal of toxicity and (ii) Recovery of valuable metals. Cadmium is one such metal. Traces of cadmium has been identified as deleterious to aquatic ecosystem and human health. Waste containing high concentration of toxic metals either separately or in combination is extremely toxic to all living organisms. The sources of cadmium pollution are industrial discharge mining waste, metal plating and water pipes. Cadmium occurs in nature in association with sulphide ores. It replaces Zn biochemically, causes high blood pressure and kidney damage, destroys testicular tissue and RBC. Cadmium is toxic to aquatic biota. Its permissible limit is 0.01 mg/L (US Standard). In the present work, two coal samples and their eight chemical treated

samples were used as adsorbents for the removal of cadmium from aqueous solution considered as waste water.

## **EXPERIMENTAL**

### **Collection and preparation of sample**

#### **Collection of sample**

Coal samples were collected from North and South Tisra collieries of Lodna area, BCCL, Dhanbad. The samples were collected from three different layers viz. top layer, middle layer and bottom layer.

Coal samples from top and middle layers were collected from North Tisra Colliery and samples from bottom layer only were collected from South Tisra colliery.

#### **Preparation of sample**

The coal samples collected from the two collieries were first crushed by jaw crusher to 12.5 mm and then by roll crusher to -3 mm size. From the crushed coal, samples for proximate analysis and other tests were collected by coning and quartering. Thereafter, the samples were further ground to -72 mesh in a pulveriser before carrying out the analyses.

#### **Chemical treatment of coal**

Crushed coal samples of -72 mesh size were subjected to different types of chemical treatments to alter their chemical and physical characteristics. These are :

- (i) Alkali treatment
- (ii) Acid treatment
- (iii) Alkali treatment followed by acid treatment (Alkali-acid treatment)
- (iv) Acid treatment followed by alkali treatment (Acid-alkali treatment)

#### **Alkali treatment**

200 g coal with 300 mL of 25% w/v aqueous sodium hydroxide was refluxed for 6 hours at atmospheric pressure at a temperature of 150-160°C. The mixture was then cooled, filtered using a Whatman No. 40 filter paper and washed subsequently several times with

distilled water till it is free from alkali and the residue was dried in a moisture oven at a temperature of 110°C till constant weight.

### **Acid treatment**

200 g coal with 300 mL of 50% v/v HCl was refluxed for 6 hours at atmospheric pressure at a temperature of 150-160°C. The mixture was then cooled, filtered using a Whatman No. 40 filter paper and washed subsequently several times with distilled water till it is free from acid. The residue was dried in a moisture oven at a temperature 110°C till it gets a constant weight.

### **Alkali-acid treatment**

50 g of alkali treated coal was refluxed with 100 mL 50% v/v HCl for 6 hours at atmospheric pressure. The mixture was then cooled, filtered using a Whatman No. 40 filter paper, and washed repeatedly with distilled water till it is acid free. The coal sample was then dried in a moisture oven at a temperature of 110°C till it gains a constant weight.

### **Acid-alkali treatment**

50 g of acid treated coal was refluxed with 100 mL of 25% w/v aqueous sodium hydroxide for 6 hours at atmospheric pressure and the mixture was then cooled, filtered using Whatman No. 40 filter paper and washed subsequently for many times with distilled water till it is free from alkali and then dried in a moisture oven till it gets a constant weight at a temperature of 110°C.

### **Coal characterization**

Both the coal samples were characterized by doing the proximate analysis following Bureau of Indian Standard Methods<sup>6</sup>.

### **FT-IR studies**

FT-IR studies of two raw coal samples and eight chemically treated coal samples were carried out using a Perkin-Elmer FT-IR Spectrometer, Spectrum-2000 by KBr pellet method. Spectroscopic grade KBr (E.Merck), used for the preparation of pellets, was dried for minimum 3 hours at a temperature of 110°C to remove moisture. The coal samples were also dried for the same duration. Coal was mixed with KBr in the ratio 1 : 100 (w/w) for obtaining optimum results<sup>7</sup>. Approximately 3.5 mg of coal was accurately weighed and then ground with potassium bromide in the above ratio in an agate mortar with an agate pestle for two minutes and a pellet is made by pressing it in the mould at a pressure of 5 tons. Also a

blank pellet was prepared with pure potassium bromide for measuring the background. IR spectra were recorded in the range  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  (average of 4 scans)

### **Scanning electron microscopy studies**

Scanning Electron Micrographs (SEM) of above ten chemical treated and untreated coal samples were taken at the Electron Microscopy Laboratory of Indian Association for the Cultivation of Science, Jadavpur, Kolkata using HITACHI, S-415A, Scanning Electron Microscope.

### **Adsorption studies**

Batch adsorption experiments were carried out in a temperature controlled shaking machine by agitating 50 mL of aqueous solutions of the sorbate at different concentrations with 1.0 g of the sorbent in 250 mL of conical flasks. The speed of the agitation was maintained at 55-60 of the Variac reading to ensure comparable agitation. The process was continued for three hours at a temperature of  $30^{\circ}\text{C}$ . At the end of the predetermined time, the sorbate and the sorbent were separated by vacuum filtration and the filtrate was then analyzed by Atomic Absorption Spectrophotometer, Perkin-Elmer, 2380, for its metal ion content.

### **Preparation of standard stock solution**

250 mL of stock solution of 1000 mg/L strength of cadmium was prepared as follows :

Cd (II) : 0.5079 g of AR grade cadmium chloride ( $\text{CdCl}_2, 2.5\text{ H}_2\text{O}$ ) (SD Fine) was dissolved in 250 mL of distilled water.

## **RESULTS AND DISCUSSION**

### **Effect of chemical treatment of coal on its characteristics**

The two coal samples, North Tisra and South Tisra, have been treated with alkali, acid, alkali followed by acid and acid followed by alkali to modify its characteristics. The effect of these chemical treatments have been studied by the following tools : (a) Proximate Analysis (b) FT-IR Spectroscopy, and (c) Scanning Electron Microscopy.

### **Effect of chemical treatment on proximate analysis of coal samples**

Proximate analysis of all the raw and chemically treated coal samples have been carried out and result are presented in Table 1. The effect of chemical treatment on different

parameters such as moisture, ash, volatile matter and fixed carbon are discussed below.

**Table 1: Proximate analysis of raw and chemically treated coal samples**

Coal sample	Moisture (%)	Ash (%)	V.M (%)	F.C (%)
Raw north tistra (Coal-1)	0.7	34.4	20.0	44.9
Alkali treated Coal-1	0.2	32.7	19.6	47.3
Acid treated Coal-1	0.4	30.3	17.4	52.1
Alkali-acid treated Coal-1	0.4	28.2	17.6	54.0
Acid-alkali treated Coal-1	0.2	29.7	17.7	52.2
Raw South Tistra (Coal-2)	0.9	33.2	20.3	45.6
Alkali treated Coal-2	0.6	32.7	18.9	47.8
Acid treated Coal-2	0.3	29.8	17.7	52.2
Alkali-acid treated Coal-2	0.4	26.9	18.1	54.6
Acid-alkali treated Coal-2	0.5	29.3	17.5	52.7

### Effect of chemical treatment on moisture

It is clear from Table 1 that the moisture content of treated coals is less than that of the corresponding raw coals. In case of North Tistra Coal (Coal-1). The moisture content was 0.7%, which has been reduced to 0.2% in case of alkali treated, and acid-alkali treated coals, where as it has been reduced to 0.4 % in case of acid treated and alkali-acid treated coals. In case of South Tistra coal (Coal-2) the moisture percentage has been reduced from 0.9 to 0.6, 0.3, 0.4 and 0.5 in case of alkali treated acid treated, alkali-acid treated and acid-alkali treated coals, respectively. Thus, the moisture content of treated coals in all the cases is less than that of the corresponding raw coals. The very low moisture content in raw coal indicates that it is coking coal and its porosity is least. When acid or alkali is added to coal, only the acid soluble or alkali soluble portion of the mineral matter will be removed. It is known that when alkali is added to any coal followed by distilled water washing, trace amount of alkali remains with washed coal unless it is acid treated further. The above data can be explained on this basis. The trace amount of alkali attracts some moisture depending upon its capacity. That is the reason why (i) Moisture contents of raw coals are more than treated coals, and (ii) The moisture contents of alkali, and acid alkali treated coals are more than acid, and alkali-acid treated coals.

### **Effect of chemical treatment on ash content**

From Table 1, it is obvious that the ash content of chemically treated coals are less than that of raw coals, which had 34.4% and 33.2% ash in case of North Tisra (Coal-1) and South Tisra (Coal-2) respectively. The maximum reduction in ash percentage has been observed for alkali-acid treated coals in both cases, (28.2 and 26.9 for Coal-1 and Coal-2, respectively). Alkali treatment alone did not reduce the ash percentage significantly (32.7 in both Coal-1 and Coal-2), but acid treatment reduced it to 30.3 and 29.8, respectively for the two samples. In case of acid-alkali treatment, ash reduction marginally improved to 29.7 and 29.3 in case of Coal-1 and Coal-2, respectively.

Acid treatment is a common chemical method for ash reduction. In the present study, the coals were subjected to moderately drastic treatment conditions and this resulted in reducing the ash content by about 2%. Demineralization of coal by acid is not expected to change coal structure significantly. A large part of the mineral matter present in coal may not be soluble in acid in the form in which they exist. This may be a possible reason for the relatively low reduction in ash content by acid treatment.

Alkali treatment of coal is not expected to reduce ash content to a very large extent, as the solubility of mineral matter in alkali solution of moderate concentration is not very high. However, this treatment is expected to make some significant changes on the chemical nature of the mineral matter as well as on the surface functional groups on coal.

Acid treatment of alkali treated coal produced the best results as far as ash reduction is concerned. Similar observation has been made earlier by Sharma and Gihar<sup>8</sup>. This increase in ash reduction can be explained as due to the conversion of acid insoluble mineral entities to acid soluble form by alkali treatment. It has been reported that Kaolinite type minerals are converted into a crystalline sodium derivative,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1.8 \text{SiO}_2 \cdot 1.5 \text{H}_2\text{O}$  by moderately concentrated NaOH solutions at 378 K<sup>9,10</sup>. This sodium derivative is not very soluble in alkali and water but is moderately soluble in mineral acid solutions. This is the reason, why the ash reduction achieved is highest by this method. Acid-alkali treatment slightly improved the ash reduction from that of acid treatment alone. This may be due to the removal of acid insoluble mineral matter by alkali solution; however, this increase is only marginal.

### **Effect of chemical treatment on volatile matter**

In all the cases, there is a reduction in the volatile matter percentage by chemical treatment (Table 1). The reduction is more in the case of acid treated coal samples rather

than alkali treated ones. This change may be due to carbonates and other mineral matter occurring in coal which on acid treatment/alkali treatment decomposed/solubilized followed by its removal from coal, resulting in lower volatile matter content. However, no oxidative change is expected from hydrochloric acid treatment, as HCl is not an oxidizing acid. NaOH treatment may cause oxidative changes on the coal surface.

### **Effect of chemical treatment on fixed carbon**

From Table 1, it is obvious that the percentage of fixed carbon has increased by chemical treatment. As expected, when the moisture, ash and volatile matter contents reduced, proportionately the fixed carbon contents will go up.

### **FT-IR spectra of raw coal samples<sup>11</sup>**

Comparison of the two FT – IR spectra (North Tisra and South Tisra raw coals) indicate that the two are similar in nature. The broad band appearing around  $3300\text{ cm}^{-1}$  is due to hydroxyl (OH) groups. The bands at around  $3030$  to  $3050\text{ cm}^{-1}$  is caused by aromatic CH stretch. The intensity of band at  $2950\text{ cm}^{-1}$  is very weak and indicates that  $\text{CH}_3$  content of this coal is small. There are absorption bands present at  $1599\text{ cm}^{-1}$  indicating carbonyl groups. There are strong absorption bands at  $1032\text{ cm}^{-1}$  and  $1009$ - $1010\text{ cm}^{-1}$ , which indicate the presence of Kaolinite. This is not surprising, since these coals are of high ash content. There are bands at  $913$ ,  $540$  and  $470$ - $474\text{ cm}^{-1}$ , which are also ascribed to kaolinite. There are also absorption bands in between  $3750$ - $3400\text{ cm}^{-1}$  indicating OH vibrations. There is a band present at  $3620\text{ cm}^{-1}$  indicating inner hydroxyl groups<sup>12</sup>. The absorption band at  $1700\text{ cm}^{-1}$  indicate carboxyl group.

These FT-IR spectra indicate that the coal samples do not contain much of hydroxyl groups attached to carbon skeleton and are having a moderately cross-linked structure. There is also indication of the presence of carbonyl groups in the coal. The low intensities of band at  $850$ ,  $810$  and  $750\text{ cm}^{-1}$  indicate low aromaticity of the coal<sup>13</sup>.

### **FT-IR spectra of alkali treated coal samples<sup>11</sup>**

There are some difference in the spectra of alkali treated coals with respect to the spectra of respective raw coals. Other than the change in intensities of bands at  $2912$ ,  $1600$ ,  $1032$  and  $540\text{ cm}^{-1}$ , the intensity of the band at  $1653\text{ cm}^{-1}$  increased due to alkali treatment, which indicate some increase in the carboxyl/carbonyl groups in the coals. There is no significant reduction in the intensities of the mineral peaks. This is in agreement with the proximate analysis results, which also indicate that alkali treatment do not significantly reduce mineral content of coal.

**FT-IR spectra of acid treated coal samples<sup>11</sup>**

The acid treatment of coal has not significantly altered the characteristic peaks of the coal samples. There is, however, some reduction in the intensities of mineral peaks. This is consistent with the observation that mineral acid treatments simply remove soluble mineral matter from coal and do not significantly alter the coal structure.

**FT-IR spectra of acid-alkali treated coal samples<sup>11</sup>**

There are some significant differences between the spectra of raw coal and acid-alkali treated coal. There is a new broad peak at around  $3395\text{ cm}^{-1}$  and the intensities of peak at  $1600\text{ cm}^{-1}$  has significantly increased compared to that of raw coals. The mineral peaks at  $1032$  and  $1010\text{ cm}^{-1}$  have completely disappeared but a new strong peak at  $984\text{-}999\text{ cm}^{-1}$  has appeared. Similarly, the sharp peak at  $913\text{ cm}^{-1}$  has complete disappeared. This clearly indicates a change in the chemical structure of mineral matter present in the coal samples due to the acid-alkali treatment. The effect on the characteristic spectrum of the organic part of the coal sample is similar to that of the alkali treatment of the sample alone; i.e. the bands due to carbonyl/carboxyl groups have become more prominent. There is also evidence of phenolic OH as well in these spectra.

**FT-IR spectra of alkali-acid treated coal samples<sup>11</sup>**

Alkali-acid treatment has caused significant changes in the FT-IR spectra of both; North and South Tisra coals. There are significant reductions in the intensities of peaks at  $1033$  and  $1010\text{ cm}^{-1}$ . The peak at  $912\text{ cm}^{-1}$  also has a reduced intensity. Indications of oxygen groups in the two treated coals are present and are same as expected due to alkali treatment. The significant effect of alkali-acid treatment is the reduction in the intensity of mineral peaks.

**Scanning electron microscopic studies of raw and chemically treated coal samples<sup>11</sup>**

To study the morphological changes in the two coals, Scanning Electron Microscopy studies were carried out.

**SEM of raw coal samples<sup>11</sup>**

The scanning electron micrographs of raw North Tisra and South Tisra coals were recorded at two different magnifications. Scanning electron microscope has been used for the analysis of coal and coal products for the determination of sulphur content, iron content

and mineral matter in coal<sup>14</sup>. With the help of SEM, the morphology and interrelationships of mineral in coal was studied.

The micrographs show that the coal powder is irregularly shaped with almost comparable grain sizes.

### **Effect of chemical treatment of coal on their scanning electron micrographs<sup>11</sup>**

The scanning electron micrographs of alkali treated North and South Tisra coals were recorded. It was observed that there is no drastic change in the morphology of the samples except for some indentations and breakages, which are apparent. There appears to be some reduction in the grain sizes as well.

The scanning electron micrographs of acid treated North and South Tisra coals were also recorded. These micrographs show that the grains have started crumbling and a more irregular shape is evident. This is obviously due to the leaching out of inorganic material from coal.

The scanning electron micrographs of alkali-acid treated North and South Tisra coals were recorded. There is a clear evidence of leaching out of mineral matter in these micrographs. Due to the indentations caused by leaching, the morphology of these treated coals have also changed as compared to that of raw coals. This clearly indicates more effective demineralization and a consequent increase in porosity for the alkali-acid treated coals.

The scanning electron micrographs of acid-alkali treated North and South Tisra coals were also recorded. This also indicate leaching and crumbling but not to the same extent as that of alkali-acid treated coals.

It can be concluded from the SEM study that the alkali-acid treatment has caused maximum changes in the morphology of coal samples. Acid and acid-alkali treatment also caused some changes and the alkali treatment alone caused only small visible changes in the morphology of coal. It is also evident from the study that the surface area and porosity increased due to different chemical treatments carried out.

### **Adsorption of Cd (II) by coal samples**

The results of studies of adsorption of Cd (II) on raw coals are presented in Table 2 and that for chemically treated coals are presented in Table 3.

**Table 2: Percentage adsorption of cadmium on raw coals at different initial concentration of solutions**

Initial conc. of solutions mg/L	Percentage of Cd adsorbed (%)	
	North Tisra	South Tisra
20	14.00	15.50
40	8.88	32.75
60	9.88	37.33
100	6.53	32.90

**Table 3: Percentage adsorption of cadmium on different chemically treated and untreated coal samples from solutions of different concentrations**

Coal samples	Percentage adsorption of solution (%)			
	20 mg/L	40 mg/L	60 mg/L	100 mg/L
Raw North Tisra (Coal-1)	14.00	8.88	9.88	6.53
Alkali treated Coal-1	32.00	31.75	38.00	28.74
Acid treated Coal-1	15.70	17.55	9.62	3.97
Alkali-acid treated Coal-1	10.50	9.08	8.68	5.30
Acid-alkali treated Coal-1	90.90	91.33	78.42	28.20
Raw South Tisra (Coal-2)	15.50	32.75	37.33	32.90
Alkali treated Coal-2	95.50	96.88	90.83	69.75
Acid treated Coal-2	20.25	12.20	22.17	12.40
Alkali-acid treated Coal-2	13.00	11.50	10.67	6.80
Acid-alkali treated Coal-2	97.90	97.40	96.05	79.15

### Adsorption of Cd (II) on raw coal samples

There are several studies<sup>15-22</sup>, which report the efficacy of coal as an adsorbent for heavy metal ions. Our study also show that coal is a moderately efficient adsorbent for the removal of Cd (II) from aqueous solutions.

Table 2 shows that North Tisra coal has adsorbed 0.14 mg/g to 0.33 mg/g of Cd (II) from solutions containing 20 mg/L to 100 mg/L of Cd (II), whereas South Tisra coal has adsorbed 0.15 mg/g to 1.64 mg/g of Cd (II) from solutions of same concentrations. There is increase in the amount of Cd (II) adsorbed with increasing concentration of solution. South Tisra coal adsorbs substantially more Cd from solutions compared to North Tisra coal. This difference cannot be explained with the help of the proximate analysis (Table 1) or the FT-IR spectra of the two samples. The FT-IR spectra are similar with similar features. However, there is difference in the intensities of different peaks observed as well as minor shifts in the peaks. This does not indicate with any certainty, any significant difference in the structures of the two coal samples. The ash, volatile matter and fixed carbon content are also comparable. However, in this study porosity of the samples were not determined. Coal porosity plays a very important role on the physical and chemical behavior of coal, since it is mainly through the internal pore structure that coal comes into contact with the reactive environment<sup>23</sup>. For the complete characterization of coal, data on pore structure, pore volume, surface area, and pore size distribution are needed. This could not be carried out during the present study. Therefore, the difference in the adsorption capacities of the two coal samples for Cd (II) cannot be explained satisfactorily without conducting further investigations as mentioned above.

### **Adsorption of Cd (II) on alkali treated coal samples**

Alkali treatment of both North; Tisra and South Tisra coals resulted in considerable enhancement in the amount of Cd (II) adsorbed by them from solution (Table 3).

In the case of Cd (II) adsorption (Table 3), there is substantial increase in the amount adsorbed after alkali treatment. From solution of 20 mg/L concentration, the amount adsorbed increased from 0.14 mg/g to 0.32 mg/g, and from 100 mg/L solution, it has increased from 0.33 mg/g to 1.44 mg/g for North Tisra coal. The corresponding values for South Tisra coal is 0.15 mg/g to 0.95 mg/g, and 1.64 mg/g to 3.47 mg/g, respectively. The amount adsorbed for the other two concentrations viz. 40 mg/L and 60 mg/L are also higher with respect to the values for raw coals.

It is obvious from these observations that the changes caused by alkali treatment on coal structure have tremendously improved its capacity to adsorb metal ions. This may be due to the changes in the organic as well as mineral part of the coal structure. The increase in the oxygen groups in the coal structure might have improved the ion exchange capacity of coal increasing its ability to adsorb metal ions. The changes in the mineral part also may be playing an important part in this regard. There might be some increase in the porosity and

also change in pore size distribution due to the alkali treatment. Some micropores, which were not accessible earlier, might have been made accessible by the alkali treatment.

### **Adsorption of Cd (II) on acid treated coal samples**

Table 3 presents the results of adsorption study of Cd (II) on acid treated coals. For both; North Tisra and South Tisra coals, acid treatment resulted in no significant increase in the amount of Cd (II) adsorbed.

For both; North Tisra and South Tisra coals, acid treatment resulted in no significant increase in the amount of Cd adsorbed, rather it reduced the adsorption at higher solution concentrations. This is contrary to the expectation that reduction in ash and the resulting increase in porosity improve the adsorption capacity of coal. The reduction in adsorption capacity due to acid treatment may be explained as due to the change in the ion exchange capacity of coal due to the treatment.

### **Adsorption of Cd (II) on alkali-acid treated coal samples**

From the proximate analysis (Table 1), it can be seen that alkali-acid treatment reduced the ash content to the greatest extent and from SEM studies, it can also be seen that the porosity has also increased to the maximum extent. It is, therefore, expected to show very good adsorption characteristics. However, these samples also behaved in a similar manner to that of acid treated coals.

Cd (II) adsorption (Table 3) on alkali-acid treated North Tisra coal have reduced from 0.14 mg/g to 0.11 mg/g from 20 mg/L solutions, and 0.33 mg/g to 0.27 mg/g from 100 mg/L solutions. Observations are similar for 40 mg/L and 60 mg/L solutions. In case of South Tisra coals also, a similar trend is observed. It is obvious from this that ash reduction is not the single most important factor, which improves the adsorption characteristics of coal. The surface characteristics such as ion exchange capacity and surface charge plays a more important role in determining the amount of metal ion adsorbed by the coal sample.

However, the reduction in adsorption of Cd (II) ions by alkali-acid treatment is less than that of alkali treatment alone. Here, the difference may be due to the reduction in the ash content and increase in porosity of alkali-acid treated coal over alkali treated coals.

### **Adsorption of Cd (II) on acid-alkali treated coal samples**

Even though acid-alkali treatment has reduced the ash content only slightly more than that of acid treated coals, the amount of metal ions adsorbed has increased drastically.

Table 3 presents the results of adsorption study of Cd (II). For both; North and South Tisra coals, the amount of Cd (II) adsorbed from solutions of different concentrations have increased considerably, especially at lower concentrations of 20 mg/L and 40 mg/L. For North Tisra coal, it increased from 0.14 mg/g to 0.91 mg/g from 20 mg/L solution, and 0.18 mg/g to 1.83 mg/g from 40 mg/L solution. Corresponding values for South Tisra coal are 0.15 mg/g to 0.98 mg/g and 0.66 mg/g to 1.95 mg/g, for these solutions, respectively. At higher concentrations, the increase is not that substantial. This increase is due to the changes in the morphology as well as the chemical characteristics of the coal surface caused by the acid-alkali treatment. This also proves that alkali treatment can significantly improve the adsorption capacity of coal towards different metal ions.

### **Comparison of the effect of different chemical treatments on the adsorption capacity of coal**

In the present study (Table 3), it can be seen that alkali treatment improves the adsorption capacity of coal for Cd (II). Since mineral matter do not have great tendency for adsorbing metal ions, reduction in ash content is expected to increase the adsorption capacity. However, acid treatment and alkali- acid treatment, which reduced maximum ash content did not improve the adsorption capacity of coal, rather it showed a tendency to reduce the amount of metal ions adsorbed, where as alkali treatment and acid-alkali treatment, which did not reduce mineral matter as much as acid and alkali-acid treatment, improved the adsorption capacity of coal. This indicates that it is not only the reduction in ash but also changes in the chemical characteristics of coal surface by different chemical treatments, which play very important role in deciding the adsorption behavior of coal towards the metal ions.

## **CONCLUSION**

The major conclusions from this study are the following :

- North and South Tisra coals are not as efficient for the adsorption of Cd (II).
- Different chemical treatments of coal resulted in structural and morphological changes in coal as shown by proximate analysis, FT-IR spectra and scanning electron microscopy.
- Alkali-acid treatment resulted in maximum reduction in ash content.
- Alkali treatment and acid-alkali treatment resulted in significant improvement in the adsorption capacity of coal, with acid-alkali treated coal giving best results, with 90% removal of Cd (II).

- Alkali-acid treatment, which reduces maximum mineral matter, has not produced the best adsorbent indicating that the adsorption capacity is determined by the changes in the chemical characteristics of the coal surface rather than reduction in mineral matter. Alkali treatment causes more structural changes than acid treatment and results in better ion exchange capacity.

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