International Journal of Application or Innovation in Engineering & Management (IJAIEM)
Web Site: www.ijaiem.org Email: editor@ijaiem.org, editorijaiem@gmail.com
Volume 2, Issue 7, July 2013 ISSN 2319 - 4847

A comparative study on the removal of heavy metals by adsorption using fly ash and sludge: A review

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ABSTRACT

Increased industrial activities have resulted in the generation of large amounts of wastewater polluted with heavy metals. Adsorption is recognized as an effective and economic method for low concentration heavy metal wastewater treatment. Activated carbon is the commonly used adsorbent, the major drawback being the high cost. Low cost adsorbents from waste materials have been tried by different researchers. The current research is focussed on the need to find an economical adsorbent for the removal of heavy metals from aqueous solutions. Both fly ash and sludge are produced in large scale and cause major disposal problems. This paper reviews the use of sludge and fly ash as an adsorbent for the removal of heavy metals from aqueous solutions which meets the dual goals of disposal and treatment. It is evident from the existing literature that both fly ash and sludge can be effectively used as an adsorbent for heavy metal removal. Different modes of operation and activation methods to improve the adsorption capacity are the future scope for the research.

Keywords: Adsorption, activated carbon, fly ash, sludge, heavy metal, activation

1. INTRODUCTION

The presence of heavy metals in the environment is of major concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment [1]**.** It is a well known fact that heavy metals can damage nerves, liver, and bones and could also block functional groups of essential enzymes. Conventional methods for removing dissolved heavy metal ions include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment, application of membrane technology, evaporation recovery and biological treatment [2]. Although all the heavy metal wastewater treatment techniques can be employed to remove heavy metals, they have their inherent advantages and limitations [3]. Among all these methods, adsorption process is considered better than other methods because of convenience, easy operation and simplicity of design. Further, this process can remove/ minimize different types of pollutants and thus have wider applicability in water pollution control. A fundamentally important characteristic of good adsorbents is their high porosity and consequent larger surface area with more specific adsorption sites [4].

Activated carbons display high adsorption capacity; but the high cost presents a major drawback for practical applications, especially in the field of industrial effluent treatment where activated carbons may play a very useful role. Efforts have been made to develop low cost adsorbents for the removal of heavy metals from aqueous solutions. A number of natural and synthetic adsorbents like agricultural waste's carbon [5]-[7], clay [8], neem leaves [9], cooked tea dust [10], zeolites [11], teak leaves activated carbon [12], cashew nut shell activated carbon [13], fly ash [14] etc have been studied by various researchers for the removal of heavy metals.

Fly ash is one of the residues generated in combustion, and comprises the fine particles that rise with the flue gases. Fly ash is generally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys of coal-fired power plants, and together with bottom ash removed from the bottom of the furnace. It is one of the numerous substances that cause air, water and soil pollution, disrupt ecological cycles and set off environmental hazards[15]. Fly ash has potential use in wastewater treatment because of its major chemical components, which are alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, and its physical properties such as porosity, particle size distribution and surface area. Moreover, the alkaline nature of fly ash makes it a good neutralising agent[16].

The sludge removed from drinking and waste water treatment plants generates growing amounts of waste, which have to be managed. Sludge disposal is now recognized as one of the most important issues by all environmentalists. Fly ash and sludge which cause major disposal problems have been tried for the removal of heavy metals which serves the dual purpose of waste management and waste water treatment. This review article discusses about the usage of fly ash and sludge as an adsorbent for heavy metal removal from aqueous solutions.

2. DISPOSAL PROBLEMS OF FLY ASH AND SLUDGE

In India, about 90 million tons of fly ash is produced per year from burning approximately 200 million tons of coal per year producing ash ponds that occupy 65,000 acres of land. Nearly 73% of India's total installed power generation capacity is thermal, and 90% of it is coal-based. The power requirement of the country is rapidly increasing with increased growth in the industrial sectors. As a result, the quantity of ash produced is also on the increase. The World Bank has cautioned India that by 2015, disposal of coal ash would require 1000 m^2 or 1 km^2 of land per person. Fly ash management therefore poses a serious environmental problem for India and requires considerable research and development. At present, approximately 10% of the ash is used for ash dikes and land fill, and approximately 3% of the ash is used in other construction industries. Thus, the use of fly ash as an adsorbent is an attractive alternative from both an economical and environmental point of view[17]. Approximately 32% of the total fly ash produced in Europe is used as cement raw material, as constituent in blended cements and as addition for the production of concrete. In 2008, about 18 million tonnes of fly ash were used in the construction industry and for production purposes in underground mining [18]. The high temperature of burning coal turns the clay minerals present in the coal powder into fused fine particles primarily composed of aluminium silicate. Fly ash produced thus possesses both ceramic and pozzolanic properties [15].

Sludge disposal is a worldwide problem and a wide variety of disposal routes have been adopted as directed by local conditions. The final resting place of the sludge is either on the land, in the air or in the water. Disposal of sewage sludge to the ocean is now banned because of its perceived environmental effects. Due to the unstable nature of biomass, inadequate sewage sludge disposal may cause environmental impact and health problems. In order to achieve acceptable volume-reduction and stabilization of sewage sludge, many sludge incineration facilities were built and operated. Although, this reduction is sufficient to stabilise the sludge, a large volume remains for disposal. There is the possibility of energy recovery in the form of heat, which in turn can be used in various stages throughout the process. The flue gases leaving the incinerator at a temperature of approximately 850°C can be passed through a combustion air preheater. This results in no fuel requirement for combustion process, smaller furnace and a reduced volume of flue gases to be treated. The re sidue of sewage sludge produced from incineration facilities, i.e. the sewage sludge ash (SSA), is primarily an inorganic and stable material. The SSA predominantly contains silicon oxide and aluminium oxide. Although sludge incineration can help to stabilize and reduce the volume of sewage sludge, the SSA still needs to be wasted and disposed. In order to minimize the need of final disposal, many studies have been dedicated to develop reuse technologies of SSA. Among those feasible reuse technologies, most utilize SSA as a recycled material since it is rich in silicon oxide and aluminium oxide [19]. Disposal of waste sludge is a major economical factor in operation of wastewater treatment plants, 30–50% of the annual operating costs are related to sludge dewatering alone [20]. Therefore, it is pressing to seek a cost effective and innovative solution to the problem caused by the sludge disposal.

3. COMPOSITION OF FLY ASH AND SLUDGE

Fly ash material solidifies while suspended in the exhaust gases and is collected by electrostatic precipitators or filter bags. Since the particles solidify while suspended in the exhaust gases, fly ash particles are generally spherical in shape and range in size from 0.5 µm to 100 µm. Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3) and calcium oxide (CaO). Table-1 gives the chemical composition of Indian coal [21] .

Table 1: Chemical composition of Indian coal ashes

Compounds	Fly ash	Pond ash	Bottom ash
SiO_2	38–63	37.7–75.1	23–73
Al_2O_3	27–44	11.7–53.3	13–26.7
TiO_2	0.4–1.8	0.2–1.4	0.2–1.8
Fe_2O_3	3.3–6.4	3.5–34.6	4–10.9
MnO	0–0.5	bd–0.6	bd–0.3
MgO	0.01–0.5	0.1–0.8	0.1–0.7
CaO	0.2–8	0.2–0.6	0.1–0.8
K_2O	0.04–0.9	0.1–0.7	bd–0.56
Na_2O	0.07–0.43	0.05–0.31	bd–0.3
LOI	0.2–3.4	0.01–20.9	0.61–51.6

The composition and properties of the water treatment sludge depends typically on the quality of treated water as well as on types and doses of chemicals used during the water treatment. Depending on the quality of the treated water, the

water treatment sludge contains suspensions of inorganic and organic substances. Typically hydrated alumina oxides and iron oxides are present (this depends on coagulants used for the treatment). Table.2 shows the average composition of the water treatment sludge [22].

Table 2 Typical composition of the alumina and iron sludge (average values)

Indicator	Alumina sludge	Iron sludge
pH	7.6	7.97
Total dry mass %	5.46	3.15
Ignition loss%	31.6	28.8
R_2O_3%	31.2	28.9
Al_2O_3 %	28.5	2.76
Al %	15.07	-
Fe_2O_3 %	2.7	27.6
Fe %	1.88	19.5
Ca %	6.78	5.66
Mg %	1.56	1.32
Mn %	0.19	0.10
N total %	0.006	0.008
P total %	0.002	0.003

4.SLUDGE BASED ADSORBENTS AND THEIR PERFORMANCE

Sludges obtained from water treatment plant, waste water treatment plant, activated sludge and sludges from various industries have been tried by many researchers. Sludge also has been treated differently before trying as an adsorbent.

4.1. Water treatment sludge

Groundwater treatment plant sludge (GWTPS) was used as an adsorbent for heavy metal removal and at optimum conditions 100% of Zn(II) and Cu(II) were removed at initial concentrations of 10 mg/L and 65 mg/L of Zn(II) and Cu(II) respectively [23]. Factors that affect Zn(II) and Cu(II) removal from aqueous solutions were pH of solution, dosage of adsorbent, initial metal concentrations and contact time. Alum sludge was recycled using a chemical precipitation process to promote the removal of lead metal in wastewater [24].. The removal of lead from synthetic wastewater was found to be effective when reused sludge was employed thereby reducing the fresh alum dosage. Lead hydroxide co precipitated with alum sludge in alkaline conditions.

Spent alum-derived water treatment sludge, a material which is often disposed of in landfills, can be employed as an effective adsorbent for sorption of Cr(III), Pb(II) and Cr(VI) from aqueous solutions25. Adsorption capacity was strongly dependent on initial metal ions concentration, initial pH and dosage. Experimental data can be fitted well to Freundlich and Langmuir equations. Kinetic data is strongly correlated to a pseudo-second-order kinetic model and for Cr(III) and Pb(II), the adsorbent surfaces can be regenerated using 0.1 M HNO_3. A comparative study using seven inorganic solid wastes showed that water treatment sludge has a substantial capacity to adsorb metal cations and this is attributable to the amorphous nature of the hydroxyl-Al present and therefore its high surface area [25].

Aluminium based water treatment residuals can be beneficially used to remove water borne Selenium concentrations [26]. Studies conducted using dewatered alum sludge found that it has a high ability for phosphorous removal and pH plays a key role in the adsorption process [27].

4.2. Sewage sludge

Studies were conducted using primary, secondary, mixed and physiochemical treatment and agro-processing industry sludge for the removal of chromium [28]. The results revealed that physiochemical treatment sludge had the best adsorption capacity for chromium. Kinetic adsorption studies showed that almost complete removal of chromium in solution was reached in the first two hours of reaction with all types of sludge. Kinetics and isotherms of biosorption of Zn(II) onto pre-treated powdered waste sludge obtained from a paint wastewater treatment plant was studied by Kargi and Cikla, 2006 [29]. The Langmuir isotherm best fitted the data. The maximum biosorption capacity for Zn(II) ions was found to be 82mg/g of sludge.

Batch adsorption experiments using municipal sewage sludge coated with iron oxide was found to be a good adsorbent for the removal of Cd2+, Cu2+, Pb(II) and Ni2+. The iron oxide coated sludge had higher surface area, pore volume and iron content, compared to uncoated sludge. The suitable pH value in the extraction was 7 for adsorption of Cd2+ and Ni2+ [30].
Studies on the removal of three basic dyes from aqueous solutions by adsorption on sewage treatment plant biosolids as an adsorbent were carried out and the results showed that the biososorption of basic dyes into STP biosolids was found to be effective, efficient and promising and the biosolids could be considered as a low cost adsorbent for the decolourization of industrial effluents [31].

4.3. Sludge derived materials

The adsorbent derived from sewage sludge was found to be suitable for the removal Cd^{2+}[32]. The efficiency of adsorption of Ni^{2+} from aqueous solutions varied with pH, adsorbent dosage, initial ion concentration and time. Four different types of materials were made from dried sludge and tested for the removal of methylene blue [33]. It was found that dried sewage sludge has a high potential for the removal of methylene blue. Activated carbon remains the best adsorbent but dried sewage sludge could find some practical interests due to its low cost.
Two different sewage sludge based adsorbents were made and used for the removal of Hg(II), Pb(II), Cu(II) and Cr(III) . The product obtained by $ZnCl_2$ activation showed a better development of surface and porosity than the product obtained by pyrolysis process. Equilibrium data was well suited to the Langmuir model and showed the capacity order Hg(II) > Pb(II) > Cu(II) > Cr(III) [34]. The produced activated carbons from sewage sludge have a remarkable surface area and found to be a good adsorbent for the removal of organic compounds such as crystal violet, indigo carmine and phenol from aqueous solutions [35] .
Urban sewage sludge was subjected to two different procedure via microwave irradiation and used for the removal of Cu(II) from aqueous solutions. The kinetic study demonstrated that the adsorption process followed the second order kinetic equation [36]. A review on the effectiveness of different sewage sludge based adsorbents showed that the properties of the adsorbents were highly dependant upon both the production/conversion method and the nature of sludge itself [37].

4.4. Sewage sludge ash

Studies were conducted using carbon based adsorbents from sewage sludge to remove metals from water [38]. It was found that carbon based adsorbents prepared from sewage sludge pyrolysis was effective for the removal of Na^{+}, K^{+}, Ca^{++},and Mg $^{2+}$ from saline waters. The percentage of ion adsorption followed the sequence Na^{+}> K^{+}> Ca^{+}> Mg^{2+}.
Sewage sludge ash was found to be a good adsorbent for the removal of nickel and cadmium. Equilibrium in the adsorption of Ni(II) and Cd(II) on sewage sludge ash was reached at two hours and the optimum pH for maximum adsorption was 6 and the metal ions removal was nearly constant for pH > 6. This may be attributed to the surface charge development of the sewage sludge ash and the concentration distribution of metal ions since both of them are pH dependent. Langmuir isotherm better fitted the experimental data [39].
Sewage sludge ash can be used as an effective adsorbent for copper removal from wastewater and the efficiency was greater than 98% [19]. The primary mechanisms of copper removal by sewage sludge ash included electrostatic attraction, surface complex formation and cation exchange. Carbons with different adsorbent properties were produced from urban sewage sludge- one by single pyrolysis and the other with chemical activation by $ZnCl_2$. Both were able to adsorb materials although carbon with activation displayed higher capacity. Metal adsorption was also highly pH dependant [40].

4.5. Different sludges

Batch equilibrium sorption experiments were used for four types of sludge, which were drinking water treatment plant sludge, landfill leachate sludge, anaerobically digested sewage sludge and sewage sludge. Sewage sludge removed cadmium most efficiently from aqueous solutions [41]. The capacity of dairy sludge to remove Pb(II) and Cd(II) was investigated by Sassi et al. Equilibrium uptake increased with increased metal ion concentration for Pb(II) and Cd(II) and temperature increase from 20^0C to 40^0C enhanced metal uptake [42].
Waste sludge samples obtained from a paint industry wastewater treatment plant was dried, ground and pre-treated with 1% H_2O_2 to improve the biosorption capacity. The powdered waste sludge (PWS) was sieved to different mesh sizes and used for biosorption of zinc(II) ions from aqueous solution. Maximum biosorption capacity was found to be 82 mg/g29. Batch adsorption experiments were carried out for the removal of Pb(II) from aqueous solutions using clarified sludge collected from steel plant as an adsorbent and the adsorption capacity was obtained as 92.51 mg/g of adsorbent [43]. Freundlich isotherm fitted better. Biosorption experiments were performed using different pre-treated activated sludge as bioadsorbent for Cu^{2+}, Cd^{2+} and Ni^{2+}. Pre-treatment with NaOH was found to improve the adsorption capacity of the sludge whereas the treatment with HCl reduced it. The treated and untreated sludge showed great affinity towards Cu^{2+}, Cd^{2+} and low affinity towards Ni^{2+} [44].

Activated sludge was treated with NaOH for the biosorption of heavy metals and found that the adsorption capacity of the sludge was improved by treating the sludge with NaOH solution when compared to untreated sludge [45]. pH had a clear influence on the sorption capacity of activated sludge for removal of heavy metals and it was found that the optimum value was equal to 4 at which the adsorption capacity of the sludge was found to be higher. Acid treatment with activated sludge biomass can effectively remove Cr(VI) from aqueous solutions and was remarkably pH dependent [46]. Dried activated sludge can remove Cu(II) and Pb(II) from aqueous solutions and the process followed pseudo-second order equations. The equilibrium data fitted well to both Langmuir and Freundlich isotherms [47]. Activated sludge has distinct potential for Pb(II) and Hg(II) sequestration in an acidic cationic exchange basis. Desorption tests demonstrated that hydrochloric acid is a powerful agent to leach the sequestered metal ions from the biosolids [48]. pH had a clear influence on t he sorption capacities of activated sludge for Cu, Cd, Ni, Zn and Pb. The maximum sorption uptake of the studied metals by activated sludge showed the decreasing order Pb>Cu>Cd>Zn>Ni [49].

The modifications done to various types of sludges and maximum uptake under optimum conditions are given in Table 3.

Table 3.Modifications done on sludge and maximum uptake under optimum conditions

Material	Modification	Operating condition	Uptake under optimum condtions	References
Ground water treatment plant sludge	Dried, ground and sieved	pH - 2 to 3	100% of Zn(II) and Cu(II)	Ngatenah et al., 2010
Recycled alum sludge	Recycled using a chemical precipitation process	pH -11.6	96-98% Pb removal	Chu, 1999
Water treatment sludge	Treated with alum and activated carbon	pH-3 to 6	Pb^{2+} - 0.3mmol/g Cr^{3+}- 0.37mmol/g	Zhou and Haynes,2011
Water treatment sludge	Acid pretreatment with 0.10 M HNO_3	pH- 6	0.479mmol/g Pb(II) and 0.107 mmol/g Cd(II)	Zhou and Haynes, 2011
Aluminium based water treatment sludge	Air dried and passed through 2mm sieve size	pH- 6.5	1.4-2.1 mg/g Se(VI)	Ippolito et al., 2009
Dewatered alum sludge	Dewatered, air dried, ground and sieved	pH=4.3	0.7-3.5 mg/g P	Yang et al., 2006
Wastewater sludge	Dewatered in filter press and dried	pH-6	25.8 mg/g Cr	Faout et al., 2008
Industry waste water treatment plant sludge	Pretreated with 1%hydrogen peroxide, dried, ground and sieved	pH- 5	82 mg/g Zn(II)	Kargi and Cikla, 2006
Sewage sludge	Dried, crushed and sieved to size less than 0.2mm and treated with Fe(NO3) $_3$9H2O	pH-12	17.3 mg/g Cu 14.7 mg/g Cd 7.8 mg/g Ni 42.4 mg/g Pb	Phuengprasop et al., 2011
Sewage sludge	Dried in an oven and sieved	pH 8-9	23.2 mg/g dye	Alam, 2004
Sewage sludge	Dewatered, dried in oven, sieved to size between 1 and 3 mm, activated with ZnCl2, and treated with N_2 at 850 ^{0}C.	pH-5.5 to 6	16.7 mg/g Cd2+ 9.09 mg/g Ni2+	Zhai et al., 2004
Sewage sludge	Dried, pyrolysed and chemically activated	NA	147 mg/g methylene blue with dried sludge	Fostoy et al.
Sewage sludge	Chemical activation with	pH-5	137.2 mg/g Hg(II)	Otero et al., 2009

	$ZnCl_2$ followed by pyrolysis	pH-4 pH-4 pH-3	46.3 mg/g Pb(II) 31.7 mg/g Cu(II) 9.9 mg/g Cr(III)	
Sewage sludge	Dried, powdered, treated with $ZnCl_2$, filered and heated in a microwave under a nitrogen flow, washed with HCl, dried and ground	pH-5	3.88 mg/g Cu(II) for sludge with single pyrolisis 10.56 mg/g for sludge with chemical activation	Wang et al., 2006
Sewage sludge ash	Heated in an inert atmosphere at 450 ^{0}C	NA	76.78% Na+ 66% K+ 35.12% Ca2+ 42.84% Mg2+	Gasco et al., 2005
Sewage sludge ash	Dewatered sludge incinerated at 600^0 C, ground and screened	pH-6	7.65 mg/g Ni 7.1 mg/g Cd	Elouear et al., 2009
Sewage sludge ash	Dewatered and burned in an incinerator at 700 ^{0}C, ground and sieved	pH-4-6	4.139 mg/g Cu(II)	Pan et al., 2003
Sewage sludge	Chemical activation with $ZnCl_2$ followed by pyrolysis	pH-5-6 pH-4 pH-4 pH-3	175.4 mg/g Hg(II) 64.1 mg/g Pb(II) 30.7 mg/g Cu(II) 15.4 mg/g Cr(III)	Rozada et al., 2008
Sewage sludge	Treated with 1 N HNO_3 solution, washed, deionized and dried in an oven.	pH-5	0.38 mmol/g Cd	Choi and Yun, 2006
Dairy sludge	Dried, ground and sieved	pH-5	148.6 mg/g of Pb(II) and 66.7 mg/g of Cd(II)	Sassi et al., 2010
Paint industry sludge	Dried, sieved and ground and treated with 1% H_2O_2	pH-5	82 mg/g of Zn(II)	Kargi and Cikla, 2006
Basic oxygen furnace sludge	Ground, homogenized, dried at 105 ^{0}C and cooled	pH-5	92.51mg/g Pb(II)	Naiya et al., 2009
Activated sludge	Washed, oven dried ground, sieved and treated with 0.2M NaOH	pH-5	133.3 mg/g Cu2+ 91.7 mg/g Cd2+ 58.8 mg/g Ni2+	Al-Qodah, 2006
Activated sludge	Activation with NaOH and centrifuged	pH=4	18.08 mg/g Cd 3.94 mg/g Cu 4.06 mg/g Ni	AjayKumar et al., 2009
Activated sludge	Dried, ground, sieved and treated with HCl solution	pH-2	226 mg/g Cr(VI)	Wu et al., 2010
Activated sludge	Centrifuged, washed, dried and ground	pH-2-4	65.1 mg/g Cu(II) 81.2 mg/g Pb(II)	Xuejiang et al., 2006
Activated sludge	Dried, treated with NaOH, rinsed with water, dried and ground and treated	pH-3.5 for Pb(II) pH-5.8 for Hg(II)	18.61 mg/g Pb(II) 19.3 mg/g Hg(II)	Mehmet Kilic et al., 2008
Activated sludge	Centrifuged, dried and ground	pH- 4 for Cd, Cu and Pb pH-5 for Ni and Zn	0.25 mmmol/g Cd,0.30 mmmol/g Cu,0.15 mmmol/g Ni,0.69 mmmol/g Pb, and 0.24 mmmol/g Zn	Hammaini et al., 2007

5. FLY ASH BASED ADSORBENTS AND THEIR PERFORMANCE

Fly ash as such or converted to zeolite or zeolite like material with a large cation exchange capacity and specific surface area have been tried for the removal of heavy metals from aqueous solutions.

A study conducted using dried and ground fly ash for the removal of lead and copper ions from aqueous solutions bybatch adsorption experiments showed that lead and copper ions were adsorbed onto the fly ash very rapidly within the first 20 min, while equilibrium was attained within two hours for both lead and copper ions [50]. The hydration of fly ash increased with pH between 10 and 13 and at this pH values higher degree of precipitation of metal ions can be expected, thereby enhancing the removal of heavy metal ions from solution by the fly ash. This investigation revealed that increase in temperature decreases uptake of metal ions by the fly ash and that the metal ion uptake by fly ash depends on the metal ion type. Batch adsorption experiments conducted using fly ash for the removal of zinc and cadmium showed that the maximum adsorption of Zn^{2+} and Cd^{2+} was found to occur at pH 7.0– 7.5 [51]. Equilibrium time was found to be two hours. The Langmuir model was more applicable than the Freundlich model. It was seen that the extent of adsorption increases with an increase in initial concentration, dosage of fly ash and temperature.

Agglomerated fly ash was used for removing arsenic from solutions. Experimental data of arsenic adsorption onto fly ash agglomerates can be fitted by a Freundlich isotherm, while kinetics follows a pseudo second order model. The circulation mode was preferable to the batch mode [52] .

Batch adsorption experiments conducted for the removal of copper from wastewater using fly ash showed that the percentage removal of copper (II) was found to increase with decrease in initial concentration of copper(II). Major adsorption was observed within 1 hour upto initial concentration of 50 mg/l. Adsorption increased with temperature showing it as an endothermic process. In column studies, the maximum uptake of copper (II) was achieved at a flow rate of 0.50 ml/min. Freundlich model fits the isotherm data well [53].

Fly ash was used in packed columns at different lengths and wastewater containing harmful chemicals was allowed to pass through these columns [54]. It has been found out that the concentration of harmful chemicals was reduced to acceptable values. Also the adsorption efficiency increased as a result of the increased mass transfer units in proportionality with the length of the columns.

Batch experiments were conducted using modified fly ash by a hydrothermal treatment of the ash with NaOH [55]. The modified fly ash samples exhibited much greater specific surface areas and cation exchange capacities than the unmodified ash. The adsorption of lead from aqueous solution by these modified ashes was found to occur readily. The synthesised products show a greater adsorption capacity than similar cheap materials such as clay or moss peat.

Batch adsorption studies conducted using treated fly ash for the removal of Cr (VI) from wastewater showed that removal efficiency was decreasing with increase in the initial pH. The rate of adsorption was faster in the initial periods and adsorption obeyed second order rate equation. The equilibrium data obtained for the adsorption of Cr(VI) was well described by Koble-Corrigon isotherm model19.

Zeolites derived from Indian fly ash was used for the removal of Cu^{2+}, Co^{2+}, and Ni^{2+} from aqueous solutions by conducting batch studies [56]. It was observed that the metal uptake increased with the increasing concentration, pH and temperature. All sorption data fitted to the Langmuir equation. Sorption capacity of the zeolite was quite higher than that of fly ash at acidic pH having the selectivity order $Cu^{2+} > Co^{2+} > Ni^{2+}$.

Studies have shown that modifying fly ash with NaOH solution would significantly enhance the adsorption capacity depending on the treatment temperature, time, and base concentration [57]. The adsorption isotherm can be described by the Langmuir and Freundlich isotherm equations. The removal efficiency for copper and nickel ions were from 30% to 90% depending on the initial concentrations. The increase in adsorption temperature enhanced the adsorption efficiency for both heavy metals. The pseudo second-order kinetics fitted better for the dynamic adsorption of Cu and Ni ions. The unburned carbon in fly ash plays an important role for adsorption. The unburned carbon can be converted to activated carbon, which will enhance the adsorption capacity [58].

Studies were conducted using zeolites derived from coal fly ash and found that the removal could be described by Pseudo second order model and Langmuir equations [59]. For tested concentration of 300 mg/l the adsorption capacity varied as $Cu^{2+} > Cr^{3+} > Zn^{2+} > Co^{2+} > Ni^{2+}$. Temperature is the most influential parameter for removal of Cu2+ and Zn2+ when studies were conducted using different fly ashes [60]. Removal efficiency of Cu^{2+} and Zn^{2+} is a function of fly ash quality, lime and silica-alumina composition. Also mixing of different fly ashes does not have a significant impact on the Zn removal and slight increase in the removal of copper. Fly ash was used to examine it as an adsorbent for heavy metal cations. The sorption rates were very high. Over 90% of the total adsorption was obtained in 10 minutes reaction time [61]. Coal combustion ash was used for Cadmium removal in aqueous solutions and observed a monolayer adsorption with an uptake of 67 mg/g [62]. Mechanical sieving and demineralization were able to beneficiate the ash, by significantly improving the carbon content and porosimetric characteristics. Fly ash has been demonstrated to be a potential heavy metal adsorbent for industrial wastewater . The Cd(II) and Zn(II) adsorption were 0.27 mg/g and 0.05 mg/g respectively [63].

Study showed good percentage removal of five metallic ions (Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}) by fly ash/ lime mixing [64]. An adsorbent concentration around 122 g/ L and a solution temperature of 660 C lead simultaneously to a high adsorption and a low desorption. Alkalinity of fly ash is an important factor for metal removal and pH control is required. Precipitation occurs for all metallic ions at pH 10 [65].

Fly ashes with different quantities of carbon and minerals were tested for Cu(II) removal [66]. Carbon fraction of fly ash was found to be a very significant parameter for removal of Cu(II). The specific surface area of fly ash increased around 0.6m2 per percentage of carbon fraction.

Fly ash has been investigated for its direct use as an adsorbent in both gaseous and aqueous applications [67]. 11 different adsorbents were compared for the removal of heavy metals out of which one was fly ash. It was found that fly ash has significantly higher affinity towards heavy metals mainly present as cationic or non charged species compared to those present as anionic species [68].

Fly ash possesses the adsorption capacity for removal of heavy metal ions and organic compounds in leachate from solid waste landfill. The use of fly ash in leachate treatment is recommended in order to remove the heavy metals before discharging the treated leachate into nearby water courses. The fly ash after the utilization for the adsorption of heavy metals can be effectively disposed in the secured landfill along with hazardous waste [69].

The adsorption studies conducted to remove dyes using fly ash was highly pH dependent and the optimum pH for maximum adsorption was found to be at pH 7.0. The Langmuir isotherms had higher coefficients of determination and lower chi-square values at all temperatures, suggesting that the Langmuir isotherm was the best-fitting isotherm. The adsorption data showed good agreement with the pseudo second-order kinetic model for different sorbent concentration. The optimum pH for the removal of Cr VI using Bagasse fly ash after treatment was 1.0. The sorption data correlated well with the Freundlich and Langmuir models. The removal of adsorbate decreased with increasing metal ion concentration and so the removal of even trace quantities of pollutants from the solution, was not expected to pose any special problem in the system under investigation. The material can be utilized for Cr (VI) removal from wastewater even in the presence of other metal ions and surfactants [70].

The modifications done to fly ash and maximum uptake under optimum conditions are given in Table 4.

Table 4: Modifications done to flaysh and maximum uptake under optimum conditions

Material	Modification	Operating conditions	Uptake (mg/g)	References
Modified fly ash	Dried, ground and sieved	pH-6.4	22 mg/g Pb 21.5 mg/g Cu^{2+}	Alinnor, 2007
Fly ash agglormerates	Mixed with water for 1 hour and cured for 1 week	Continuous flow and batch adsorption	Circulation -2.17 mg/g As Batch – 2.23 mg/g As	Polowczyk et al., 2010
High calcium fly ash	Mixed with water and filtered	pH-7-7.5	2.778 mg/g Zn^{2+} 0.714 mg/g Cd^{2+}	Bayat, 2002
Fly ash	Washed, filtered, dried and ground	pH-4 and temperature 50^0C	98% removal Cu	Nath et al., 2007
Fly ash	No modification	Coal ash packed column of 6 cm diameter	90% removal Hg	Abdelhadi et al., 2011
Modified fly ash	Mixed with NaOH solution, filtered and dried	pH-5	300 mol/100g Pb	Woolard et al., 2000
Modified fly ash	Treated with conc.H2SO4 and heated in oven	pH-1-3	21 mg/g Cr	Gupta and Babu
Zeolite derived from fly ash	Alkali fusion method	Ph-3.5 Temperature 310 ^{0}K	2.325x10-3 mol/g Cu2+ 1.871 325x10-3 mol/g Co2+ 1.568 325x10-3 mol/g Ni2+	Mishra and Tiwari, 2006
Treated fly ash	Treaed with NaOH solution	pH- 6.2 temperature- 40 ^{0}C	90% removal Ni 70% removal Cu	Wang et al., 2006

Zeolite derived from coal fly ash	Hydrothermal treatment of coal fly ash using NaOH	pH-3 Temperature 25 ^{0}C	13.72 mg/g Co2+ 41.61 mg/g Cr3+ 50.45 mg/g Cu2+ 8.96 mg/g Ni2+	Hui et al., 2005
Fly ash	From different power plants	pH-5	4.2 mg/g Cu 1.3 mg/g Zn	Hequet et al., 2001
Fly ash	Dried and calcinated at 800 ^{0}C	pH-4.6	100% removal of Cu and Mn 92.85% removal of Fe	Daci et al., 2010
Fly ash	Mechanical sieving and demineralized by treating with HCl.	Size of particle of adsorbent>100µm	67 mg/g Cd	Montagnaro and Santoro, 2009
Fly ash	Dehydrated in oven at 103 ^{0}C and sieved through 75 µm sieve	pH- 8.6-9.0 pH - 5.5-6.5	0.27 mg/g Cd(II) 0.05 mg/g Zn(II)	Weng and Huang, 1994
Modified fly ash	Mixed with lime and dried for 24 hours at 105^{0}C.	NA	97% of Cd2+ 84% of Cu2+	Ricou et al., 2001
Modified fly ash	Acidified and dgested in a digester	pH-5	2.2-2.8 mg/g Cu	Lin and Chan,. 2001
Bagasse fly ash	Treated with H2O2,washed with water, dried at 100 ^{0}C, powdered, ground and sieved	pH-1 Temperature-300C	5 x 103 mol/g Cr	Gupta et al., 1999
Fly ash	Acidified, digested and baked	pH-5	2.2-2.8 mg/g Cu	Lin and Chang, 2001

6. CONCLUSION

Activated carbon is normally used for adsorption process which is costly. To replace the expensive activated carbon, a wide range of inexpensive adsorbents have been investigated. Large quantities of fly ash and sludge are produced in India which creates serious disposal problems. This paper has provided a review of the use of sludge and fly ash as an adsorbent for the removal of heavy metals. Both have been found to be very effective for the removal of heavy metals from aqueous solutions. This review has also referred to some modification done on sludge and fly ash for increasing the capacity of adsorption.

Further research is required to utilise both fly ash and sludge in improved ways for getting maximum removal of heavy metals. For the successful application of using sludge and fly ash as adsorbents for heavy metals in real life situations, improvement in the adsorption quality by chemical or any type of modification is needed. Different modes of operation can be tried for maximum adsorption of heavy metals. Also behaviour of the adsorbent need to be tested with real industrial effluents where different types of heavy metals are present and analysing the adsorption capacity.

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