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ROASTED CHINA CLAY AS A POTENTIAL ADSORBENT FOR THE REMOVAL OF HEAVY METALS FROM WATER AND WASTE WATER

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Abstract- *Environmental contamination of water due to toxic heavy metal ions is becoming a serious threat to the environment and human health in particular due to their detrimental accumulation in living tissues, soil and water bodies. Utilization of one waste material to control pollution caused by another is of high significance in the remediation of environmental problems. Clays are abundantly available natural material which has remarkable ability to adsorb heavy metals either in their natural form or after treating with some suitable chemicals. Many types of clays have been employed in removing heavy metals from industrial effluent. Researchers have studied the extent of uptake of different metals with the tested clays under different conditions such as pH, time of clay residence in solution with different concentration of metal and clay's mass. Langmuir, Freundlich adsorption isotherms are commonly used for fitting experimental data. Conventional technologies for the removal of heavy metals from wastewater are proving expensive due to non-regenerable materials used and high costs. Adsorption is an emerging technique offering the use of economical alternative materials as adsorbents for the removal of heavy metals from waste water. Roasted china clay is a waste of ceramic industry which is available free of cost in bulk. It has great potential to remove heavy metals ions from wastewaters. This paper is a review for the use of various clays to exhibit different affinities towards different metals and hence its importance to be employed as an effective adsorbent. For commercial use of roasted china clay to remove metal ions from wastewater, emphasis should be given to the selection of metal to get high sorption capacity. Adequate understanding of sorption mechanism and development of low cost methods facilitate better prediction of metal sorption.*

Key words-Adsorption, Langmuir, Fruendlich, regenerable, remediation, roasted china clay.*

I. INTRODUCTION

This review covers literature pertaining to the removal of heavy metals from water and wastewater using natural and modified clays as an adsorbent. In recent years, there have been increased concern about heavy metals released into the environment due to their cumulative toxic effects and serious environmental impact [1]. These metals, which find many useful applications in our life, are very harmful if they are discharged into the natural water resources posing serious health hazards [2] [3]. Heavy metal containing wastewaters cause detrimental effects to all forms of life upon direct discharge in to the environment [4] as they get accumulated in the soil, plants and water bodies [5] [6]. Different alternative techniques have been described in the literature for the removal of heavy metals including chemical precipitation [7], ion exchange, electrodialysis [8]), membrane separation [9]. All these methods have various disadvantages specifically, high capital investment and operational cost, low efficiency, low selectivity, high energy consumption and generation of residual sludge [10]. Adsorption has emerged as an alternative method to overcome the shortcomings of conventional methods for heavy metal removal [11] [12]. There have been many investigations on the use of different types of clays to remove heavy metals from wastewaters. In this article roasted china clay was used an adsorbent to remove metal ions from aqueous solutions. The effects of several parameters such as contact time, initial pH of the solution, initial metal ions concentration and adsorbent dose on metal removal are presented. In addition, the adsorption isotherms were described by using Langmuir and Freundlich models and kinetic experimental data were correlated by the pseudo first order and second order kinetic models.

II. ADSORPTION THROUGH ROASTED CHINA CLAY AND OTHER CLAYS

Ahmad et al. studied the use of Roasted China Clay (RCC) as an alternative adsorbent for the removal of Cr(VI) from aqueous solution by batch process. It was found that 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 concentration 25 mg/L and remove 69.84% of Cr(VI) of concentration 150 mg/L. The value of $R^2 \approx 0.9694$ and $R^2 \approx 0.9329$ 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. The RCC was found to be very effective and environment friendly adsorbent which can remove sufficient amount of Cr(VI) from aqueous solution in very small period of contact time (20 minutes) [13].

Ahmad et al. explored the feasibility of using Fired Ceramic as adsorbent for the removal of lead ions from aqueous solutions under different conditions. Batch studies were conducted to investigate the influence of pH, contact time, adsorbent dose and metal ion concentration on the adsorption of lead by fired ceramic. It was found that adsorption of lead on fired ceramic was a fast process as equilibrium was established within 2 hrs. The process was pH dependent. Maximum amount of Pb(II) (96.320%) was removed from aqueous solution at pH ranging 4-6. The experimental data was best fitted to Langmuir isotherm as indicated by the highest value of correlation coefficient (R^2 = 0.9917). Kinetic data showed the applicability of both pseudo first and pseudo second order model as indicated by the values of correlation coefficients (R^2 = 0.9974 and 0.9982). The findings showed that fired ceramic can be employed as potential adsorbent for the elimination of Pb(II) ions from aqueous solution as it is cost free adsorbent which is locally available in bulk [14].

Chooaksorn and Nitisoravut developed a novel technique for Ni(II) ions removal from aqueous solution which allowed simultaneous filtration and adsorption using chitosan coated ceramic membrane. The chitosan coated membrane was found to have maximum adsorption capacity of 123 mg/g which was comparable to those using chitosan nanoparticles from treated water. There were two Ni(II) adsorption mechanisms - column studies and breakthrough curves which showed rapid sorption of Ni(II) ions onto chitosan surface followed by the slower intra-particle diffusion of Ni(II) ions inside chitosan structure [15].

Ghorbel-Abid and Trabelsi-Ayadi investigated the interaction of Cr(III) and Cd(II) ions in solution with the local landfill clay of Jebel Chakir located in the northwest of Tunis (Tunisia, North Africa). Adsorption properties of natural clay and Na-purified clay in a chromium and cadmium rich aqueous solution by batch technique were studied. It was found that the uptake of Cr(III) by the purified clay was very fast and the quantity removed from the solution reached a maximum value within 15 min after mixing the purified clay and within 1 h for the natural clay, although the latter removes greater quantities of Cr(III) ions compared to the Na-purified clay. The uptake of Cd(II) reached maximum value within 2 h after mixing the purified clay, and 3.5 h for the natural clay. The Study indicated that the smectic clay JCK could be used as an efficient low-cost adsorbent. In single-element system, an increase in the pH-enhanced adsorption capacity for chromium was observed. The adsorption capacities of Cr(III) and Cd(II) by purified Jebel Chakir Clay were 64.5 and 62.5 mg/g, respectively. The removal efficiency was found to be strongly modified when the two metals are present in the solution. 110 mg/g increase for chromium uptake and 20 mg/g decrease for cadmium was observed in binary-element system. Their results provided further support of reaffirming that certain clays could be a promising agent in the fight against heavy metal pollutants in waste landfills when used as pollution barriers in waste storage sites [16].

Jia et al. functionalized a Japanese volcanic soil, Akadama clay, with metal salts ($FeCl_3$, $AlCl_3$, $CaCl_2$, $MgCl_2$, $MnCl_2$) and tested for Cr(VI) removal from aqueous solution. $FeCl_3$was selected as the most efficient activation agent. To investigate the independent or interactive contribution of influencing factors (solution pH, contact time, adsorbent dose, and initial concentration) to Cr(VI), adsorption was employed onto Fe-functionalized AC (FFAC). It was found that the initial concentration contributed most to adsorption capacity of Cr(VI) (53.17%), followed by adsorbent dosage(45.15%), contact time (1.12%) and the interaction between adsorbent dosage and contact time (0.37%). The adsorption was found to be pH dependent from 2 to 8. The adsorption selectivity of Cr(VI) was evaluated through analyzing distribution coefficient, electrical double layer theory, as well as the valence and Pauling's ionic radii of co-existing anions (Cl^-, SO_4^{2-}, and PO_4^{3-}). EDX and XPS analyses was carried out to demonstrate the adsorption mechanism of Cr(VI) onto FFAC which included electrostatic attraction, legand exchange, and redox reaction [17].

Hijjaji and Beraa carried out a comparative study on acid-treated montmorillonite-rich clay and amines (methylamine, morpholine, and aniline)-modified clay adsorbents for their abilities to remove chromate from aqueous solution. The rate of adsorption was found to be controlled by the intra-particle diffusion and mass transfer through the liquid film. It was observed that chromate adsorption was an endothermic process and took place spontaneously by physisorption.Various types of clays used were saturated clay (AN), acid treated clay (AA), methylamine–clay and morpholine– clay (A–Me, A–Mo) were type V, whereas those of aniline– clay (A–An) were type III. The maximum uptakes were found to be 105, 29, 15, 11, and 10 mol/kg for A–An, AN, A–Mo, AA, and A–Me, respectively [18].

Musso et al. studied sorption of Cu(II) and Zn(II) on three natural clays meeting the international requirements for use as liners by means of batch tests. The purpose was to determine the retention capacities of the clays for metal cations commonly present in urban solid waste leachates. Langmuir model was the best found to describe the sorption processes, offering maximum sorption capacities from 8.16 to 56.89 mg/g for Cu(II) and from 49.59 to 103.83 mg/g for Zn(II). The total amount of metal sorption was strongly influenced by the total specific surface area, the presence of carbonates and the smectite content of the clays. The results indicated the suitability of the tested clays for contributing towards the retardation of Cu(II) and Zn(II) transport through clay liners [19].

Jassim et al. produced ceramic purifier (CP) from a mixture of Iraqi raw materials, using Bentonite as a Clay, Porcelanite as a Silica, and Limestone as a flux by semi-dry compressing method and firing them at 1200˚C. The ceramic disc purifier could remove, on an average percentages of removal, 99.98% of turbidity, 78.86 % of the electrical conductivity , 81.61 % of the total dissolved solids, 73.45 % of Ca^{++}, 49.69 % of Na^{+}, 55.63 % of NO_3^-, 37.54 % of HCO_3^-.The results showed that CP has excellent adsorption ability for solutes of seven heavy metals, Mn, Fe, Pb, Cd, Co, Cu and Zn, at concentrations of 1 mg/L each and 10 mg/L each. The adsorption capacity of CP according to Freundlich model was: Pb>Cd>Cu>Zn>Mn>Co>Fe; the maximum capacity was for Pb (3.694 mg/g) and minimum was for Fe (1.517 mg/g). According to Langmuir model the adsorption capacities of CP were: Fe>Co>Mn>Zn>Pb>Cd>Cu; the maximum capacity was for Fe (1.337 mg/g), and minimum was for Cu (0.394 mg/g) [20].

Mohamed and Mosa conducted a study on the removal of some heavy metals ions (Hg^{2+}, Pb^{2+}, and Zn^{2+}) from aqueous solution by adsorption process using commercially activated carbon (Merck 2514), silica and ceramic as adsorbents. Adsorption process was carried out at the pH range 5.3 to 5.5 at room temperature. When three layers of adsorbents were used, it was observed that the percentage of adsorption increased and attained 100% removal for all element ions. The decrease in textural parameters like pore diameter and pore volume is known to be the influencing factors for the adsorption efficiency [21].

Gladysz-Plaska et al. studied the adsorption of La, Eu, and Lu on different forms of red clay: T-clay (thermally modified), R-clay (raw, unmodified), Na-clay (sodium form), H-clay (acid form), and HDTMA-clay (surfactant-modified form), in an initial concentration range of 10^{-4}–10^{-3}mol/ dm^3 at pH range of 2–10.They found that among the different forms of red clay, thermally modified clay (T-clay) is the most active lanthanide sorbent and HDTMA-clay has the lowest, but still sufficient affinity for lanthanides, i.e. 18 % of the adsorbent's cation exchange sites can be occupied by Eu in the equilibrium conditions. The study indicated that HDTMA-clay played an important role in the stabilization of nuclear wastes which contain both lanthanides and organic impurities. Finally it was stated that red clay is a good sorbent for lanthanides and as such it can potentially serve as a geological barrier for nuclear wastes [22].

Wei and Hai-Cheng studied the adsorption of sulphate in aqueous solutions onto organo-nano-clay prepared by natural zeolite and cationic surfactant cetyltrimethylammonium bromide (CTAB).The uptake of sulphate increased with the increase of contact time and temperature, and decreased with the increase of dosage. The maximum adsorption capacity was found to be 38.02 mg/g at 40 °C. It was suggested that chemisorption was the rate-controlling step for adsorption of sulphate onto organo-nano-clay. Meanwhile both intra-particle diffusion and boundary layer diffusion also contributed as well. The adsorption of sulphate onto organo-nano-clay was the result of: (1) ion-exchange between sulphate anions and the counterion Br− ions of adsorbent in solutions and (2) complex-precipitation occurring between sulphate anions and CTAB cations [23].

Sdiri et al. observed that the Calcareous clay of the Coniacian–Early Campanian Aleg formation, Tunisia, has high removal capacities due to the presence of carbonate impurities and has potential to be used as metal sorbent. The adsorption of Cu(II)and Zn(II) in single and binary systems fitted the Langmuir isotherm. In binary system, the adsorption capacity decreased for each metal due to competitive effect. The removal of Cu(II) ions showed greater potential than the removal of Zn(II) in the presence of Cu(II). It was found that good adsorptive capacities could be achieved under the operating conditions of 60 min contact time, pH 6, and clay concentration of 1 g/L at 25 ˚C. The results indicated the predominant role of carbonate impurities in the removal of Cu(II) and Zn(II). The negative ΔG values confirmed the feasibility of sorption process and their spontaneous nature. It was concluded that the use of natural clay from the Aleg formation as a starting material, to develop clay based cost-effective adsorbents with enhanced surface area and strong adsorptive capacities for various environmental pollutants in aqueous systems, could be envisaged [24].

Prakash et al. evaluated the influence of clay on the adsorption of heavy metals like copper and cadmium from simulated industrial wastewater on Chitosan and clay blend with ratio of (1:1), (1:2), and (2:1). The adsorption study was conducted in the pH range of 3 to 8. It was found that the percentage removal of copper increased with increase in pH from 3 to 5, after which there was a regular decrease in the percentage removal of copper with increase in pH up to 8. Clay provides enough adsorbable sites to overcome mass transfer limitations. The number of adsorbable sites for cadmium was more compared to copper, and thus the rate of recovery of cadmium was faster than copper. The percentage removal of cadmium is more than copper at all times on clay over nylon 6. Thus, it was concluded that the difference in adsorption was due to the influence of clay in the adsorption of heavy metals in comparison to synthetic polymer, nylon 6 [25].

Soon-Do et al. prepared porous ceramics by mixing fly ash from a thermal power plant with waste glass to resolve the environmental waste recycling problems. The mechanical milling method and annealing procedure was applied in which powder mixtures consisting of waste glass powder (70 wt %) and fly ash (30 wt %) was used at various heat treatment temperatures of 600, 650, 675 and 700 ˚C to obtain porous ceramics with a variety of structural and mechanical properties. An easy method for controlling the pore size and pore volume of porous ceramics utilizing waste resources (waste glass and fly ash) was developed. It was found that an irregular pore size in the ceramics matrix decreased and disappeared because the pores kept on shrinking as the heat treatment temperature was increased from 600˚C to 700˚C. Consequently, a more compact porous ceramics was produced at 700˚C than at 600˚C.600˚C was the most suitable heat treatment temperature for generating a porous ceramic containing the proper pore size and pore volume with good physical properties. In future, it was proposed to explore the possibility of applying porous filter ceramic to waste water adsorption and recycling problems [26].

Melichova and Hromada studied adsorption properties of natural betonite from lieskovec (Slovakia) for the removal of Pb^{2+} and Cu^{2+} ions from aqueous solutions by batch process. The adsorption of metal ions increased with the initial solution pH, initial metal ion concentration and contact time but decreased with the amount of adsorbent. The maximum adsorption capacity of the adsorbent for Pb^{2+} and Cu^{2+} ions calculated from the Langmuir isotherm was found to be 32.68 and 11.34 mg/g, respectively [27].

Zhao et al. used natural Akadama clay for Cr(VI) removal from aqueous solution. Cr(VI) adsorption on natural Akadama clay reached equilibrium in 180 min. The removal efficiency was 46.8% without pH adjustment. It increased to 73.8% at the optimum initial pH of 2. The maximum adsorption capacity was found to be 4.29 mg/g at an initial concentration of 50.0 mg/L and adsorbent dosage of 5 g/L [28].

Kalhoria et al. used Light weight Expanded Clay Aggregate (LECA) modified with an aqueous solution of magnesium chloride ($MgCl_2$) and hydrogen peroxide (H_2O_2) to remove Cr(VI) from aqueous solutions. The effect created by magnesium chloride on the modification of the LECA surface was greater than that of hydrogen peroxide solution. It showed a substantial increase in the specific surface area having a value of 76.12 m^2/g for magnesium chloride modified LECA, while 53.72 m^2/g and 11.53 m^2/g were found for hydrogen peroxide modified LECA and natural LECA, respectively. Maximum sorption capacities were found to be 198.39, 218.29 and 236.24 mg/g for natural LECA, surface modified LECA with H_2O_2 and surface modified LECA with $MgCl_2$, respectively. It was also observed that spent natural and surface modified LECA with $MgCl_2$ was best regenerated with HCl solution, while LECA surface modified with H_2O_2 with HNO_3 concentrated solution [29].

Djebbar et al. showed that activated Natural clay is a promising adsorbent for phenol removal from aqueous solution. They found that activated natural clay had monolayer adsorption capacity equal to 15 mg/g at pH 5.0 and adsorption process was very fast and physical in nature. The extent of the phenol removal increased with decrease in the initial concentration of phenol and contact time of solution. As the amount of the adsorbent was increased, the percentage of phenol removal increased accordingly [30].

Zhivaeva et al. studied the adsorption of high molecular mass acrylamide–sodium acrylate copolymers with a degree of ionization of 7–34% from concentrated aqueous solutions on Khvalynsk clay granules. It was carried out under dynamic conditions in the absence of inorganic electrolytes at an initial concentration of copolymer in the solution 2 g/L. It was found that copolymer adsorption decreases with an increase in the content of the adsorbent. The influence of the degree of polymer chain ionization on adsorption of copolymer macromolecules on the adsorbent surface was discussed. It was observed that copolymer with a low degree of ionization is adsorbed more intensely than the others [31].

Rao and Kashifuddin showed pottery glaze as an excellent adsorbent for the removal of Cu(II) ions from aqueous solution. The effects of contact time, pH, dose, concentration and temperature on adsorption of Cu(II) by batch process was studied. Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) were also studied and kinetic data was evaluated by using pseudo-first order and second order kinetic model over a wide range of concentrations. It was found that chemisorption process was involved [32].

Erraisa et al. conducted a comparative study using standard clays, namely kaolinite, KGa-2, smectite, SWy-1 and illite IMt-2 to provide a better understanding of the role played by the different clay species as well as the nature of the adsorption processes involved. Tunisian raw clay (Fouchana) composed of different species of clay minerals (kaolinite, smectite and minor illite) has efficiency for removal of anionic dye Reactive Red 120 (RR120) from aqueous solutions. Batch adsorption experiments were performed at ambient temperature and pH of the dye solutions. Acid-basic properties of the solid surfaces, electrophoretic mobility of particles, cation exchange capacity, amount of exchangeable cations and specific surface area were investigated. Kaolinite in the Fouchana raw clay was found to play a major role in anionic dye adsorption mainly due to its acidic surface sites and also due to exchangeable aluminium (III) cations acting as bridges between the clay mineral and the dye molecules. Smectite and illite most likely played a secondary role by adsorption on exchangeable calcium (II) and dissociated Al (III) OH groups [33].

Du et al. studied the adsorption mechanism of fluoride (F) on four clay minerals (kaolinite, montmorillonite, chlorite, and illite) under different F^- concentrations and reaction times by probing their fluoride superficial layer binding energies and element compositions using X-ray photoelectron spectroscopy (XPS).It was observed that at high F^- concentrations (C_o = 5–1000 mg/L), the amount of F^- adsorbed (Q_f), amount of hydroxide released by clay minerals, solution F^- concentration, and the pH increased with increasing C_o. As the C_o increases, F^- along with other cations are adsorbed to form a quasi-cryolite structure. At C_o>100 mg/L, new minerals precipitate and the product depends on the critical Al^{3+} concentration. At Al^{3+}>10–11.94 $molL^{-1}$, cryolite forms, while at Al^{3+}<10–11.94 $molL^{-1}$, AlF_3 is formed. At low C_o (0.3–1.5 mg/L), proton transfer occured, and the F^- adsorption capabilities of the clay minerals increased with time [34].

Salim and Munekage studied the kinetics adsorption of lead from aqueous solution using silica ceramic in batch methods. The effect of solution pH, initial metal ion concentration, temperature and adsorbent mass on metal ion removal was taken into consideration. It was found that the maximum Pb removal achieved was 2.7 mg/g of silica ceramic. The findings showed that silica ceramic has excellent potential for the removal of lead from waste water [35].

Bhakta et al. performed experiment to draw a mercury adsorption stoichiometry of ceramic and activated carbon from aqueous phase in two parts - first part dealt with the effect of three different pH 4, 7 and 10, whereas second part was designed to determine the effect of three temperatures 15, 25 and 35°C.SEM-EDS analysis of adsorbents clearly showed highly uneven and porous surface structure of activated carbon as compared to ceramic. Ceramic contains SiO_2 (73.65%) as a major constituent with negligible amount of metals, whereas C (98.46%) is the only constituent in activated carbon. Activated carbon exhibited 15 to 52% (experiment on pH effect) and 49 to 70% (experiment on temperature effect) higher adsorption efficiency than that of the ceramic. It was inferred that the activated carbon is a proficient Hg adsorbent compared to the ceramic because of having greater available Hg adsorptive total surface area than ceramic. On contrary, high ionic competition on the surface of ceramic prevents more Hg adsorption from aqueous phase which was entirely absent in activated carbon. The highest Hg adsorption in ceramic and activated carbon occurred at pH 7 and 4, respectively. Highest temperature (35°C) applied exhibited a higher rate of adsorption (ceramic 32-35% and activated carbon 0.13-0.84%) than the remaining temperatures. Therefore, temperature (35°C) of the medium promoted the used adsorbents to remove higher quantity of Hg from water phase due to surface group activity of adsorbents, ionization and movements of Hg ions which increased with increasing temperature leading to higher rate of Hg adsorption [36].

Nita et al. prepared micro-particles from non-toxic biopolymer obtained by dropping aqueous solutions of sodium alginate in a calcium chloride solution to investigate the removal of bivalent ions (Pb^{2+}, Cd^{2+}) from synthetic wastewater. Alginate adsorbent materials were tested due to its known affinity for the bivalent metal ions. It was found that microparticle beads which contained gas forming agent in 1:1 ratio was more efficient in removing these ions [37].

Mohapatra et al. investigated As(V) removal efficiency by different clay minerals as a function of solution pH, time, As(V) concentration and temperature. The arsenic mobility was determined by the As(V) released from the loaded samples by leaching with various aqueous solutions. The maximum adsorption capacity was calculated by fitting the Langmuir equation to the adsorption isotherms which was found to be 0.86, 0.64, and 0.52 mg As(V)/g of kaolinite, montmorillonite and illite, respectively. Among the studied clay minerals, kaolinite proved to be the best As(V) adsorbent and montmorillonite had strong retention capacity [38].

Kan et al. investigated the adsorption characteristics of tourmaline for Cu(II), Pb(II), Zn(II) and Cd(II) as well as their selectivity on tourmaline. The adsorption on tourmaline was found to depend on experimental conditions, particularly the pH medium and initial concentration of the metal ions. The adsorption capacity of tourmaline for single metal was found to decrease in the order of Pb>Cu>Zn>Cd and inhibition dominance in two metal systems was Pb>Cu, Pb>Zn, Pb>Cd, Cu>Zn, Cu>Cd and Cd>Zn. Thus it was concluded that tourmaline preferred adsorption of Pb over Cu, Zn and Cd [39].

Zhai and Li studied the adsorption kinetics of 100~mg/L arsenite with two types of clay minerals (kaolinite and montmorillonite) in three types of solutions (calcium chloride, sodium sulfate, sodium bicarbonate), respectively. The adsorption capacity of montmorillonite towards arsenic was found lower than kaolinite. It was also observed that the changes of diffuse coefficient could be used to explain the adsorption trend on clay mineral surface. At the beginning of the reaction, diffuse coefficient, D_i, was large, which decreased with the progress of the reaction attaining equilibrium gradually. The results indicated that the adsorption processes of As(III) was controlled by the reaction rate and diffusion factor. The half-life of As (III) adsorbed on kaolinite was nearly 10 hours and half-life of As (HI) on montmorillonite was approximately 11 hours. With increasing concentrations of calcium chloride and sodium bicarbonate, the adsorption capacities of As (1II) enhanced but the increasing concentration of sodium sulfate reduced the adsorption of As (III). The adsorption of As (III) could be promoted by bicarbonate anions and calcium cations and restrained by sulfate anions. Adsorption at the sourish aqueous medium (pH=8) favoured the removal of As (III) [40].

Green-Ruiz evaluated the ability of the mineral clay montmorillonite to remove mercury from aqueous solutions. Studies on effects of mercury concentration and pH of the solutions were carried out. It was found that optimum pH for the effective adsorption lies between 6.0 to 7.5 and rate of adsorption increased with increase in mercury concentration [41].

Papandreou et al. examined the potential of ceramic structures produced in the form of pellets in a laboratory scale pelletizing machine by using coal fly ash as adsorbent for the removal of heavy metals. Morphology of adsorbent, physical and chemical characterization was studied by SEM, XRD and AAS which showed that fly ash is composed of spherical, oval and irregular particles. Ceramic structures showed good adsorption and low desorption capacity which can effectively remove copper, lead and cadmium ions from aqueous solutions. Furthermore, removal of heavy metals strongly depended on the solution pH as well as on the properties of fly ash structures (e.g Porosity).A preliminary mechanism for the adsorption on fly ash surface correlated with the formation of metal surface species on the surface hydroxyl sites (SiOH, AlOH, and FeOH) have been discussed [42].

Kamel et al. assesed the adsorption of heavy metals such as Pb(II), Cu(II), Fe(III), Mn(II) and Zn(II) on kaolinite clay. Kaolinite is easily available at low cost and it is a good ion exchanger having high metal adsorption capacity. The affinity of kaolinite clay for the sorption of investigated metal ions was in the order-: $Cu^{2+}> Fe^{3+}>Pb^{2+} = Mn^{2+}> Zn^{2+}$. The desorption percentage for Fe^{3+}, Pb^{2+}, Mn^{2+}, Zn^{2+} and Cu^{2+} from kaolinite clay by distilled water was very low, almost zero but regeneration using saturated solutions of HCl was the most suitable [43].

Muminov and Gulyamova studied the adsorption of polar organic substances (methanol, pyridine and acetonitrile) and water from the vapour phase on microporous adsorbent prepared by the substitution of polyhydroxyaluminium (PHAM) ions for the sodium ions of natural montmorillonite clay. The series of adsorption isosters were measured, and the differential isosteric heats of adsorption were calculated over the wide range of fillings. The heats of adsorption of polar substances from vapour phase on the PHAM over the whole filling range were found higher than their heats of adsorption on the initial Na-montmorillonite [44].

Atun and Kilislioglu investigated the adsorption behaviour of Cs ions on montmorillonite-type clay in the presence of potassium ions, using a radiotracer technique. The initial concentration of K^+ added to CsCl was between 10.4 and 10.1 mol/L. The addition of K^+ to the CsCl solution at different concentrations reduced the amount of Cs^+ adsorbed on the clay. The ratio of Cs^+ exchanged calculated from a linearized form of Langmuir plot was in agreement with the ion exchange isotherms of CsK ions. It was concluded that the surface of montmorillonite exhibits slightly higher affinity for Cs than for K [45].

Seng et al. used De-oiled spent bleaching clay activated either by acid treatment followed by heat activation or by heat activation alone at temperatures between 200 and 800°C as adsorbent for the removal of Cr(VI) and Ni(II) ions. The adsorption capacities of Cr(VI) for both series studied, increased as the activation temperature increased until 300˚C and decreased at higher temperatures. At lower pH, more than 95 % of the Cr(VI) was adsorbed from a solution with initial concentration of 1 mg/L per gram of adsorbent activated at 300˚C.Two maximal values of adsorption capacities of Ni(II) were observed at activation temperatures of 200 and 500˚C for acid-treated samples, whereas these were at 200 and 700˚C for the non-acid treated samples. The amount of Ni(II) adsorbed increased with the pH of the solution for all samples studied. The maximal adsorption capacities of the adsorbents in solution containing initial Ni(II) concentration of 5 mg/L per 0.5 g of adsorbent and at pH 6 were found to be 44 and 42%, respectively, for the acid-treated sample activated at 500˚C and for the non-acid treated sample activated at 700˚C [46].

Neubauer et al. studied the influence of hydroxamate siderophore desferroxamine B (DFOB) on the adsorption of Cu, Zn and Cd on Na-montmorillonite and kaolinite. In montmorillonite suspension, heavy metal sorption was enhanced by DFOB due to electrostatic interactions. In kaolinite suspensions DFOB drastically diminished heavy metal sorption. The different effects of DFOB on heavy metal sorption by kaolinite and montmorillonite is due to the large difference in their permanent negative surface charge. The effect of DFOB on the adsorption of heavy metal ions on montmorillonite and kaolinite decreased in the sequence Cu > Zn > Cd in accordance with complex stability constants [47].

Lin and Puls investigated six clay minerals [halloysite (IN), M-kaolinite (sedimentarykaolinite), EPK-kaolinite (weathered kaolinite), illite(MT), illite/montmorillonite (MT), and chlorite (CA)]for the adsorption/desorption and oxidation/reduction of arsenic. It was observed that the halloysite and the chlorite had much greater As(V) adsorption (25–35 folds) than the other clay minerals. The clay minerals had lower As(III) adsorption than As(V) adsorption which was affected by pH. Desorption of arsenic from the clay minerals was significantly influenced by the aging process. The quantities of extractable As(III) and As(V) decreased with increasing aging time. The less extractability of arsenic may have resulted from: (1) arsenic initially adsorbed to the clay surfaces may have diffused into internal pores of the clay aggregates and (2) the dehydration of retained arsenic on the clays could have led to enhancing the bonding of As(III) or As(V) to the clay [48].

Hongping et al. studied the interaction between minerals and heavy metals through the selective adsorption experiment of Ca-montmorillonite, illite and kaolinite to Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} and Cr^{3+} ions at different conditions. It was found that Cr^{3+} is most effectively sorbed by all the three minerals. Pb^{2+} showed a strong affinity for illite and kaolinite while $Cu^{2+}$for montmorillonite. The amount of heavy metals adsorbed by minerals increased with increasing pH of the solution [49].

Sanchez et al. studied the adsorption of some heavy metals in industrial waste water on different silicate minerals. These adsorbents (mainly clay minerals) are readily available, inexpensive materials and offer a cost-effective alternative to conventional treatment of wastes from the metal finishing industry. The Findings showed that some mineral species are suitable for the purification of such residual waters down to the limits prescribed by current legislation concerning industrial wastes. The clays with the greatest specific surface area (Orerasepiolite and Vallecassepiolite) and clays with the greatest CEC (bentonite) showed the strongest adsorption capacity for Zn^{2+}.It was found that the sepiolite (Orera) may be used as a low-cost adsorbent for the effective retention of Zn^{2+}, Cd^{2+} and Cu^{2+} and, to a lesser extent, of Ni^{2+}. The retention of the metal cations follows the sequence: $Cd^{2+}> Cu^{2+}> Zn^{2+}> Ni^{2+}$. The adsorption of the four metal ions increased with the increase in pH. The adsorption of Cd^{2+} decreased slightly with the increase in ionic strength. As the particle size of the adsorbent decreased, adsorption increased [50].

Ajmal et al. investigated the leaching of heavy metals (zinc, lead, cadmium, chromium, copper, manganese, nickel and cobalt) from glazed surfaces of tea mugs under different conditions. The leachates used were: tea at 80˚C, orange juice at room temperature and 4% acetic acid at room temperature, 40˚C and 60˚C, respectively. It was found that concentration of metal leached in tea were in the range (in microgram/l): Zn, 343-1262; Cd, 25-349; Fe, 122-342; Cr, 66-945; Cu, 135-853; Mn, 166-424 and Ni, 70-134. The concentration of heavy metals extracted by 4% acetic acid at room temperature were found in the range (in microgram/l): Zn, 18-192; Fe, 143-372; Cu, 51-190; and Mn, 0-48; at 40˚C (in microgram/l): Zn, 118-837; Fe, 124-639; Cu, 230-722; and Mn, 30-63 and at 60˚C (in microgram/l): Zn, 33-900, Fe, 83-576; Cu, 90-685 and Mn, 43-778, respectively [51].

III. CONCLUSIONS

Activated carbon normally used for adsorption process proves costly. To replace the expensive activated carbon, a search for a wide range of inexpensive adsorbents has been taken into task. The process of adsorption for the removal of heavy metals from solution has been extensively studied on various types of clay based adsorbents which were found to be very efficient and cost effective. Relatively shorter time, acid pH range and high affinity for metal ions was observed. Metal sorption has been generally described by using Langmuir and Fruendlich models. The utilization of one waste material to control pollution caused by another is of high significance in the remediation of environmental problems. The use of inexpensive and efficient material (clay along with Roasted china clay) for the removal of heavy metal ions have been reviewed. It was observed that roasted china clay is itself a waste material produced in bulk by ceramic industries which has to be disposed off. Roasted China Clay has the ability to adsorb high concentration of heavy metals making it suitable for removing heavy metal ions from dilute aqueous solutions. The method of removing heavy metal ions from wastewater by using clay based adsorbent has proved to be more efficient, cost effective and eco-friendly than the conventional physico-chemical methods.

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