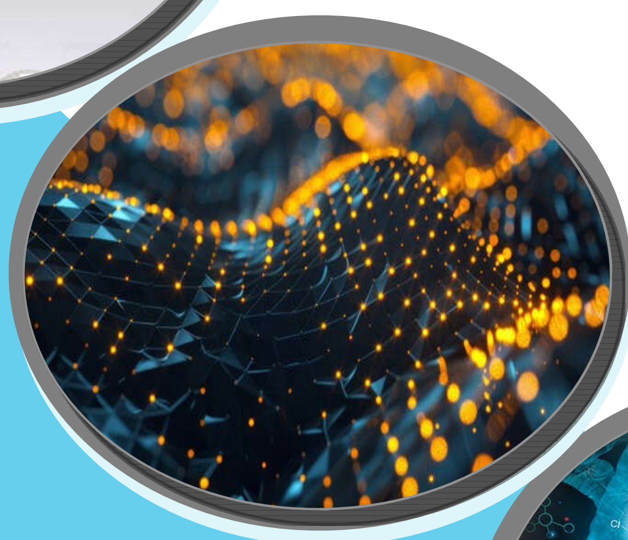
BIOLOGICAL, CHEMICAL AND PHYSICAL APPROACH TO MATERIALS AND ITS APPLICATIONS



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Biological, Chemical and Physical approach to materials and its applications

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APPLICATION OF CENOSPHERE FROM FLY ASH BASED MATERIALS IN CONTAMINANT ADSORPTION FROM WATER SYSTEM: A BRIEF DISCUSSION

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ABSTRACT

Pollution caused by production of fly ash due to combustion of different fuels is a serious environmental issue. Reuse of these fly ashes and their components for different purposes may be a solution to this problem. Cenosphere separated from fly ash finds applications in different fields. In this review, utilization of cenosphere and its related materials for adsorption of contaminants from aqueous system is discussed. Cenosphere is a potential adsorbent material due to its porous morphology and large surface area. Therefore, cenosphere and related materials are now a days become materials of interest as adsorbent for adsorption of different contaminants such as synthetic dye molecules, fluoride, metal ions from water system.

Keywords: Cenosphere, Adsorption, Contaminants

1. INTRODUCTION

Production of ash during combustion of fuels like coal, oil, biomaterials, domestic waste etc. and its adverse effects on environment is a global issue in the modern world. A large area of land already has been converted to ash dumps to deposit the ashes released from huge number of thermal power plants situated different parts of the world and this area is expanding day by day (Kizelshteyn, Dubov, Shpitsgluz, and Para- da 1995, Zyrynov and Zyrynov 2009, Shpirt, Clare and Persikov 1990, Sear 2001, Drozhzhin, Piculin, and Kuvaev 2005, Fenelonov, Mel'gunov and Parmon 2010). Reuse of these ashes and conversion of them to some value added product may be helpful in this regard to reduce size the ash dumps as well as environmental pollution. The most abundant component of ash is alluminosilicate microspheres some of which have extremely low density (Fenelonov et al. 2010). These can enter to ash settling reservoirs in thermal power plants and accumulate at the external surface of the reservoir. They can easily be carried away by wind and rain and can even enter to respiratory tracts which increase the chance of cardiovascular diseases (Fenelonov et al. 2010, Chock, Winkler, and Chen, 2000, Anderson, Bremner, Atkinson, Har-rison and Walters, 2001).

However, the microspheres have several unique properties and therefore have potential applications in different fields if they can be collected and utilized with proper technologies (Fenelonov et al. 2010). Microspheres can be divided into two types: plerospheres and cenospheres. In plerospheres, some fine microspheres or particles of minerals get entrapped in some hollow microspheres [Fisher, Chang and Brummer, 1976, Goodarzi and Sanei, 2009, Liu, Sun, Wang, Wang and Zou, 2016). The cenosphere word was derived from two Greek words namely kenos and sphaira which means hollow and sphere respectively (Ngu, Wu and Zhang, 2007). They are hollow, low bulk density (range of bulk density is from 0.2 to 0.5 g cm^{-3}) ash fraction and which collected from the surface of ash lagoon. A cenosphere is composed of a cavity which is surrounded by perforated or solid mineral shell. Such cavity is generally filled up with gas. The mineral shell is composed with silica, alumina, oxides of iron and other elements such as CaO, MgO, Na_2O, K_2O, TiO_2 etc (Ngu et al. 2007). Cenospheres which are obtained from fly ash by density separation technique in water medium have either spherical and single-ring type structure or irregular and network type structure (Ngu et al. 2007). Cenospheres have some specific properties like spherical morphology, low density, heat resistance capacity, high insulation, high thermal stability, low chemical reactivity etc (Ngu et al. 2007). These properties make cenosphere a versatile material for applications in number of fields such as lightweight construction products, polymer composites, different types of foams, catalysis and adsorption (Ngu et al. 2007, Shao, Jia, Zhou and Liu, 2008, Sharma, Sharma, Das and Boukherroub, 2022). In this article, application of cenosphere and cenosphere based material as adsorbent for different toxic materials have been discussed.

2. CHARACTERISTICS OF CENOSPHERE

2.1 Physical Properties

As already discussed, the density of cenosphere is very low (much lower than water). According to Ngu et al. (2007), the apparent density (i.e. the density of the cenosphere particles excluding the voids among them) of ash cenosphere generally ranges between 0.4 − 0.8 g cm^{-3} and their bulk density lies between 0.2 − 0.5 g cm^{-3}. Due to this low apparent density, cenospheres float on the surface of ash lagoon and therefore can be easily separated from other components of fly ash of ash lagoons (Ngu et al. 2007). The size of the cenospheres particles ranges between 5 − 500 µm, though, generally it lies between 20 – 200 µm (Ngu et al. 2007).

2.2 Chemical Compositions

The chemical compositions of cenospheres collected from different sources are different. According to some authors, for cenosphere formation, presence of minimum 5 % iron oxide in ash is necessary (Anshits et al. 2000, Liu et al. 2016). But, high production of cenosphere from low iron oxide containing ash (0.54 % by weight) is also reported (Ngu et al. 2007). Table 1 represents the chemical composition of some cenosphere samples of different sources (Fomenko, Anshits, Solovyov Mikhaylova and Anshits, 2013, Kolay and Singh, 2001, Fedyaeva, Poshelyuzhnaya, Rakhmatulina, Zakharov and Fisenko, 2019).

Oxides of	**Sample 1 Composition (wt.%)** (Fomenko et al. 2013)	**Sample 2 Composition (wt.%)** (Kolay and Singh, 2001)	**Sample 3 Composition (wt.%)** (Fedyaeva et al. 2019)
Silicon	64.64	52.53	50.5
Alluminium	20.85	30.01	32.5
Iron	4.05	7.53	1.8
Calcium	2.24	1.15	2.6
Sulphur	0.24	0.02	0.00
Sodium	0.93	0.02	0.5
Potassium	3.19	1.98	0.6
Magnesium	1.85	0.32	0.00
Titanium	0.31	1.79	1.3
Phosphorous	0.00	0.45	1.8
Carbon	0.00	0.00	8.4
loss on ignition	0.72	4.20	0.00

Table 1. Chemical compositions of three cenosphere samples

2.3 Thermal Properties

Cenospheres are reported have a high thermal stability. When cenospheres are heated, the different gases or entrapped in the cavities escapes at approximately 300°C. At about 330°C, the water molecules dissolved in cenosphere get escaped (Kolay and Singh, 2001). In a study performed by Kolay and Singh (2001), DTA-TGA analysis of cenosphere showed more than 90 % weight loss at about 300 °C. An endothermic peak was also observed in the DTA curve at about 330 °C due to loss of dissolved water molecules. However, no weight loss peak was observed above this temperature in the DTA-TGA curve on heating the sample up to 800 °C indicating the stability of the cenosphere skeleton. Vassilav et al. (2004) studied the thermal behavior of some ceramic cenosphere concentrate samples by DTA and TGA analyses. They obtained about 63 % weight loss in the temperature range 230–330° C due to liberation of fluid inclusions locked in cenosphere wall voids. They reported that the pore moisture is liberated and dehydration of gypsum completes at about 150°C. An exothermic reaction takes place in the range (210–600) °C due to burning of char. In the temperature range (600 – 690) °C, decomposition of calcite occur which shows an endothermic peak in the DTA curve. Similarly, dolomite get decomposed at (690–1070) °C, anhydrite get decomposed at 1270°C. The softening of glass starts at (1300–1330) °C and complete glass fusion occurs at 1450°C.

3. UTILIZATION OF CENOSPHERE IN REMOVAL OF CONTAMINANTS FROM AQUEOUS SYSTEM

Cenospheres as well as other fly ash based materials have drawn considerable attentions of the researchers as potential adsorbent materials for adsorptive removal of contaminates like dye molecules, fluoride, heavy metals from water system. Tiwari et al. (2015) carried out some modifications in cenospheres studied its utilization in adsorptive removal of disperse dyes from aqueous system. They first separated cenospheres from coal fly ash through wet method and leached out the metals from it to get the modified cenosphere. The modified cenosphere was used for adsorption of disperse blue 79:1 and disperse orange 25 from aqueous medium. The effect of different parameters such as pH, dose of adsorbent, concentration of adsorbate, agitation speed, temperature and time of contact is reported. The adsorption capacity for both the dye molecules was decreased with increase in temperature. Maximum adsorption capacity is reported to be achieved at pH 6 at all temperatures. Adsorption capacity of both the dye molecules also increases with increase in the adsorbent concentration. Maximum adsorption capacity is reported to achieve at 40 mg L^{-1} adsorbate concentration and at 140 rpm agitation speed for both the dye molecules. The equilibrium contact time is 100 min for disperse orange 25 and 120 min for disperse blue 79:1. They obtained maximum 78% adsorption for disperse blue 79:1 and 81 % adsorption for 81% for disperse orange 25 on to modified cenosphere under their experimental conditions. Pseudo second order kinetic model was the best fit kinetic model and Langmuir isotherm model was the best fit isotherm model for both of the adsorption studies. Sahoo et al. (2013) carried out alkali treatment to coal fly ash to reduce the amount of Si and Al and to increase the percentage of carbon. The alkali treated fly ash was used for adsorptive removal of different metal ions namely Al, Ni, Zn, Pb, Fe and Mn from acid mine drainage water. The alkali treated fly ash had also larger surface area and higher pH value than the raw fly ash. The rate of adsorption of metals on to alkali treated fly ash was non-uniform. The adsorption rate was rapid initially for the first 3 h; after that the rate becomes slower. The amount of metal adsorption was increased with increase in the concentration of adsorbent and optimum concentration was achieved at adsorbent concentration of 120 g/L. Maximum adsorption efficiency was reported to be 99, 96, 94, 92, 89 and 60 % for Al, Fe, Pb, Zn, Ni and Mn respectively. Two isotherm models namely Freundlich and Langmuir models were studied for the adsorption process which showed Freundlich model to be more appropriate suggesting that the heterogeneous nature of the adsorption process. The adsorption process for Ni, Zn, Pb, Fe and Al in this study is governed by chemisorption whereas adsorption of Mn is governed by intra-particle diffusion. They also reported that the metal ions can be desorbed from the adsorbent surface in acidic media. Xu et al. (2011) studied the adsorption of fluoride from aqueous solution using of magnesia loaded cenosphere (MLC) derived from fly ash as adsorbent. The fly ash cenospheres were impregnated with magnesium chloride solution to prepare MLC and used as adsorbent for adsorption of fluoride from aqueous solution. The adsorption process is monolayer type adsorption as suggested by the best fitting of isotherm study data to Langmuir isotherm model. The adsorption kinetics of fluoride adsorption on MLC surface followed the pseudo-second-order model. Maximum adsorption of fluoride ions on MLC was obtained at pH 3.0 and 318 K temperature. They also performed column adsorption experiments in a fixed bed reactor which was packed with MLC. The breakthrough time was increased with increase in amount of MLC was decreased with increase in the concentration of fluoride. On the other hand, with increase of fluoride concentration, the exhaustion time was decreased. Columns with large amounts of MLC and high flow rate increase the column performance. The adsorbent materials were recovered by pumping 0.2 M NaOH solution through the MLC loaded column. Olabemiwo et al. (2017) compared adsorption of cadmium from contaminated water on polyelectrolyte-coated fly ash (PEFA) and raw fly ash (RFA). They obtained up to 99 % removal of Cd by using PEFA as adsorbent while with RFA, only 27% removal was obtained under same experimental conditions. This clearly indicates the superiority of PEFA as adsorbent towards heavy metal removal from aqueous system over RFA.

FUTURE SCOPE OF STUDY

Fly ash based cenospheres and related products have potential applications as adsorbent materials towards the removals of a number of contaminants from water system. Cenospheres can be separated from the fly ash using simple, cost effective and environment friendly processes. Removal of contaminants from water using adsorption is also proven to be an effective process due to its simplicity and cost effectiveness. However, there is a tremendous need of study in recent future to develop processes for large scale generation of cenosphere with low cost and its use for adsorption of water pollutants released from industries, coal mines etc. before releasing into main stream.

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