

Removal of Chromium (III) and Arsenic (III) by using Coal Ash as Adsorbent

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ABSTRACT: The adsorption of Cr(III) and As(III) by using coal ash from thermal power plants in batch mode, The effect of adsorbent agitation speed, dose, pH, contact time and agitation speed on the adsorption of Cr(III) and As(III) by coal ash is examined. Adsorption equilibrium was achieved in 50–55 min. The Langmuir, Temkin and Freundlich adsorption isotherms were used to observed sorption phenomena. The maximum Cr (III) removal was 2.62 mg of Cr per gram of coal ash and As (III) removal was 2.45 mg of As per gram of coal ash as evaluated from Langmuir isotherm. The heat of sorption was in the range 3.75–3.87 kJ/mol as calculated from Temkin isotherm. Best results were obtained at pH > 5. It is proposed that low rank coals ash can be used for removal of toxic metals like Chromium and Arsenic from industrial waste water effluents.

KEYWORDS: chromium(III), arsenic(III), coal ash, adsorbent, natural abundance, coal dosage.

I. INTRODUCTION

Chromium and arsenic are natural components of the earth crust. They enter our bodies via drinking, air, food and water. In traces, some heavy metals are essential to maintain the metabolism of the human body. However, at higher concentrations, they are poisonous. Heavy metals are dangerous as they bio accumulate. Generally Chromium and arsenic are approximately rank is 20th in natural abundance available material, consisting 0.00005% of the earth crust, its concentration in most rocks are found in finer grained argillaceous sediments and phosphorite. Chromium and arsenic are gathered by natural weathering reactions, biological activity, waste discharge, agricultural use of arsenical pesticides metal mining geochemical reactions and anthropogenic activities. Chromium and arsenic is a hard acids and Forms complexes with nitrogen and oxides. Cr(III) and As(III) behaves like a soft acid, forming complexes with sulphides, Inorganic forms of Chromium and arsenic most often exist in water supplies.

Chromium and arsenic occurrence in the environment, it causes toxicity, health hazards, and the techniques used for speciation analysis. Long term drinking water supplies causes skin, lung, kidney, bladder Chromium and arsenic in natural waters is a worldwide problem.

The WHO standard guideline of 10 ppb (0.01 mg/L) has been adopted as the drinking water standards. Comparison of main Chromium and arsenic removal technologies are Oxidation/precipitation, Coagulation/electrocoagulation/co precipitation, ion-exchange techniques, Membrane techniques, Nano filtration, Reverse osmosis, Electro dialysis and other techniques are Foam flotation, Solvent extraction, Bioremediation. Metal chromium is used for making steel while chromium are used for chrome plating, dyes and pigments, leather tanning, and wood preserving, Removal of heavy metal pollution is an important problem especially in industrial effluents.

II. COAL ASH

Coal ash is obtained from thermal fired power plants; it is a huge amount of by product coal. Coal ash disposal requires large quantities of land and water. Present coal ash applications are limited to civil engineering works uses including cement and brick preparation and manufacture of road bed, other uses include road base construction, soil amendment, zeolite synthesis, and use as a filler in polymers. Coal ash used as a good adsorbent, Resource recovery from coal ash is one of the most important issues in waste water management worldwide. Coal ash contains the major

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Chemical compounds are aluminium and silicates. Chromium and arsenic removal from water, Kinetic and equilibrium experiments were performed to evaluate the Arsenic and chromium removal efficiency by coal ash.

Sample	Moisture	Volatile matter	Ash	Fixed C	% sulphur	Heating value(Btu/lb)	IR spectra(cm^{-1})
Coal	5.0%	25.0%	20.0%	50.0%	1.2%	10,988	3820,2928,2357,1688, 1575,1558,1463

Natural and anthropogenic arsenic and chromium contamination of water sources causes serious health problem, especially for small communities in rural areas. The physical, chemical properties of the adsorbents were characterized by XRD, XRF, FTIR, SEM and NMR analysis. Batch experiments conducted that coal ash could provide effective removal Arsenic and chromium, The effect of adsorbent dose, pH, contact time and agitation speed on the adsorption of Cr (III) and As (III) by both the coals fly ash were investigated. Adsorption equilibrium was carried in 50–55 min. The Langmuir, Freundlich and Temkin adsorption isotherms were used for removal of chromium Cr (III) and As (III) from waste water effluents.

Chromium and Arsenic removal by three widely available low-cost adsorbents coal ash (inorganic waste materials), green waste compost (organic waste by products), and lignite (natural organic resources) .The selected adsorbents were also characterized by spectroscopic analyses. Coal contains many toxic metals, Chromium and arsenic is two of those, which is significantly toxic for aquatic and terrestrial life including human being.

III. EXPERIMENTAL

Coal ash is collected from thermal power plants .The coal is crushed with laboratory le crushers and powdered with disc pulverizer, and sieved to 0 meshes (ASTM). The powdered coal was dried in an oven at 106 ° C for 12 h, and stored in plastic containers. The proximate methods of analysis of the coal were carried out by using standard methods (ASTM D5142-90).

Standard solutions:

Stock solution of Cr (III) and As (III) (1000 ppm) was prepared with appropriate weighed quantity of chromium chloride and arsenic chloride. Standard solutions of the desired concentrations (10–100 ppm) were obtained by successive dilutions of solution.

Equipment and apparatus:

Calorific value of the coal ash is determined with oxygen bomb calorimeter using standard method. IR spectra were recorded with perkinElmer BX Model FTIR Spectrometer. Sample was prepared grinding 3 mg of coal ash with 2–3 drops of accelerators. Digital pH-meter was used pH adjustment. Standard solutions are taken of HCl (0.1M) and NaOH (0.1M) were used for pH adjustment along with standard buffers solutions to the pH constant. A PerkinElmer Atomic Absorption Spectrometer was used for the determination of chromium concentrations in the solutions. The instrument was calibrated by standard method and absorbance of the solutions was measured. The absorbencies of all solutions were recorded at a wavelength of 7.8nm emitted by hollow cathode lamps suitable to determine the Cr (III) and As (III) of heavy metals.

Effect of process parameters:

A series of experiments was conducted to study the effects of parameters are coal dose, pH, contact time and agitation speed, adsorption for the sample solution (50 ppm, 50 mL). To study the effect of certain parameter, that parameter has been varied gradually keeping the other three constant. Measuring (100 mL) flasks were washed and dried in an oven at 106 ° C for 30 min. After sorption under certain conditions, contents of the flasks were placed and filtrate was subjected to atomic absorption for determination of chromium (358.1nm) and arsenic (390.2nm).

The effects of the coal dose are Cr(III) and As(III) adsorptions were studied by varying the coal dose from 0.25 to 2.50g (0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 2.25 and 2.50 g). Ten measuring flasks were taken and sample solution was added to each. Sieved coal ash was added each flask and pH was adjusted to 9. Flasks were agitated with

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orbital shaker (top loaded) at 240 rpm for 50 min and subjected to atomic absorption spectrophotometer instrument after filtration.

The effects of the pH were carried by varying the pH from 1 to 10 (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10). Ten measuring flasks were added sample solution. Coal ash (3 g) was added to each and pH values were adjusted by adding HCl (0.1 M) or NaOH (0.1 M) using potential hydrogen meter. The flasks were agitated on orbital shaker at 250 rpm for 50 min, solutions were filtered and analysed to determine concentration of Cr (III) and As (III) oh heavy metals.

The effects of the contact time on Cr(III) and As(III) adsorption were studied by varying the time of contact from 5 to 60 minutes (5,10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 min). Sample solution was taken in twelve measuring flasks. 2 g coal was added to each. pH of each sample was adjusted to 9 and agitated at 240 rpm for different process of time intervals. After filtration, absorption for Cr (III) and As (III) was taken on atomic adsorption.

The effects of agitation speed were studied in the range 25–300 rpm (25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275 and 300 rpm). Twelve measuring flasks were taken and sample solution was added to each. Dry sieved coal (3 g) was added to all samples. Flasks were agitated at different speeds for 50 min at pH 9. The contents of flasks were filtered to separate coal ash and filtrates were subjected to atomic adsorption process.

IV. RESULTS AND DISCUSSION

Coal analysis:

Coal ash is obtained from thermal power plants in Visakhapatnam of Andhra Pradesh .The analysis of coal ash has revealed that coal ash have high percentages of volatile matter, moisture, and sulphur. Results are shown table 1. High sulphur content and low calorific value makes the coal ash.

Bands are corresponding to aromatic carboxylic groups and hydroxyl groups, the active centre of the coal ash for metal take are shown in table 1. The IR spectrometer confirms the presence of these groups in the coal sample used for analysis of study. Hence, this process may be considering suitable for adsorption.

Effect of amount of coal dose:

The effect of the coal dose on Cr (III) and As (III) adsorption was studied by varying the adsorbent dose from 5 to 60 g/L using 50 ppm Cr (III) and As (III) solution at pH 9.0 for time interval of 40 min. From figure 1, it is observed that adsorption increases with increase in coal concentration. Maximum removal of chromium was 85% for dose of 50 g/L of coal ash and arsenic was 89% for dose of 50 g/L of coal ash for 50 ppm, initial concentration of Cr (III) and As (III) solution. The increase in adsorption with the increase in amount of coal dose is due to the fact that more surface area of coal ash is available for adsorption or in other words more active sites are available. It is also observed that adsorption process with more coal dose requires less contact of time to attain standard equilibrium process.

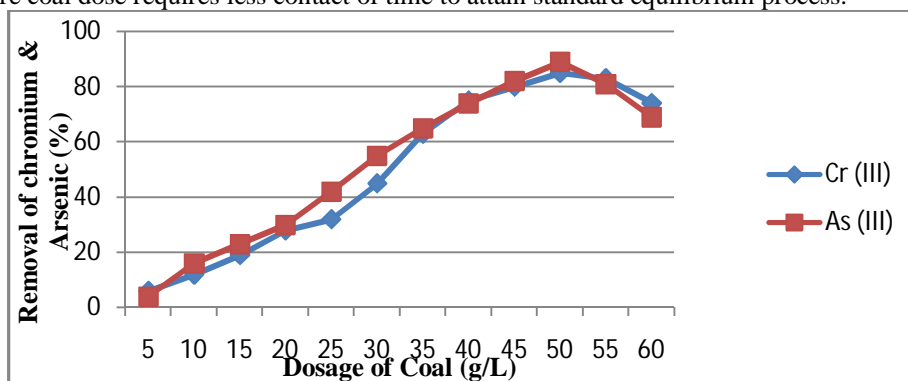


Fig.1. The effect of amount of coal on adsorption of Cr (III) and As (III) ions

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Effect of pH:

The effect of the pH on Cr (III) and As (III) adsorption was studied by varying the pH from 1 to 10. The results are shown in figure 2.

Graph has significantly shown that affects adsorption and maximum adsorption occur at PH - 9 Carboxyl and hydroxyl groups are the active centres of the natural polymer for ion-exchange method. Carboxyl or hydroxyl groups are able to take part in the ion exchange process according to Equations of 1 and 2. Where R is only aromatic, sorption occurs only with phenolic groups, not occur with aliphatic hydroxyl alcohol groups.

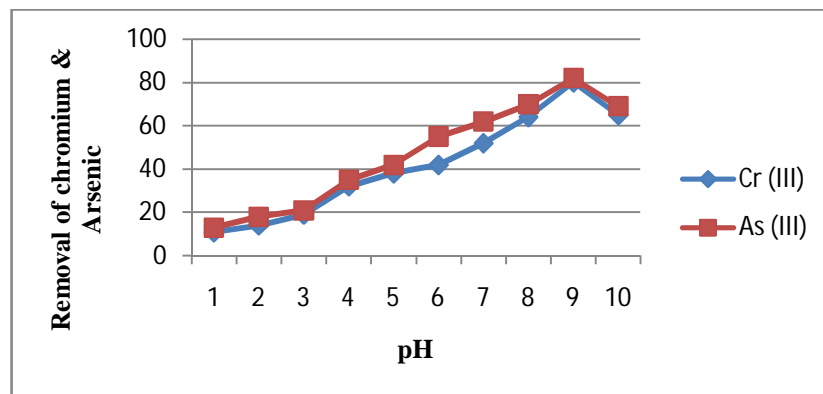
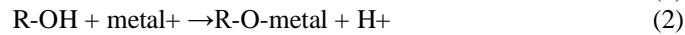
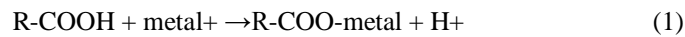


Fig.2.The effect of pH on absorption of Cr (III) and As (III) ions

As the pH values rises removal of Cr (III) and As (III) efficiency increases for coal ash and the best results are obtained at pH 9. At very low pH, functional oxidized groups (carboxylic and phenolic on which adsorption takes place) of the coal ash are used and thus, active sites of coal ash for binding of metal ions available in small quantity, thus, removal of Cr(III) and As(III) efficiency decreases. At pH > 9, insoluble Cr (III) and As (III) hydroxide starts precipitating from the prepared solution. So, finally it is concluded that pH of the solution should be on higher side in order to get good results but should not exceed the value of pH-9.

Effect of contact time:

The effect of the contact time on Cr (III) and As (III) adsorption was studied by varying the contact time from 5 to 60 min. The flasks were agitated placed on orbital shaker at 240 rpm with the adsorbent dose of 40 g/L. The results are shown in figure 3. Increase in removal of Cr(III) and As(III) efficiency with increase in contact time is due to the fact that more time becomes available for metal ions to make a complex compounds with coal ash. Initially removal occurs immediately as soon as the metal and coal ash powder came into contact, but after those easily available active sites are become unavailable, metal needs time to find out more active sites for binding to form stable complex. It is concluded that metal and coal ash should be in contact for at least contact time is 50 min in order to get better results. Adding more coal ash powder will require less time of contact attain standard equilibrium process.

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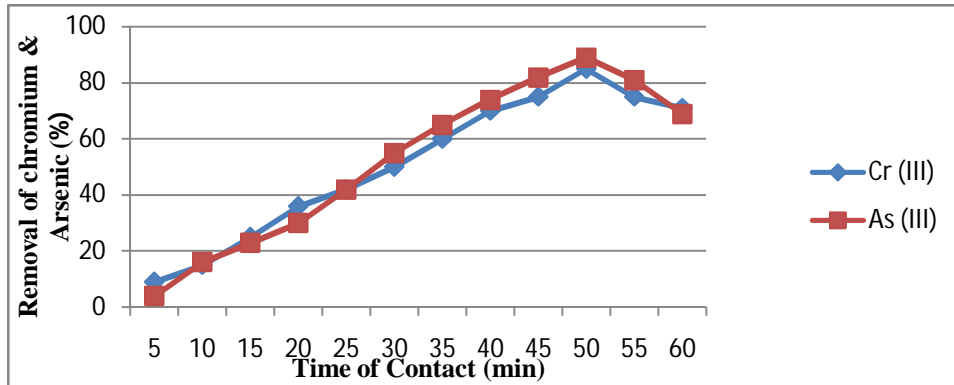


Fig.3.The effect of contact time on adsorption of Cr (III) and As (III) ions

Effect of agitation speed:

Effect of agitation speed on adsorption of Cr (III) and As (III) of heavy metal was discussed shown figure 4, it can be easily seen that shaking speed significantly affects the adsorption. With increasing shaking speed, adsorption increases for both removals of Cr (III) and As (III) by coal ash. If shaking speed is slow, coal instead of reading in the sample, accumulates and various active sites are buried under the top layers of coal. So, removal occurs only by top layers and the under buried layers do not take part in the process they have no contact with metal. This indicates that shaking rate should be sufficient to assure that all the surface binding sites are readily available for Cr (III) and As (III) metals uptake.

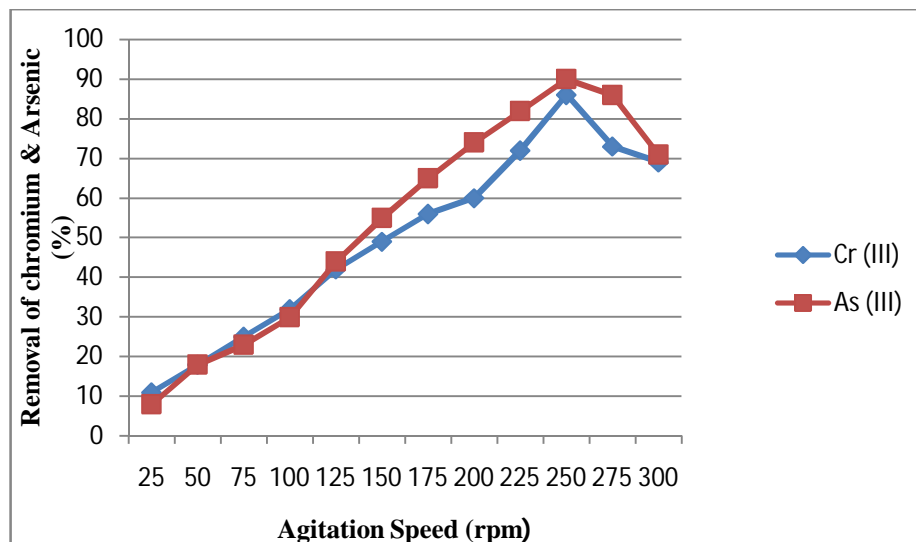


Fig 4. The effect of agitation speed on adsorption of Cr (III) and As(III) ions

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Adsorption isotherms:

The Langmuir, Temkin and Freundlich isotherms were plotted according to Equations 3, 4&5 respectively.

$$q = \frac{Q_{max} b C_e}{1 + b C_e} \quad (3)$$

$$q = K_f (C_e)^{1/n} \quad (4)$$

$$q = K_T \ln C_e + b_T \quad (5)$$

Where q (mg/g) is the amount of metal adsorbed per unit mass of adsorbent and Ce (mg/L) is the equilibrium concentration of adsorbate in solution after adsorption. Qmax (mg Cr/g coal) and b (Langmuir adsorption coefficient, a constant) are Langmuir parameters. Kf is Freundlich adsorption coefficient. bT (kJ/mol) is Temkin adsorption potential of adsorbent and KT is the Temkin adsorption coefficient.

The Langmuir, Freundlich and Temkin isotherms parameters are given in Table 2. The smaller value of 1/n indicates formation of relatively stronger bonds between Cr (III) and As (III) on active sites of coal ash.

Description	Langmuir parameters		
	Qmax (mg metal/g coal)	b	R2
Chromium(III)	2.62	0.15	0.98
Arsenic(III)	2.45	0.12	0.98

Description	Freundlich parameters		
	1/n	Kf	R2
Chromium(III)	0.46	0.50	0.98
Arsenic(III)	0.45	0.48	0.98

Description	Temkin parameters		
	bT (kJ/mol)	kT	R2
Chromium(III)	3.70	1	0.98
Arsenic(III)	3.67	1	0.98

Recovery of Cr (III) and As (III):

Recovery of metals is important process to make economical by recovering metals and by regenerating the adsorbent. The Purpose of HCl addition was to lower the pH as adsorption is favoured at higher pH, so, lowering the pH as desorb the metal. The chromium recovery was 25.65% for coal ash and Arsenic recovery was 24.6% .This can be attributed to bond strength of coal ash and metals. Bond formed between coal ash and chromium is relatively stronger than bond between Arsenic and coal ash. Since both bonds are not very strong as indicated by Temkin isotherm, so the metal is recoverable to some extent and coal ash can be used again.

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V. CONCLUSION

Coal ash from thermal fired power plants has been used for removal of Cr (III) and As (III) ions. pH of 9.0, contact time of 50 min and agitation speed of 250 rpm were found to be optimum for maximum Cr(III) and As(III) uptake by coal ash. The maximum Cr (III) removal was 2.62 mg of Cr per gram of coal ash and arsenic removal was 2.45 mg of As per gram of coal ash as evaluated from Langmuir isotherm. Relatively stronger bonds are formed between coal ash and Cr (III), arsenic as evaluated from Temkin isotherm. It is concluded that coal ash can be used for removal of Cr (III) and As (III) from effluents of electroplating, tanneries and textiles.

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