Removal of Cr (VI) from Aqueous Metal Solution using Roasted China Clay

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ABSTRACT

This study was focused on the use of Roasted China Clay (RCC) as an alternative adsorbent for the removal of Cr(VI) from aqueous solution. As Cr(VI) above permissible limit is toxic for biological systems and carcinogenic for both animals and plants, therefore it is a matter of great interest to remove it from aqueous systems. Batch experiments were conducted to determine the potential of RCC as an adsorbent by studying the effect of initial metal ion concentration, contact time, adsorbent dose and pH of solution on adsorption of Cr (VI). The maximum adsorption (81.66%) was found at pH 3 with initial metal ion concentration 50 mg/L. Adsorption of Cr(VI) ions depends upon the initial concentration of metal ions. 0.5 g of RCC was able to remove 93.34% of Cr(VI) of conc. 25 mg/L and remove 69.84% of Cr(VI) of conc. 150 mg/L. The value of R² ≈ 0.9694 and R² ≈ 0.9329 for Freundlich and Langmuir plots respectively suggested that adsorption of Cr(VI) by RCC obey Freundlich model more appropriately than Langmuir model. Kinetic models plotted for the obtained results showed that the adsorption of Cr(VI) by RCC is of second order reaction. FTIR and SEM analysis had been carried out to study the functional group and surface morphology of the adsorbent. The adsorption capacity of Roasted China Clay was found greater than most of the clay based adsorbents reported. Kinetic studies showed that experimental data was best described by pseudo second order model.

Keywords: Adsorption, Chromium, Roasted China Clay, FTIR, SEM, Morphology, Functional group.

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Introduction

Chromium is an essential nutrient for plants and animal metabolism. Chromium species is mainly exists in two different oxidation states in aqueous solution. Cr(III) is considered as an essential trace element for the maintenance of effective glucose, lipid and protein metabolism in mammals (Kotash et al., 2000). On the other hand, Cr(VI) which is present as either dichromate (Cr₂O₇²⁻) in acidic environment or chromate (CrO₄²⁻) in alkaline environments can be toxic for biological systems (Shankar et al., 2005) and carcinogenic for both humans and animals (Mungasavalli et al., 2007). Therefore, the toxicity and biological activity of the Chromium not only depends on the total amount but also on its chemical form (Kot et al., 2000; Dehiram et al., 2005).
Chromium in its hexavalent form being toxic is introduced into the water bodies from different industrial processes such as tanning, electroplating, metal processing, paint manufacturing, steel fabrication and agricultural runoff (Shrivastava et al., 2008). According to USEPA the maximum permissible limits in waste water and portable water for chromium is 1.0 mg/L and 0.05 mg/L respectively (Park et al, 2005). However when accumulated above the lethal limit, it is a carcinogen particularly to lungs through inhalation. Excessive intake of chromium by humans also leads to hepatic and renal damage, capillary damage, gastrointestinal irritation and central nervous system irritation (Wan Ngah et al., 2008). The ingestion of chromium causes pain, vomiting, nausea, diarrhea and hemorrhage (Browning et al., 1969). The toxic effects of chromium on both lower and higher plants have been reported (Shanker et al., 2005). Hence in order to reduce pollution, it is essential to remove Cr(VI) ions from industrial waste water before discharging into the natural environment.

The common methods for the removal of heavy metals from waste waters are chemical precipitation, ion exchange, electro-dialysis, membrane filtration and sorption of metal oxides. These methods have certain drawbacks namely, high cost, low efficiency, generation of toxic sludge or other waste that requires disposal treatment and imply operational complexity (O’Connell et al., 2008; Dada et al., 2013). The chemical methods have proved to be expensive, less efficient and increases pollution load on the environment (Barakat, 2011). Adsorption has advantages over the other methods due to its simple design with sludge free environment involving low investment (Crini, 2005; Kurniawan et al., 2005).

In recent years, numerous low cost natural materials such as glazed tea mugs, saw dust, fruit peel of orange, rice husk (Ajmal et al, 1997;1998;2000;2003), coconut fibers (Igwe et al., 2008), palm shell (Onundi et al., 2010), potato peel (Aman et al., 2008), tea waste (Amir et al., 2008), ground nut shell (S. Idris et al., 2012), chemically modified chitosan (Dai et al., 2010), neem leaves (Parineeta et al., 2013), local landfill clay (Ghorbel-Abid et al., 2011), natural clay (Sdiri et al., 2014), chitosan coated ceramic membrane (Wanida et al., 2015), kailonite clay (Kamel et al., 2004), treated old paper (Ossman et al., 2013) and tourmaline mineral (Jiang et al., 2006) ceramic water purifiers made of Iraqi Betonite type (Bp11) (Jassim et al., 2014), powdered waste sludge (PWS), dried activated sludge biomass (Ashfaq, 2011a,b), terminaliaarjuna (Rao et al., 2014), flyash (Ashfaq, 2012), potteryglaze ( Rao et al., 2012) have been used to remove chromium and other heavy metals from water and waste waters.

Materials and Methods

Preparation of Adsorbent

In the city of Khurja, pots, toys and many other decorative articles are manufactured from ceramic powder which is a mixture of china clay, animal bone, quartz and feldspar. The moulded paste of the mixture exhibit binding property after heating. First ceramic powder is converted into a semi-solid paste to mould it to various shapes of pots and toys. After firing the paste becomes hard and porous which is known as Roasted China Clay(RCC). But during the process of Firing, some of the articles breaks or get deshaped which are thrown away as waste. This thrown away waste were collected, grinded into fine particles and sieved through 100 mesh size and used as adsorbent to remove Cr(VI) from aqueous solution.
Characterization of Adsorbent

To observed the surface morphology of the adsorbent before and after adsorption of Cr(VI), SEM analysis was employed by using Scanning Tunneling Microscope, JEOL-JSM 6510 LV at USIF (University Sophisticated Instrumentation Facility) Aligarh Muslim University, Aligarh.

The types of binding groups present on the adsorbent (RCC) were identified by using Perkin-Elmer Fourier Transformer Spectrophotometer (FTIR) Version 10.03.08 by using KBr pellet technique in the wavelength range 450-4000 cm\(^{-1}\) at Instrumentation Lab, Department of Chemistry, AMU, Aligarh.

Adsorbate Solution

All the chemicals used in the study were of analytical grade, either from Merck Pvt. Ltd. A stock solution of 500 mg/L of Cr(VI) was prepared by dissolving required amount of potassium chromate, K\(_2\)CrO\(_4\) in double distilled water in a 500 ml standard flask. This stock solution was used to prepare the working solutions of desired concentrations for all experiments. pH values of the solutions was adjusted by adding 0.1 mol/L NaOH or 0.1 mol/L HCl.

The concentrations of Cr(VI) in the solution before and after adsorption were measured by using GBC-902 Atomic Absorption Spectrophotometer (AAS) at the instrumentation lab, Department of botany, AMU, Aligarh.

Batch Adsorption Studies

Batch process were conducted at room temperature 27±1\(^\circ\)C to study the adsorption of Cr(VI) ions on RCC. An accurately weighed 0.5gm of RCC was placed in 100ml stoppered conical flask containing 50 ml of Cr(VI) ions solution of 50mg/L. This solution was shaken in a rotary shaker for about 15 min and kept for 24 hours to attain equilibrium. All the operations such as effect of pH, adsorbent dose, contact time were conducted at room temperature with 50ml Cr(VI) ions solutions of 50mg/L except during the study of effect of concentration where 25 to 200 mg/L Cr(VI) ions concentration solutions were used. After that the mixture was filtered by using whatman filter paper No. 41. The concentration of Cr(VI) ions in filtrate was analysed by AAS.

Effect of pH

The effect of pH on the adsorption of Cr(VI) was studied by batch process as follows: 50 ml of 50 mg/L (Initial concentration) metal solution was taken in a 100 ml conical flask. The pH of the solution was adjusted by adding 0.1 M HCl and 0.1 M NaOH solutions by using Systronic-09 digital pH meter. This solution was treated with 0.5 gm of adsorbent and after attaining equilibrium, final concentration of Cr(VI) in the solution was determined by AAS.

Effect of Contact Time

A series of 100 ml conical flasks, each having 0.5 g adsorbent and 50 ml solution of 50 mg/L Cr(VI) concentration were shaken in a rotary shaker at predetermined intervals. The solution of the specified flask was taken out and filtered. The concentration of Cr(VI) in the filtrate was determined by AAS.

Effect of Adsorbent Dose

A series of 100 ml conical flasks, each containing 50 ml solution of 50 mg/L Cr(VI) concentration were treated with varying amount adsorbent (0.1 – 1.0g) and shaken in
a rotary shaker at predetermined intervals. The solution of the specified flask was taken out and filtered. The concentration of Cr(VI) in the filtrate was determined by AAS.

**Effect of Concentration**

A series of 100 ml conical flasks, having 0.5 g of adsorbent and 50 ml solution each of varying concentration from 10 - 200 mg/L Cr(VI) concentration were shaken in a rotary shaker, at pre-determined intervals. The solution of the specified flask was taken out and filtered. The concentration of Cr(VI) in the filtrate was determined by AAS.

The removal percentage (R%) of metal ions and Adsorption capacity or amount of Cr(VI) adsorbed per unit mass of adsorbent(qe) were calculated for each run by the following expression-

\[
R\% = \left( \frac{C_i - C_e}{C_i} \right) \times 100
\]

\[
q_e = \left( \frac{C_i - C_e}{m} \right) \times V
\]

where,

- \( C_i \) = Initial concentration of metal ions in the solution
- \( C_e \) = Final concentration of metal ions in the solution
- \( V \) = Volume of the solution(L)
- \( m \) = Mass of the adsorbent (gm)

**Adsorption Isotherms**

Adsorption isotherm curve is an invaluable curve describing the phenomena governing the retention (or release) or mobility of the adsorbent from the aqueous phase to a solid phase at constant temperature and pH (Allen et al., 2004; Limousin et al., 2007; Foo et al., 2010). In order to model the adsorption behaviour of Cr(VI) ions on RCC, Langmuir and Freundlich adsorption isotherm were studied. The adsorption of Cr(VI) ion concentration ranging from 25 mg/L to 200 mg/L were studied and the data obtained was analyzed with both the Langmuir and Freundlich adsorption isotherm equations.

**Langmuir Isotherm**

One of the most widely used model for describing heavy metals sorption is the Langmuir model. Langmuir relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. It is expressed as-

\[
\frac{1}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} \times \frac{1}{C_e}
\]

where,

- \( q_e \) is the amount of Cr(VI) adsorbed per unit weight of the adsorbent (mg/g) at equilibrium,
- \( C_e \) is the equilibrium concentration (mg/L),
- \( b \) and \( q_m \) are Langmuir constant related to the energy of adsorption and monolayer adsorption capacity of adsorbent (mg/g) respectively.

The linear plot of \( 1/q_e \) vs \( 1/C_e \) shows that adsorption of Cr(VI) follows the Langmuir model. The values of \( q_m \) and \( b \) were be calculated from the intercept and slope of the plots (Langmuir, 1918). The coefficient \( b \) in Langmuir equation is a measure of the stability of the complex formed between metal ions and adsorbent under specified experimental conditions (Rao et al., 2007; Ayranci et al., 2005).
Freundlich Isotherm

Freundlich isotherm is an empirical equation which was applied for adsorption of Cr(VI) and is represented as-

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

where,

- \(C_e\) is the equilibrium concentration (mg/L)
- \(q_e\) is the amount of metal ions adsorbed per unit weight of the adsorbent (mg/g).

\(K_f\) and \(n\) are the Freundlich constant designating adsorption capacity and adsorption intensity respectively. The linear plot of \(\log q_e\) vs \(\log C_e\) show that the adsorption followed Freundlich model. The values of \(K_f\) and \(n\) were calculated from the intercepts and slop of the plots (Freundlich, 1906).

Adsorption Kinetics

In order to investigate the Adsorption kinetics, the Lagergren first order (Lagergren, 1898), pseudo first-order (O’Shannessy et al., 1996) and pseudo second order kinetics models (Singh et al., 1988; Ho and Mckay, 1999) were applied. The pseudo second order model may be represented the data more appropriately when the value of correlation coefficient is greater than 0.99 (\(R^2 > 0.99\)).

The pseudo first-order kinetic equation of Lagergren is represented as:

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t)
\]

The above equation can be integrated to yield a linearized form as

\[
\log (q_e - q_t) = \log q_e - k_1 t / 2.303
\]

where,

- \(k_1\) = Lagergren rate constant for adsorption (min\(^{-1}\)),
- \(q_e\) = Amount of metal adsorbed at equilibrium (mg g\(^{-1}\))
- \(q_t\) = Amount of metal adsorbed (mg g\(^{-1}\)) at any time \(t\).

Time, \(t\) was plotted against \(\log(q_e - q_t)\) and the values of \(k_1\) and \(q_e\) was determined from the slope and intercept of lines of the plot.

The equation of pseudo second order model is:

\[
\frac{dq_t}{dt} = k_2 (q_e - q_t)^2
\]

Integration and rearrangement of equation above yielded the following equation

\[
t / q_t = 1 / k_2 q_e^2 + 1 / q_e t
\]

where,

- \(k_2\) = Equilibrium rate constant of second order kinetics model (g mg\(^{-1}\) min\(^{-1}\)),
- \(q_e\) = Equilibrium capacity
- \(q_t\) = Adsorption capacity at any time \(t\).

The time \(t\) was plotted against \(t/q_t\) and the values of \(k_2\) and \(q_e\) was determined from the slope and intercepts of lines of the plot.

Results and Discussion

Characterization of Adsorbent

The SEM images of RCC before and after adsorption shown in Fig. 1 and 2 shows that surface of RCC is irregular and rough with almost non compact structure which means that it has considerable number of pores of different shapes and sizes, where appropriate
conditions exists for Cr(VI) ions to be trapped and adsorbed in these pores. The bright spots in the images before adsorption show the presence of tiny holes on the surface of RCC. After treatment with metal ions, the bright spots become dark grey and black which reveal that the adsorption of Cr(VI) has occurred on the surface of RCC by means of physisorption (Sudha et al., 2007; Arivoli et al., 2007; Weber et al., 1967). The SEM images also illustrates that the adsorbent surface before adsorption seems to be less denser while after adsorption it becomes denser showing the adherence of Cr(VI) ions on the surface. Hence, adsorptive characteristics of RCC are expected to be highly effective.

**SEM Images**

**FTIR Images**

The types and structure of binding groups present on the surface of RCC were identified in the wavelength range 450-4000 cm⁻¹. The FTIR spectra of RCC recorded before and after adsorption are shown in Fig. 3 and 4. The FTIR spectrum showed a characteristic broad peak at 3441.81 cm⁻¹ due to the presence of hydrogen bonded –OH group (Rao et al., 2011), while small peak at 2925.76 cm⁻¹ indicates the presence of C-H stretched bond in alkanes. The peaks between 900 and 1100 cm⁻¹ might be due to the presence of metal oxides (Coates, 2000) as metal oxides generally give absorption band below 1000 cm⁻¹ arising from interatomic vibration (Wang et al., 2013; Anandan et al., 2011). The peaks between 500 and 800 cm⁻¹ indicates the presence of C-X bonds (X = Halogen). When FTIR spectra of untreated RCC is compared with Cr(VI) treated RCC the shifting of bands towards lower and higher frequencies was observed. Shifting of band from 3441 to 3438 cm⁻¹ indicates the interaction of Cr(VI) ions with –OH group. All the changes in the spectra of treated RCC is due to the metal bonding process on the surface of RCC.

**Batch Studies**

**Effect of pH of Metal Ions Solution of Adsorption**

The pH of the solution is one of the important controlling parameter in the adsorption process. The solution of Cr(VI) metal ion of concentration 50 mg/L was treated with 0.5gm of adsorbent at various pH ranging 1 to 14. The percentage removal of Cr(VI) at various pH values is shown in fig. 5. It has been observed that the percent removal of metal ion decrease as pH value of the solution increase. Hence RCC show higher adsorption at pH 3 (81.66%). At a higher pH, Cr(VI) ion gets precipitated as their hydroxides which decreases the rate of adsorption and subsequently the percent removal of metal ions (Pagnonelli et al., 2003; Lugolugo et al., 2009).

**Effect of Concentration of Metal Ion on Adsorption**

The effect of Cr(VI) concentration in the solution for five different concentrations (25, 50, 100, 150 and 200mg/L) is shown in fig.6. It has been observed that the adsorption capacity of Cr(VI) increases from 2.33 mg/gm to 14.18 mg/gm whereas the adsorption percentage decreases with the increase in concentration of metal ion on solution. This was due to the fact that empty adsorbent sites adsorbed Cr(VI) ions rapidly at lower concentration but at higher concentration adsorption of Cr(VI) ions occurred by diffusion (slower step) into the inner sites of the adsorbent. The maximum adsorption observed at 25 mg/L (93.34%) and minimum adsorption observed at 150 mg/L (69.84%).
Effect of Contact Time

Adsorption of metal on adsorbent used increases with increasing contact time. The Cr(VI) uptake versus time curve in fig.7 shows that equilibrium is attained in 20 min, where maximum adsorption percentage was 80.34%. The adsorption percentage of metal versus time is single and continuous line leading to saturation, suggesting a monolayer adsorption on the surface of adsorbent. The equilibrium time of 20 minutes investigated in the present work was much shorter than other adsorbents reported earlier for Cr(VI) adsorption.

Effect of Adsorbent Dose

The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion in the solution. The Adsorption percentage of Cr(VI) at different doses of adsorbent is shown in fig. 8. It was observed that increasing the adsorbent dose increased the percentage removal of Cr(VI) upto 96.66%. The adsorption percentage of Cr(VI) increases with the increase of adsorbent dose, due to increase in surface area of adsorbent leading to more adsorption sites.

Fig.1 SEM Image of RCC before adsorption

Fig.2 SEM Image of RCC after Adsorption
Fig. 5 Effect of pH on Adsorption of Cr(VI)

Conc.: 50 mg/L; Contact Time: 2 hours; Ads. dose: 0.5gm
**Fig. 6** Effect of Concentration of Cr(VI) on its Adsorption

**Fig. 7** Effect of Contact Time of Adsorption of Cr(VI)

Initial conc. 50 mg/L; Ads. Dose: 0.5gm; pH: 3

**Fig. 8** Effect of Adsorbent Dose on Adsorption of Cr(VI)

Initial concentration: 50 mg/L; Contact Time: 24 hours; pH: 3
Fig. 9 Langmuir Adsorption Isotherm Plot for Adsorption on RCC

Fig. 10 Freundlich Adsorption Isotherm Plot for Adsorption on RCC

Fig. 11 Pseudo First Order Plot for the Adsorption of Cr(VI) on RCC
Adsorption Isotherm

Adsorption isotherm curve is an invaluable describing the phenomena governing the retention (or release) or mobility of the Cr(VI) ions from the aqueous phase to a solid phase at constant temperature and pH (Allen et al., 2004; Limousin et al., 2007; foo et al., 2010). The Langmuir and Freundlich isotherms were used to fit the experimental data of the adsorption of Cr(VI) at 27 °C. In order to evaluate the fitness of the experimental data on Langmuir model, \(1/q_e\) were plotted against \(1/C_e\) as shown in Fig. 9 and on Freundlich model, \(\log q_e\) were plotted against \(\log C_e\) as shown in Fig. 10 respectively. The linearity of the graph and values of the correlation coefficient \(R^2\) showed that the experimental data were more appropriately fitted on Freundlich model. Moreover the values of the correlation coefficients suggests that adsorption of Cr(VI) ions on RCC occurs by the formation of homogeneous monolayer followed by multilayer formation.

Adsorption Kinetics

To find out the validity of the obtained experimental data on Pseudo first and second order equation, graph of \(\log (q_e - q_t)\) vs time, \(t\) and \(t/q_t\) vs time, \(t\) was plotted as shown in Fig. 11 and Fig.12. A straight line was obtained and the value of correlation coefficient \(R^2 \approx 0.9998\) as observed in Fig. illustrate that adsorbate-adsorbent system obeyed Pseudo second order model. Furthermore, the applicability of Pseudo second order model confirmed that Cr(VI) ions during adsorption form multilayer on the surface of particles of RCC.

In conclusion, the present study was to evaluate the RCC as possible potential adsorbent for removal of Cr(VI) from synthetic wastewater by batch process. It was found that the adsorption of Cr(VI) ions by RCC was pH dependent and the optimum pH for the maximum removal (81.66%) of Cr(VI) from aqueous solution was 3 and obeying Freundlich model more appropriately than Langmuir model. From the study of kinetic models plotted for the obtained results showed that the adsorption of Cr(VI) by RCC is of second order reaction. It is also important to remark that the Roasted China Clay is economic and easily available material and after treatment with heavy metals a very low amount of sludge is produced which may be disposed off without causing any harm to the environment. The results showed that the Roasted China Clay has been found very
effective and environment friendly adsorbent which can remove sufficient amount of Cr(VI) from aqueous solution in very small period of contact time (in this case 20 minutes). Hence, RCC can be utilized in wastewater treatment containing Cr (VI) as pollutants without any chemical treatment.

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