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Removal of Chromium (VI) From Aqueous Solution Using Modified Bentonite Clay and its Application on Tanneries Waste Water

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Abstract. Adsorption is one of the best methods for removing metals from aqueous medium. In the present study, bentonite clay was used as an adsorbent for heavy metal Cr^{+6} removal from the synthetic solution as well as actual waste water collected from local tanneries. Bentonite was used with and without chemical modification to improve removal efficiency. The adsorbent was modified with HCl, H_2SO_4 and NaOH. The batch adsorption technique was applied to study the effect of pH, initial concentration of metal ions, adsorbent dose and shaking time on the adsorption process. The chemical oxygen demand and biological oxygen demand of tannery effluents were significantly reduced upto 77.6% and 81.2%, respectively. The original bentonite clay removed upto 59%, while 98% removal was achieved with H_2SO_4 modified bentonite clay, 68% with HCl modified clay and 89% by NaOH-modified clay. Furthermore, the percentage removal efficiency was reduced by increasing the initial concentration of metal ions. The current study concluded that bentonite clay is a good adsorbent and modifications to bentonite clay can effectively improve the physical characteristics of the clay to adsorb Cr^{+6} ions. Moreover, bentonite clay is inexpensive and readily available in our country.

Keywords: adsorption method, bentonite clay, Cr (VI) metal, synthetic solutions, tanneries wastewater

Introduction

The growing demand in the global leather market has stimulated the growth of a large number of tanneries in Pakistan. According to the recent statistics released by Ministry of Industries and Production, there are about 650 registered tanneries in the country, including small, medium and large enterprises (Tahir and Naseem, 2007). In most tanneries, chromium salt is the most widely used for tanning purposes. However, tannery operations cause severe environmental degradation due to the discharge of untreated effluent onto land and water bodies. High chromium concentration is harmful for environment and human health (Abbas *et al*., 2011).

Chromium ions naturally exist in mineral (rocks, soil) and in living system (animals and plants). Chromium (Cr) is toxic metal especially to plants and animals and is not easy to treat because it is not bio-degradable and bio-accumulated in living cells (Akpomie and Dawodu, 2015). It can form multiple oxidation states, where Cr forms Cr^{2+}, Cr^{3+} and Cr^{+6} ions, which are highly toxic, reactive and readily soluble in solutions with different pH values (Al-Essa, 2018). However, their toxicity is less compared to Cr^{+6}. Chrome ulcers, corrosive reaction on the nasal septum, acute dermatitis and allergic eczematous dermatitis are recorded on humans. In addition, there are also economic losses due to the drainage of unused chromium salts in wastewater, which accounts for almost 25-30% of the total amount of chromium used in the tanning process.

Heavy metals enter the environment through natural phenomena such as weathering and volcanic eruptions. These metals are also produced in textile industry, leather tanning industry, zinc refineries, metallurgical industries, automobile emissions, incineration of metals, mining and refining of heavy metals, cement and asbestos industries, cadmium nickel batteries, fungicides and insecticides etc. (Toor, 2010).

Over the past few years, the removal of heavy metals from water has been the subject of many developments and experimental studies. The most common methods for removal of metals from industrial effluents include chemical precipitation (Renu *et al*., 2017), pre- or post-oxidation (Lajayer *et al*., 2018), reduction (Kanamarlapudi *et al*., 2018) and ion exchanges (Renu *et al*., 2017) etc.

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Consumptive processes, such as chemical precipitation, have high operating costs. Thus, attention has been focused on non-consumptive methods that include ion-exchange and other absorption processes. In recent decades, adsorption has become an economical and feasible alternative method for removing low traces of metal from waste water. Some of the major adsorbents for commercial and laboratory use include activated carbons, decolourizing carbons, bone char, alumina, silica, bauxite, bentonite, fuller's earth, molecular sieves, peat, lignite, chitin, chitosan and ion exchange resins (Raghuvir *et al*., 2018).

The term "bentonite" is not an exact mineralogical name or any material with a definite mineralogical composition or definite chemical and physical properties. The biggest feature of this material is that it swells during processing due to the adsorption of metal ions on its surface. Bentonite clay is a 2:1 mineral with one octahedral sheet and two silica sheets that forms a layer and carries a net negative charge due to broken bonds around the edges of the silica–alumina units. This would lead to unsatisfied charges that can be balanced by the exchange of cations (Bhattacharyya and Gupta, 2008). The removal of metal ions using bentonite is based on ion exchange and adsorption mechanisms due to its relative high cation exchange capacity (CEC) and specific surface area. It is noteworthy that the bentonite clay can change its removal mechanism according to its pre-treatment.

The maximum allowable limit for Cr^{+6} in effluents is only 0.05 mg/L, but the concentration in the industrial waste water is higher. Consequently, the concentrations of Cr^{+6} must be reduced to such an extent to comply with environmental regulations (Grady *et al*., 2011; Tchobanoglous *et al*., 2003).

Considering all the above, the current study was conducted to evaluate the ability of locally available bentonite clay as an inexpensive adsorbent for the removal of Cr^{+6} from tannery waste water. To study the influence of various parameters, such as dosage of adsorbent, pH and type of adsorbent, on the adsorption process, as well as to determine the removal efficiency of various chemically modified bentonite clays for adsorption of Cr^{+6} ions.

Materials and Methods

Preparation of adsorbent. Bentonite clay of 1Kg was purchased from market in a region of Lahore, Pakistan. It was in solid hard form and greyish in colour. Clay was washed with distilled water and then dried in oven (drying oven) at 105 °C for 6 h (Moradi *et al*., 2015). The adsorbent was ground into fine particles using a mortar and pestle and sieved through a 250 µm sieve and packed in an air tight polythene bag until use to avoid moisture and labelled appropriately (Akpomie and Dawodu, 2015).

Preparation of alkali (NaOH) modified bentonite clay. Bentonite clay was added in 10% NaOH solution and left overnight. It was then filtered, washed three times and dried in an oven for 6 h at 55 °C (Rosario *et al*., 2010). The Alkali-modified clay was ground and sieved through pestle mortar and 250 µm sieve set respectively.

Preparation of acid (HCl) modified bentonite clay. The bentonite clay was dipped in 10 % HCl solution, mixed well with stirrer and kept at room temperature overnight. It is then filtered and washed 3 times with distilled water and dried in an oven at 450 °C for 4 h (Al-Essa, 2018).

The hydrochloric acid modified clay was then grounded by the help of pestle and mortar and sieved through 250µm sieve set.

Preparation of acid (H_2SO_4) modified bentonite clay. Bentonite clay was added in 10% H_2SO_4 solution and refluxed at 110°C at atmospheric pressure in a condenser equipped with a round bottom flask for 4 h. The resulting suspension was added with 300 mL of water and filtered and washed repeatedly 3 times and dried in an oven at 105 °C for 3 h.

Finally, the prepared adsorbent was kept in an air tight container for further use (Moradi *et al*., 2015)

Collection of samples. The study was conducted in two phases, first with synthetic Cr^{+6} solutions and second with original Tanneries waste water.

(A) Phase one with synthetic solutions. Preparation of synthetic solutions. The 1000 ppm of stock solution was prepared by dissolving the specific amount (2.83g) of metal salts i.e., $K_2Cr_2O_7$ in 1 L of distilled water and required concentration of Cr^{+6} ions was made by appropriate dilutions (Maheshwari and Gupta, 2015).

From that standard solution of chromium metal 5, 10, 20 and 50 ppm solutions were prepared with appropriate dilutions.

(B) Phase two with original tanneries wastewater. After the successful removal of Cr^{+6} metal ions from

synthetic solutions the results were applied on tannery waste water by batch adsorption experiments because it contains high concentrations of chromium ions in it. Dose amount of 0.25 g had adsorbed maximum concentration of the metal at a shaking time of 8 h, of all the modified and unmodified bentonite clays (T-1, T-2, T-3 and T-4).

Batch adsorption experimant. All the batch adsorption experiments were performed on an orbital shaker at a constant speed of 120 rpm using 100 mL conical flasks containing different adsorbent teratments having doses ranging from 0.05, 0.1, 0.2, 0.25 and 0.3 g/L and synthetic chromium solutions of 5, 10, 20 and 50 ppm concentration, while 0.25 g which was best dose that applied on actual tanneries waste water. The experiments were performed at room temperature (20 °C) and relative humidity (75%). The pH of the solution was maintained naturally. The other parameters such as adsorbent doses, contact time or shaking time (4 to 8 h) were varied.

All solution samples after shaking were filtered through Whatman (0.45 µm) filter paper. The concentrations of Cr^{+6} metal in treated samples were determined by UV visible spectrophotometer.

Physico-chemical characterization of samples. (*a*) *analysis of chemical oxygen demand (COD)*. 500 mL round bottom flask was taken, washed it carefully with the help of distilled water 2 mL of tannery waste water sample was poured into the round bottom flask and add 18 mL of distilled water to make the volume 20 mL in the flask. After that 10 mL of $K_2Cr_2O_7$ was measured with the help of measuring cylinder and added into the round bottom flask. Then 40 mL of distilled water and 30 mL of conc. H_2SO_4 were added in the round bottom flask to make the volume up to 100 mL. Some broken pieces of glass or glass pebbles were also added into the flask.

COD apparatus was set, and round bottom flask was put on the tripod stand, gas burner was turned on. Time was noted and refluxes the round bottom flask for 2 h.

After 2 h gas burner was turned off and flask was removed from the stand and allowed it to cool down. On cooling 2-3 drops of indicator known as Ferroin was added. Then 10 mL of FAS (ferrous ammonium sulphate) was taken in a pipette and added drop wise with constant mixing. Reading was noted at which the colour of the sample was turned blue to brick red which was the end point.

COD of all the samples can be calculated by the following formula:

$$\text{COD} = \frac{\text{Blank- sample} \times 8000 \times \text{Normality of FAS}}{20}$$

b) Analysis of biological oxygen demand (BOD). Dilution method was applied to analyse the biochemical oxygen demand of tannery waste water. Incubation bottles or glass bottles having 300 mL capacity with a ground-glass stopper and a flared mouth were used, first bottles were cleaned with a detergent, rinsed thoroughly and drained before use.

Preparation of reagent. Magnesium sulfate solution as a reagent was used in BOD analysis. It was prepared by dissolving 22.5 g $MgSO_4.7H_2O$ in distilled water and diluted to 1 L by using distilled water.

Dissolved oxygen (DO) concentrations in the samples were measured before and after the incubation period. In 300 mL incubation bottles were approximately two third of buffered dilution water added, then dosed with seed micro-organisms and stored for 5 days in the dark room at 20 °C to prevent DO production *via* photosynthesis. The dilution water blank was prepared to confirm the quality of the dilution water that is used to dilute the other samples. The membrane electrode method was used to determine initial DO on all sample dilutions, dilution water blanks.

Determination of final DO was done after 5 days of incubation, in all sample dilutions, and in all blanks by using membrane electrode method.

BOD of all the samples was calculated by the following formula reported by (Young, 1973)

$$\text{BOD}_5 \text{ mg/L} = \frac{\text{(D1 - D2) - (S)Vs}}{\text{P}}$$

(c) Colourimetric method for analysis of Cr metal. For the analysis of chromium (VI) metal concentration in both synthetic and tannery wastewater on UV Visible (SPECCORD 200) Spectrophotometer Colourimetric method was applied. In this method reagent Diphenylcarbazide was used.

Preparation of reagent. 0.1 g of Diphenylcarbazide was taken in a test tube then 10 mL of acetone was added in it and shaked until solubilize completely.

In a conical flask 10 mL of distilled water and 10 mL of filtered sample solution were added on the other hand just 20 mL of distilled water was added for blank preparation. Afterwards 0.2 mL of concentrated sulphuric acid was added and shake well. Then 0.4 mL of reagent diphenylcarbazide was added. The purple colour appearance showed presence of chromium concentration within 30 min. readings were taken on UV Spectrometer at a wavelength of 540 nm.

The same procedure was repeated for all synthetic and actual tannery wastewater samples. The amount of Cr^{+6} adsorbed per unit mass of the adsorbent was evaluated by using the following equation which is reported by (Memedi *et al*., 2017).

$$q_{Cr} = (Ci - Ct)\frac{V}{m}$$

where:

Ct [mg/L] is the concentration of the metal for a time (t) and V is the volume of the solution in a glass and m adsorbents mass.

The percentage removal of Cr^{+6} was calculated by the following equation (Rauf *et al*., 2003)

$$\%R = \left[\frac{C_i - C_f}{Ci}\right] \times 100.$$

where:

Ci is initial metal ion concentration [mg/L] and C_f is final concentration at equilibrium [mg/L].

Results and Discussion

In this research work, modified bentonite clay was used as adsorbent to absorb Cr^{+6} ions. Study was conducted in two phases: 1st phase with synthetic solutions (5, 10, 20, 50 ppm) and the 2nd phase with original tanneries waste water. Four treatments (T1- T4) were performed in 100 mL of synthetic chromium solutions as well as tanneries waste water. Contact/shaking time for all treatments was given 4 - 8 h whereas the dose rate was fixed at 0.25 g for 100 mL of waste water.

Phase one: Treatment for Cr^{+6} removal from synthetic solutions. The results in Fig. 1 showed treatment of 5 ppm synthetic Cr^{+6} solution with dose of 0.25 g. The maximum removal efficiency was shown by sulphuric acid bentonite clay (98%), then alkali treated bentonite (89%), (68%) of HCl treated clay, while least removal efficiency (56%) was of original bentonite clay after 8 h shaking as shown in Fig. 1. Colour content was reduced to 51% with a pH 5.86.

The results in Fig. 2 showed treatment of 10 ppm synthetic Cr^{+6} solution with dose rate of 0.25 g. The maximum removal efficiency was shown by sulphuric acid bentonite clay (98%) and then alkali treated bentonite (92%), (43%) of HCl treated clay while least

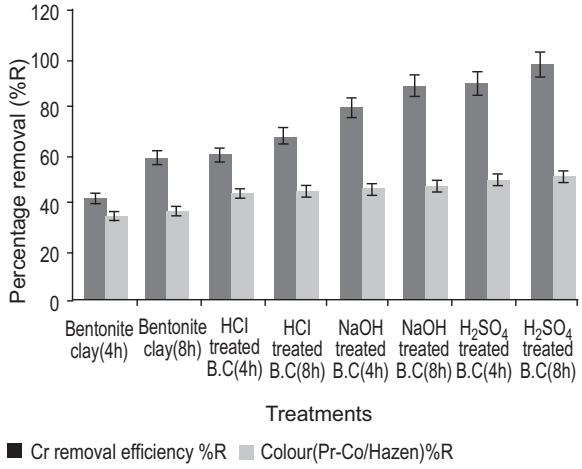

Fig. 1. Effect of different adsorbents on percentage removal of Cr^{+6} and colour at dose rate of 0.25 g in 5 ppm solution.

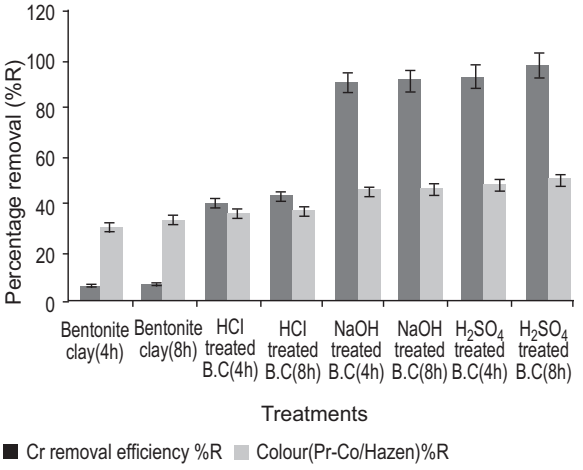

Fig. 2. Effect of different adsorbents on percentage removal of Cr^{+6} and colour at dose rate of 0.25 g in 10 ppm solution.

removal efficiency (6%) was of original bentonite clay after 8 h shaking. Colour content was reduced to 50% with a pH 5.88.

The results in Fig. 3 showed treatment of 20 ppm synthetic Cr^{+6} solution with dose rate of 0.25 g. The maximum removal efficiency was shown by sulphuric acid bentonite clay (96%), then alkali treated bentonite (70%), (60%) of HCl treated clay, while least removal efficiency (56%) was of original bentonite clay after 8 h shaking. Colour content was reduced to 52% with a pH 5.70.

The results in Fig. 4 showed treatment of 50 ppm synthetic Cr^{+6} solution with dose rate of 0.25 g. The maximum removal efficiency was shown by sulphuric acid bentonite clay (91%), then alkali treated bentonite (50%), (40%) of HCl treated clay, while least removal efficiency (37.6%) was of original bentonite clay after 8 h shaking. Colour content was reduced to 50% with a pH 4.82.

The results of the current study resemble to the previous study in which the removal of metal increased by the increase of contact time, approximately 70-80 % of maximum removal of Cr^{+6} was attained within 210 min. and the maximum adsorption was attained in 180 min (Algamal *et al*., 2018). This may be due to the presence of positively charged surface area of the adsorbent for anionic Cr^{+6} species present in the solution. The retention in the adsorption or slow adsorption of Cr ions may be explained by the electrostatic hindrance caused by already adsorbed negatively charged Cr^{+6} ions in the solution (Ghosh and Goswami, 2005).

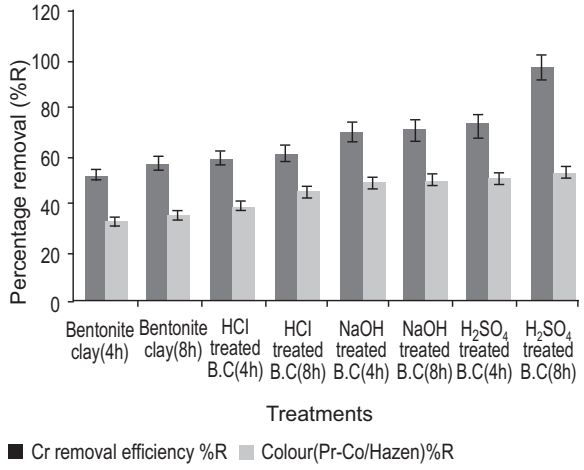

Fig. 3. Effect of different adsorbents on percentage removal of Cr^{+6} and colour at dose rate of 0.25 g in 20 ppm solution.

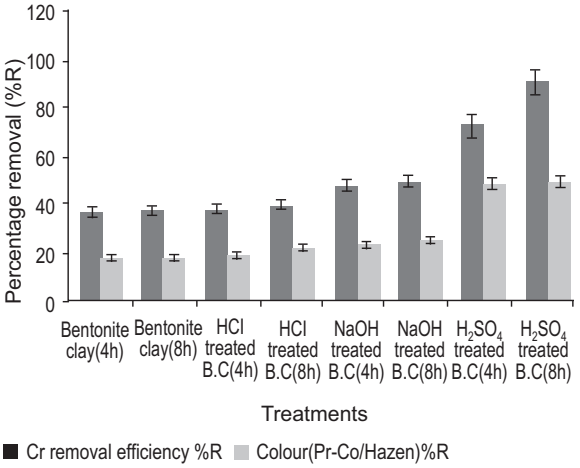

Fig. 4. Effect of different adsorbents on percentage removal of Cr^{+6} and colour at dose rate of 0.25 g in 50 ppm solution.

Phase two. Treatments with tanneries wastewater. In the 2nd phase, the similar adsorption study was conducted with original tanneries waste water. Contact/shaking time for all treatments was given 4 - 8 h, whereas the dose rate was fixed at 0.25 g/100 mL.

The results in Fig. 5 showed treatment of tanneries waste water with dose rate of 0.25 g. The maximum removal efficiency was shown by sulphuric acid bentonite clay (92.2%), then alkali treated bentonite (91.5%), (82.8%) of HCl treated clay, while least removal

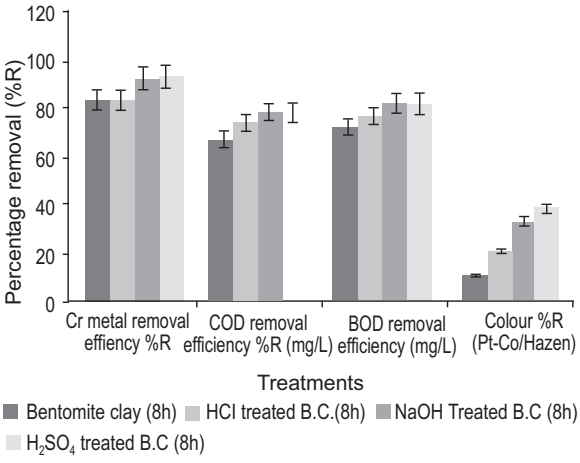

Fig. 5. Effect of bentonite clays dosage 0.25 g on tannery wastewater.

efficiency (82.5%) was of original bentonite clay after 8 h shaking as shown in Fig. 5. Colour content was reduced to 37.5%. Maximum COD was reduced to 77.6% by both H_2SO_4 and Alkali modified bentonite clays. Maximum removal in BOD of the tannery sample was done by both H_2SO_4 and Alkali modified bentonite clays which is 81.2%.

It was observed from the following study that the colour of the solution was inversely proportional to the increase of shaking time as shown in Fig. 1. Percentage of removal was increased (85%) by the modification of bentonite clay with H_2SO_4. Similar effect was also discussed in previous study (Memedi *et al*., 2017). According to that, sulphuric acid modification caused the activation of bentonite clay's surface by protonization. This protonization caused maximum adsorption of metals onto the surface of clay.

It was seen that the rate of removal of metal and colour increases by reducing the initial concentration of the Cr^{+6} ions. The 20 ppm solutions show 96% chromium removal and 50 ppm gave 91% chromium removal. It was observed in the current study that by the increase of initial Cr^{+6} concentration in the solution the removal percentage of the Cr metal was reduced, which showed similar results as the previous study of Memedi *et al*., (2017) that in the lowest value of the initial concentration the greatest degree of removal of Cr (VI) ions was obtained, 80.65%. The absorbent dosage is one of important factor that impose large contributions to the sorption process. It also determined the adsorption efficiency of the sorbent for a given initial concentration of removal of chromium (Habiby *et al*., 2020).

In tanneries waste water highest results were shown by H_2SO_4 modified bentonite clay. In the current study it was noticed that after H_2SO_4 modified bentonite clay, alkali (NaOH) modified bentonite clay also have excellent removal efficiency with high pH ranges i.e., 8.45 and so on. By increasing the concentration of NaOH leads to increase the removal percentage of chromium. This is due to the attributed complex exaction of chromium ion with negatively charged moieties formed as a result of NaOH treatment. The results of various studies showed the enhancement of chromium removal by different adsorbents modified with NaOH solutions has been reported (Ranasinghe *et al*., 2018; Bishnoi *et al*., 2007). The adsorption process is economically important because it provides an avenue for reuse of adsorbent or safe disposal (Dim *et al*., 2021). Moreover, the results showed that potential of modified bentonite clay as a suitable eco-friendly sorbent for removing chromium from tannery wastewater.

Conclusion

The current study evaluated the use of commercially available bentonite clay as an inexpensive adsorbent to remove metallic Cr^{+6} from synthetic solutions and tannery effluents. Bentonite clay was modified by acids (HCl and H_2SO_4) and by alkali (NaOH), and the best results are obtained with bentonite clay modified with sulfuric acid.

- Below is the procedure for removing chromium from treated and untreated bentonite clay:

H_2SO_4 modified bentonite clay (T-4) > alkali modified bentonite clay (T-3) >

HCl treated bentonite clay (T-2) > original bentonite clay.

- Maximum reduction in colour (83.3%) was attained as a result of treatment with H_2SO_4 modified bentonite clay. Reduction of Cr^{+6} in synthetic solution was found to be as follows:

5 ppm (98%) > 10 ppm (98%) > 20 ppm (96%) > 50 ppm (91%)

- Best dose (0.25 g/100m/L or 2.5 g /L) for the reduction of Cr was applied on tanneries waste water. The order of efficiency for removing chromium in tannery waste water was similar to that of synthetic Cr^{+6} solutions. COD and BOD were also reduced significantly up to 71.6% and 81.2% respectively. It was concluded that H_2SO_4 modified bentonite clay is best suited for the removal of Cr in tanneries waste water.
- Contact time did not affect much, only H_2SO_4 modified bentonite clay gave a noticeable difference of contact time 4 and 8 h.

Conflict of Interest. The authors declare no conflict of interest.

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