American Association for Science and Technology
AASCIT Communications
Volume 1, Issue 2
July 20, 2014 online

Synthesis of Value-added Materials from Coal Combustion Products and Biomass Ash: Environmental Application

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Keywords: Solid Wastes, Low-Cost Adsorbent, Coal Ash, Sugarcane Straw, Ecological Bricks

The world is undergoing the largest wave of urban growth in history. Increasing urbanization, growth of population with rising standards of living have contributed to increase the quantity of solid wastes generated by mining, industrial, agricultural, and domestic activities. Management of increasing amounts of solid waste has become a major challenge in many cities in developing countries. The main objective of waste management system is to maximize economic benefits and at the same time protection of the environment. The optimal solution for solid waste management is to minimize the quantity of waste both at generation and disposal stage followed by preventive environmental management action. Recycling of solid wastes is another major productive area in which considerable quantity can be utilized for manufacturing new products. Converting solid residues into value-added materials not only alleviates the disposal problem but also converts a waste material into a marketable commodity. The major solid wastes generated in Brazil are ash generated at coal-fired power plants, sludge from water treatment plant and waste biomass. To safeguard the environment, efforts are being made for recycling the wastes and utilize them in value-added applications. This article provides an overview of current research activities of our research group on the synthesis of value-added materials from Coal Combustion Products and waste agricultural biomass and their potential environmental application especially as low-cost adsorbents for the treatment of wastewater and production of ecological brick.

Coal Combustion Products

Coal Combustion Residuals, also referred to as Coal Combustion Products (CCP), are the materials produced primarily from the combustion of coal in coal-fired power plants. CCPs include the following materials: fly ash, bottom ash, boiler slag, Flue Gas Desulfurization Material (FGD), etc.

Brazil and Colombia have the most important proved reserves of coal in South America. Brazil has important reserves of lignite and sub-bituminous coal of 4559 Mt. Coal mines in Brazil are in the south and the power plants are located near these mines in the states of Rio Grande do Sul (RS), Santa Catarina (SC) and Paraná (PR).

The principal use for the coal mined in Brazil is the combustion for power generation. Approximately 1.5% of the electricity generated in the country is derived from coal-fired power plants, which account for 1.9 GW of total installed capacity. In the generation of electricity, these power plants produce approximately 4 Mt tons of ashes every year, which are composed from 65 to 85% of fly ash and 15 to 35% of bottom ash.

Brazilian coals are richer in ash (content of 20–50 wt.%) and poorer in carbon when compared to worldwide coal and coal ash disposal is a serious environmental concern. Only 30% of fly ash is applied as raw material for cement and concrete production. The remaining solid wastes are disposed in on-site ponds, nearby abandoned or active mine sites, or landfills as in other countries.

Coal fly ash samples were collected from baghouse filter, electrostatic precipitators and cyclone filter of five different Brazilian thermal power plants: Figueira, Jorge Lacerda, President Médici, São Jerônimo and Charqueadas [1]. The materials were characterized in terms of pH, conductivity, real density, specific surface area (BET method), morphological analysis, chemical composition, mineralogical composition, cation exchange capacity, humidity, loss-on-ignition among other parameters. Leaching and solubilization tests were carried out following the Brazilian NBR 10004 code. Analyses of major elements indicate a high SiO_2, Al_2O_3 and Fe_2O_3 content. The mineralogical composition of fly ashes includes mainly mullite and quartz, some amounts of magnetite and hematite and an amorphous phase. Most element concentrations were of the same magnitude, independent of the power plant, with the exception of Figueira. The fly ash from São Jerônimo power plant presents a higher content of unburned carbon and specific surface area. According to its mineralogical and chemical composition, Brazilian fly ash can be used as raw material for synthesis of zeolites using hydrothermal method.

Coal fly ash (FA) samples derived from Brazilian and Australian coal were used as supports to prepare Co oxide (Co)-based catalysts. These Co/FA catalysts were tested in peroxymonosulfate activation for sulphate radical generation and phenol degradation in aqueous solution. It was found that the FA supports did not show adsorption of phenol and could not activate peroxymonosulfate for sulphate radical generation. However, fly ash supported Co oxide catalysts (Co/FA) presented higher activities in the activation of peroxymonosulfate for phenol degradation than bulk Co oxide and their activities varied depending on the properties of the fly ash supports. Co/Brazilian fly ash showed the highest activity while Co/Australian fly ash showed the lowest [2].

Low-Cost Adsorbents

Zeolites

In our research group we have been developing zeolites synthesized from coal fly ash and bottom ash by conventionally hydrothermal treatment and fusion method. The hydrothermal activation of coal ash was optimized by applying a wide range of experimental conditions (temperature, time, alkali hydroxide concentration and solid/solution ratio).

Five different Brazilian fly ashes were used to synthesize zeolites by hydrothermal treatment. Raw fly ash materials and zeolitic products were characterized. After hydrothermal treatment, various zeolites such as hydroxy-sodalite, NaP1 and X zeolites were formed depending on sourced fly ash. Hydroxy-sodalite zeolite was formed in all samples in similar quantity. NaP1 zeolite was formed in fly ashes with high content of Ca^{2+} while X zeolite was formed fromthe fly ashes with high content of Al^{3+}. CEC values of the zeolitic materials are 40 times higher than fly ash samples, hence, the produced zeolites have a high potential for use as ion exchangers [3].

Hydroxy-sodalite zeolite (ZHS) could be synthesized from coal fly ash and used for Cd^{2+} and Zn^{2+} removal from water. Cadmium is more preferentially adsorbed than zinc on ZHS. The adsorption equilibrium time reached by ZHS for both Zn^{2+} and Cd^{2+} was 20 hours. The highest percentages of removal were obtained at pH 6 and 5 and at doses of 15 and 18 g L^{-1} for Zn^{2+} and Cd^{2+}, respectively. The adsorption capacity was 40.1 mg g^{-1} for Zn^{2+} and 60.1 mg g^{-1} for Cd^{2+} [4].

Two different Brazilian fly ashes were used to selectively synthesize pure zeolites X and A by a two-step process. The pure zeolites X and A were used in adsorption of zinc and cadmium in single and binary systems. The adsorption studies showed that zinc is more preferentially adsorbed on pure zeolites than cadmium in both single and binary systems under similar experimental conditions. Zeolite-A was presented higher adsorption than zeolite-X. The adsorption isotherms followed the Langmuir model. The adsorption capacities for zinc and cadmium on the pure zeolites ranged 156–220 mg g^{-1} and 57–195 mg g^{-1} in the single and binary ion systems, respectively. The removal of both ions by zeolites A was less affected by the presence of a competitive ion, different from zeolites X [5].

Magnetic Nanocomposites

Zeolite from fly ash-iron oxide nanocomposites were synthesized and the resulting materials were characterized. The magnetic properties of iron oxides have been combined with the adsorption features of zeolites synthesized from fly ash to produce a magnetic nanocomposite adsorbent.

Batch tests were carried out to investigate the adsorption mechanism of dyes and metal ions from aqueous solution onto magnetic nanocomposite. A series of experiments were carried out in a batch adsorption technique to obtain the effect of process variables on adsorption. The composite adsorbents after be used to adsorb contaminants in water were removed from the medium by a simple magnetic process [6-7].

The zeolite-iron oxide magnetic nanocomposite was used for the removal of U(VI) from aqueous solutions by a batch technique. The effects of contact time and initial concentration on the removal process were evaluated. The kinetic experimental data were analyzed using three kinetic equations including pseudo-first order equation, pseudo-second order equation and intraparticle diffusion model. The experimental data fit the second-order kinetic model. The Freundlich and the Langmuir models have been applied and the results indicated that the Langmuir provided the best correlation of experimental data [8-9].

Adsorbents for Dyeing Wastewaters

Synthetic dyes are used extensively by the textile dyeing industry. It is estimated that at least 10% of the dyes are lost in the dye effluent during such dyeing processes. The colored wastewater damages the aesthetic nature of water and reduces the light penetration through the water's surface and the photosynthetic activity of aquatic organisms due to the presence of metals, chlorides and other contaminants. Many of the dyes used in these industries may also be carcinogenic and mutagenic.

Textile industries feature among the eight most important sectors of the industrial activity of Brazil, occupying first place in direct employment and in billing. Among several chemical and physical treatment methods, the adsorption has been found to be superior to other techniques for the removal of dyes from aqueous solution in terms of methodology, operational conditions and efficiency. Currently, the most common procedure involves the use of activated carbons as adsorbents due to their higher adsorption capacities, but they are considered expensive.

In our research group it was proposed the use of zeolite from fly ash as an adsorbent for removal of dyes from aqueous solution. A series of experiments was conducted to examine the effects of contact time, initial concentration of dye, and adsorbent dosage on dyes removal. The adsorption kinetic of dyes onto adsorbents was discussed using the pseudo-first order, pseudo-second order and intra-particle diffusion models. The equilibrium of adsorption was modeled by Langmuir, Freundlich and Temkin models [10-13].

The studies showed that the zeolite synthesized from Brazilian fly ash can be used as an adsorbent for the removal of dyes from aqueous solution. Moreover, the dye toxicity was evaluated for dye solutions before and after the adsorption processes with *D. simlis and V. ficheri.* It was observed that acute effects were substantially reduced or was eliminated after the adsorption treatment [14-16].

Organozeolite from Fly Ash

It is known that although zeolites have little affinity toward anionic ions and organic pollutants. In order to improve water contaminant remediation performance of zeolites, cationic surfactants have been successfully used to modify their surface properties. The most commonly used surfactant for zeolite surface modification is hexadecyltrimethylammonium bromide (HDTMA-Br), in which each molecule is composed of a hydrophilic and positively charged head group, and a hydrophobic tail. HDTMA-Br may form monolayers and/or bi-layers on the zeolite surface [17].

The hydrophilic properties of zeolite are changed to hydrophobic ones, during this process and as a consequence, their affinity for organic substances increases. On the other hand, owing to the hydrophobicity of zeolite surfaces, the filtration or flotation processes of organozeolite suspensions are much easier when compared with those related to the unmodified zeolite. Moreover, surfactant-modified zeolite can simultaneously adsorb the major classes of water contaminants including organic compounds, cations, anions and pathogens. These unique multipurpose characteristics make this material applicable for the treatment of a variety of contaminated waters.

Zeolite synthesized from fly ash was modified with hexadecyltrimethyl ammonium bromide (HDTMA-Br) and hexadecyltrimethyl ammonium chloride (HDTMA-Cl) and was used as adsorbent to remove anionic dyes from aqueous solution. The unmodified and modified nano zeolites were characterized using various techniques to obtain its physical and chemical constituents. The kinetics and isotherms for dyes adsorption onto HTMA-modified nano zeolites from fly ash were studied to estimate important capacity and rate parameters which can aid in system design. The percentage of color removed by HTMA-modified nanozeolites from real textile wastewaters was in the range of 60-100%. The ecotoxicity studies showed that the wastewater contaminated with dyes after treatment with modified-surfactant zeolite should not be discarded directly into water bodies, but can be reused in industry and cleaning due to the biocidal properties of the surfactant [18-20].

Agricultural Waste as Low-Cost Adsorbent

Other line of research has been developed focusing the conversion of sugarcane straw ash, an agricultural waste of sugar industry with disposal problems, into value-added material. Brazil is the largest producer of sugarcane of the world generating 400 million tons per year, on average. An amount of 1 ton of sugarcane generates 270 kg bagasse and 144 kg trash/straw.

The sugarcane industry is seeking solutions to dispose of the wastes generated by the sugar and alcohol production processes. So, the recycling of industrial wastes from the agriculture sector is increasingly encouraged.

The sugar cane straw ash was effectively converted into the zeolitic material by alkali fusion followed by hydrothermal treatment. The effect of crystallization time was studied and the conditions optimized. The formation of the zeolite-P, major constituent, was confirmed by mineralogical and FTIR analysis. The zeolitic material from sugarcane straw ash can be utilized as low-cost adsorbent for removal of crystal violet from aqueous system. The maximum loading capacity was 93.5 mg g^{-1} and the removal percentage was 99.7% to 100% [21].

Production of Ecological Bricks

Another important residue is generated in the water treatment plants. The plants produce large quantities of sludge as a result of treatment processes of raw water such as coagulation, flocculation and filtration. The by-product from the purification process is a huge amount of waste in the form of sludge called water treatment residual or waterworks sludge, which after drying is considered to be a non-biodegradable waste material.

The common practice by most water treatment plants is disposal of sludge to the nearest watercourse around the treatment plant without prior treatment. However, the laws in Brazil are demanding a change in this behavior, and thus proper management of the sludge becomes inevitable.

Brazilian fly ashes and waterworks sludge have been also applied as by-product aggregates in the manufacture of ecological bricks (Fig. 1). Fly ash-sludge and fly ash-sludge-soil-cement bricks were molded and tested, according to the Brazilians Standards. Various mixtures were prepared by incorporating these industrial wastes in brick production. The materials were characterized by physical-chemical analysis, X-ray diffraction, thermal analysis, morphological analysis, Fourier transform infrared spectroscopy and granulometric analysis. The effects of the wastes incorporation on physical properties such as compressive strength and water absorption have been determined. The results indicate that the waterworks sludge and coal ashes have potential to be used on manufacturing soil-cement pressed bricks according to the of Brazilians Standards NBR 10836/94 [22].

Fig. 1. *Sludge from water treatment plant -coal fly ash-soil-cement bricks "Reprinted from ref. [22] with permission by the author"*

Conclusions and Future Perspectives

In our group we have been developing zeolites synthesized using coal ash samples and biomass ash by conventionally hydrothermal treatment and fusion method. Economic advantages would be obtained over chemical reagents used in processes to obtain zeolites that are relatively expensive. In addition, the synthetic zeolites were used for the removal of dyes and toxic metals from aqueous solution.

The results obtained in the project showed a great reduction in the pollutant concentration in treated waters and demonstrated the high potential of the zeolites as low-cost adsorbent material for treatment of wastewater. The utilization of synthetic zeolites as adsorbent for the treatment effluents can help to reduce the environmental impact associated to disposal of ashes.

Brazilian fly ashes have been also applied as a support for catalysts and as a by-product aggregate in the manufacture of ecological bricks.

The final goal of this project is to use the information obtained to design the synthesis of zeolites from coal ash and biomass ash in the form of a pilot plant scale. Likewise, based on the optimization in the laboratory-scale test, the ecological brick samples should be produced in the pilot-scale and commercial-scale trials.■

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References

[1] FUNGARO, D. A.; IZIDORO, J. C.; SANTOS, F. S.; WANG, S. Coal Fly Ash from Brazilian Power Plants: Chemical and Physical Properties and Leaching Characteristics. In: SARKER, P.K. (Ed.). *Fly Ash: Chemical Composition, Sources and Potential Environmental Impacts*. Hauppauge, N.Y.: Nova Science Publishers, 2013.

[2] MUHAMMAD, S.; SAPUTRA, E.; SUN, H.; IZIDORO, J. C.; FUNGARO, D. A.; ANG, M. H.; TADE, M. O.; WANG, S. Coal fly ash supported Co3O4 catalysts for phenol degradation using peroxymonosulfate RSC Advances 2 (2012) 5645-5650.

[3] IZIDORO, J. C.; FUNGARO, D. A.; SANTOS, F. S.; WANG, S. Characteristics of Brazilian coal fly ashes and their synthesized zeolites. Fuel Processing Technology 97 (2012) 38–44.

[4] IZIDORO, J. C.; FUNGARO, D. A.; WANG, S. Zeolite synthesis from Brazilian coal fly ash for removal of Zn^{2+} and Cd^{2+} from water. Advanced Materials Research 356-360 (2012) 1900-1908.

[5] IZIDORO J. C, FUNGARO, D. A.; ABBOTT, J. E, WANG, S. Synthesis of zeolites X and A from fly ashes for cadmium and zinc removal from aqueous solutions in single and binary ion systems. Fuel 103 (2013) 827–834

[6] FUNGARO, D. A; YAMAURA, M.; CARVALHO, T. E. M.; GRACIANO, J. E. A. *Zeolite from Fly Ash-Iron Oxide Magnetic Nanocomposite: Synthesis and Application as an Adsorbent for Removal of Contaminants from Aqueous Solution.* In: ANDREYEV, M. K; ZUBKOV, O. L. (Ed.). Zeolites: Synthesis, Chemistry and Applications. Hauppauge, N.Y.: Nova Science Publishers, 2012.

[7] YAMAURA, M.; FUNGARO, D.A. Synthesis and characterization of magnetic adsorbent prepared by magnetite nanoparticles and zeolite from coal fly ash. Journal of Materials Science 48 (2013) 5093–5101.

[8] FUNGARO, D. A.; GRACIANO, J. E. A.. Adsorption of Zinc Ions from Water Using Zeolite/Iron Oxide Composites. Adsorption Science and Technology 10 (2007) 729 -740.

[9] FUNGARO, D. A.; YAMAURA, M.; CRAESMEYER, G. R. Uranium removal from aqueous solution by zeolite from fly ash-iron oxide magnetic nanocomposite. International Review of Chemical Engineering (I.RE.CH.E.) 4 (2012) 353-358.

[10] FUNGARO, D.A.; BRUNO, M.; GROSCHE, L.C. "Adsorption and kinetic studies of methylene blue on zeolite synthesized from fly ash," Desalination and Water Treatment, 2, 231-239, 2009.

[11] FUNGARO, D.A.; YAMAURA, M.; CARVALHO, T. E .M. Adsorption of anionic dyes from aqueous solution on zeolite from fly ash-iron oxide magnetic nanocomposite Journal of Atomic and Molecular Sciences 2 (2011) 305-316.

[12] CARVALHO, T. E. M.; FUNGARO, D. A.; MAGDALENA, C .P.; CUNICO, P. Adsorption of indigo carmine from aqueous solution using coal fly ash and zeolite from fly ash Journal of Radioanalytical and Nuclear Chemistry, 289, 617-626, 2011.

[13] BERTOLINI, T. C. R.; IZIDORO, J. C. ; MAGDALENA, C. P.; FUNGARO, D. A. Adsorption of crystal violet dye from aqueous solution onto zeolites from coal fly and bottom ashes. Orbital: The Electronic Journal of Chemistry 5 (2013) 179-191.

[14] FUNGARO, D. A.; GROSCHE, L. C.; PINHEIRO, A. S.; IZIDORO, J. C.; BORRELY, S .I. Adsorption of methylene blue from aqueous solution on zeolitic material and the improvement as toxicity removal to living organisms Orbital: The Electronic Journal of Chemistry 2 (2010) 235-247.

[15] MAGDALENA, C. P. Adsorption of reactive Remazol Red RB dye of aqueous solution using zeolite of the coal ash and evaluation of acute toxicity with Daphnia similis. Master Dissertation. Instituto de

Pesquisas Energéticas e Nucleares, Brasil, 2010 (in Portuguese with English abstract) http://pelicano.ipen.br/PosG30/TextoCompleto/Carina%20Pitwak%20Magdalena_M.pdf .

[16] FERREIRA, C. P. Studies on the adsorption of Reactive Black 5 dye of aqueous solution using zeolite of the coal ashes. Master Dissertation. Instituto de Pesquisas Energéticas e Nucleares, Brasil, 2011 (in Portuguese with English abstract). http://pelicano.ipen.br/PosG30/TextoCompleto/Patricia%20Cunico%20Ferreira_M.pdf.

[17] FUNGARO, D. A.; BORRELY, S. I. Synthesis and characterization of zeolite from coal ashes modified by cationic surfactant. Cerâmica 58 (2012) 77-83 (in Portuguese with English abstract).

[18] FUNGARO, D. A.; MAGDALENA, C. P. Adsorption of Reactive Red 198 from aqueous solution by organozeolite from fly ash: Kinetic and Equilibrium studies. International Journal of Chemical and Environmental Engineering Systems 3 (2012) 74-83.

[19] FUNGARO, D.A.; BORRELY S. I.; CARVALHO, T. E. M. Surfactant Modified Zeolite from Cyclone Ash as Adsorbent for Removal of Reactive Orange 16 from Aqueous Solution. American Journal of Environmental Protection 1 (2013) 1-9.

[20] FUNGARO, D.A.; MAGDALENA, C. P. Counterion effects on the adsorption of Acid Orange 8 from aqueous solution onto HDTMA-modified nanozeolite from fly ash. Environment and Ecology Research 2 (2014) 97-106.

[21] FUNGARO, D. A.; REIS, T. V. S.; LOGLI, M. A.; OLIVEIRA, N. A. Synthesis and Characterization of Zeolitic Material Derived from Sugarcane Straw Ash. American Journal of Environmental Protection 2 (2014) 16-21.

[22] SILVA, M. V. Development of bricks with incorporation of coal ash and sludge from water treatment plant. Master Dissertation. Instituto de Pesquisas Energéticas e Nucleares, Brasil, 2011 (in Portuguese with English abstract) http://pelicano.ipen.br/PosG30/TextoCompleto/Mauro%20Valerio%20da%20Silva_M.pdf