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Micellar enhanced removal of ground water hardness by pseudoactivated carbon (PAC) prepared from wheat husk

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Abstract
The batch tests were conducted using four groundwater samples which showed high levels of total hardness such as 600, 800, 1088 and 1278. mg/l as $CaCO_3$, so water is not suitable for several industries. The present work aimed to evaluate the feasibility of using powdered pseudoactivated carbon (PAC) prepared from wheat husk for the removal of water hardness and also to study of impact of sodium dodecyl sulphate (SDS) micelles on the removal. The ability of 0.05, 0.1, 0.5, 1.0 and 5.0 g/l PAC to soften a ground water was investigated by shaking 50 l ml hard water with PAC at pH 5.0 and 25°C for 180 minutes. The effect of SDS was studied by running parallel tests with 10 ml of 3 g/l SDS solution. Equilibrium was attained within 120 min with PAC and 75 min with PAC + SDS. The maximum removal was found 27.8 % with 5 g/l PAC at pH 5, 250c for 600 mg/l hardness. With PAC + SDS the removal was enhanced to 81.1 % with 10 ml of 3 g/l SDS and 5 g/l of PAC for the same.

Keywords: Ground water, hardness removal, wheat husk, pseudoactivated carbon, micelles

Introduction

Hardness is the property of water which prevents lather formation with soap and increases its boiling point. It is caused by polyvalent metallic ions dissolved in water principally calcium (Ca^{2+}) and magnesium (Mg^{2+}), although other metals such as aluminium (Al^{3+}), barium (Ba^{2+}), iron (Fe^{3+}), manganese (Mn^{2+}), and strontium (Sr^{2+}) contribute to a lesser extent as they are present in small amounts. However, hardness is usually expressed in the terms of an equivalent concentration of $CaCO_3$ in ppm. Water can be categorized as soft, moderate, hard and very hard if its total hardness (TH) values that represent hardness due to all the ions present in it are <75, 75-150, 150-300 and >300 ppm as $CaCO_3$ respectively. Though moderate hardness has no known adverse effect on human health, TH higher than 300 ppm may cause heart and kidney diseases, and pain and stiffness in joints. According to the Central Pollution Control Board of India world health organization the desirable limit (DL) of TH for drinking water is 300 ppm and maximum permissible limit (PL) is 600 ppm. Hardness causes scaling of hot water pipes, boilers and other household and industrial appliances. Hard water consumes greater amounts of soaps during washing, bathing, cleaning and laundering. It may impart undesirable characteristics to the finished products in paper, beverage, dairy and allied industries. Limits on hardness for industrial uses are quite variable. For example, the maximum concentration mg/l as $CaCO_3$ for textile, shoe, pulp and paper, tannery, petroleum and metals are 120, 350, 475, 500, 900 and 1000 respectively. However, requirements for final use within a process may be essentially zero, which requires treatment for concentration reduction.

Agra city (latitude 27° 10' N and longitude 78° 5'E) popularly known as the Taj city, lies 200 km of south of Delhi and is situated on the right bank of the Yamuna river. It is 169 m above sea level and has population about 2 million. About 600 metric tons of non-segregated garbage is dumped in Shahdara landfill and 100 tons in Lohamandi, Shahganj and Bundu Katra landfills daily. It has about 200 hospitals and nursing homes, 169 foundries, 52 tanneries, 300 shoe industries, 200 marble industries, 60 dairies including milk collection centres, 900 petha industries, 60 electroplating units, 15 silver vibrators and 15 galvanizing units that contribute their own kinds of liquid wastes to enhance hardness of the Yamuna as well as groundwater.

Activated carbon (AC) has been widely used as effective adsorbent to remove aqueous contaminants, both organics such as hydroquinone and inorganics such as Cd(II), Pb(II), As(III & V), Hg (II), Co (II) and Cr(VI)[1-10]. Due to high cost it is not affordable for Indian industries to adopt this method and about 10-15% loss may be incurred during regeneration by thermal or chemical treatment. High cost of activated carbon and synthetic resins has prompted the search for cheap and non-conventional substitutes. Low cost pseudoactivated carbon (PAC) can be prepared from naturally occurring and easily available materials such as agricultural, commercial and industrial wastes. Some of such adsorbents have been widely investigated and possess remarkable adsorption capacity to abate heavy metals and organics from wastewater.

A number of studies [11-14] have investigated the enhanced removal of contaminants in the presence of surfactants. Two strategies for enhanced removal can be considered as: (1) pollutants bind up with the micelle formed by aggregation of surfactant monomers and (2) micelles adsorbed at intersurface of PAC. In other words, SDS molecules sorb onto the PAC with their anionic head groups exposed to the aqueous phase so that the PAC acts more like a cation exchange resin. Objectives of this study were to: (1) use of PAC prepared from an agro wastes for hardness removal, (2) investigate the impact of micelles on removal, (3) to elucidate interactions of PAC and surfactants with contaminants, (4) determine the suitable operating conditions to enhance removal in absence and presence of micelles.

Materials and Method

Wheat husk (WH), an easily available agro waste, was obtained from an agricultural area in Tehribagja, sun dried for 5 h and stored in plastic bags. It was crushed, washed thrice with distilled water and rinsed with 1% HCl to remove water soluble impurities particularly metal ions and surface adhered particles. Then it was kept in 0.1 N NaOH solution overnight to remove lignin and in 0.1N CH_3COOH to remove alkalinity developed due to NaOH. Thereafter it was washed well with distilled water till the wash water became colorless. Now it was dried at 110°C in an oven for 2 h to get rid of moisture and other volatile impurities. Pseudoactivated carbon (PAC) was prepared by keeping 4 parts of the above WH with 3 parts by weight of conc. H_2SO_4 in an air oven maintained at 150°C for 24 h. The carbonized WH was washed with distilled water to remove free acid (SO_4^{2-} ions). Then it was soaked in 1% w/v sodium carbonate solution overnight to remove any residual acid. Again, it was washed with distilled water and dried at 110°C for 2 h. The carbon so obtained was ground and sieved through a standard sieve to get the particle size less than 300 microns throughout the study. The composition of the PAC included 5.67 % moisture, 5.68% ash, 78.99% carbon content, 3.02% silica, 0.17% Na, 0.27% K, 0.41% Ca, 0.07% Mg, 0.06% P, 0.32% Fe and 5.34% miscellaneous components. Its pH, conductivity, specific gravity, bulk density, porosity, surface area and sodium exchange capacity were 7.8, 0.79 mS/m. 1.10 g/ml, 0.25 g/ml, 0.83 ml/g, 328.0 m^2/g and 0.53 meq/g respectively as determined by the standard methods.

Ground water sample (170) and Yamuna river water samples (65) were collected between August–September 2022 from 23 locations in Agra city. One-litre plastic bottles for sample collection were pre-cleaned by washing first with tap water, then with 50 % HNO_3 and finally thrice with distilled water. They were rinsed thrice with the sample water before collection. Groundwater samples were collected between 6 to 10 a.m. and the Yamuna river water between 6 to 8 a.m. TH was determined within 6 hours by using EDTA complex metric titration [15]. Then the samples were classified in the order of increasing hardness as A, B, C, D and E with hardness 100-250, 251–400, 401–550, 551–700, >701 mg/l respectively and results are shown in Table-1.

A surfactant like SDS has a characteristic cmc at which micelle formation occurs. The cmc value of SDS at 20°C is 8 mM or 2310 mg/l. SDS, from CDH, Delhi with about 98% purity was used without any further purification. The stock solution of 3 g/l SDS was prepared in distilled deionized water (DDW). A higher concentration than cmc, i.e., 3 g/l was taken in expectation that some surfactant losses due to sorption on PAC may not hamper micelle formation.

The interaction of SDS with contaminants and PAC was investigated in batch experiments using well characterized D and E types of surface water and groundwater samples collected from four locations in Agra city. The four such samples from St. John's College ground water, Nehru Nagar groundwater, Yamuna upstream near Grater Kailash and midstream near Water Works had TH levels 600, 800, 1088 and 1278 ppm respectively. 50 ml water sample was mixed with 1.0 ml of buffer solution (pH 5.0) and PAC dose range 0.05 to 5 g/l. The solution was continuously agitated at 120 rounds per minute (rpm) for 3 hours, followed by centrifugation at 500 rpm for 10 minutes. The supernatant was collected and immediately analyzed for TH. Parallel experiments to above in the presence of 10 ml of 3g/l SDS solution were also carried out. The supernatant was filtered through a 0.45-µm-membrane filter and TH was determined. The percentage of hardness removal was calculated using the difference between initial and final degrees of TH. The impact of pH on water softening was estimated by varying the pH from 1 to 10 using 0.1 M HCl and NaOH solutions.

Table 1: Water quality of Agra city in terms of hardness

Area	No. of samples	Average hardness	Standard deviation	Type*
Groundwater				
Left bank of Yamuna				
(a) Rambagh	10	485.50	29.60	C
(b) TransYamuna	10	499.17	23.90	C
Right bank of Yamuna				
(c) Water Works	10	342.00	50.69	B
(d) Balkeshwar	10	638.75	42.18	D
(e) Jeoni Mandi	5	500.00	36.00	C
(f) Belanganj	10	347.50	23.58	B
(g) Daresi	15	320.00	42.45	B
(h) Agra Fort	10	457.50	26.17	C
(i) Taj Ganj	18	467.78	34.22	C
Along with M.G. Road				
(j) Nehru Nagar	5	613.33	25.77	D
(k) Dayal Bagh	10	490.00	26.93	C
(l) Sanjay Place	10	603.00	33.09	D
(m) St. John’s	5	596.67	29.26	D
(n) B.M. Khan	5	590.00	9.80	D
(o) Raja Ki Mandi	5	546.66	22.44	C
(p) Gokulpura	5	477.50	23.66	C
Miscellaneous				
(q) Shahganj	12	473.00	29.78	C
(r) Jaipur House	5	330.00	19.60	B
(s) Sadar	10	476.25	26.53	C

Yamuna water				
(a) Near drain discharg.	20	1606.25	169.49	E
(b) Away drain discharg.	20	1268.57	86.98	E
(c) Near upstream	10	988.41	52.32	E
(d) Near downstream	15	1206.25	99.87	E

*Type indicates A for 100-250, B for 251-400, C for 401-550, D for 551-700, E for >700 mg/l of hardness.

Results and Discussion

Contact time and Hardness Effects

The effect of initial hardness and contact time on the sorbed amount is shown in Figure- 1 (a) and (b). Sorption capacity is found to increase with decrease in hardness or concentration of metal cations causing hardness. The number of cations adsorbed was calculated from the difference between initial H_0 and final hardness Ht at any time t. However, an equilibrium was attained within 2.0 hours with 1 g/l PAC and 1.25 hours with PAC+ SDS, which was irrespective of initial hardness. Sorption rate is very rapid during initial period of contact and about 85% of sorption reached within first 40 minutes with PAC and within 30 minutes with PAC+SDS. The rapid uptake of hardness is a great advantage for its application in continuous flow process.

Sorbent dose Effects

The study of hardness captures as a function of sorbent dose is important in establishing the optimum use of sorbent for any sorption process. The curves in Figure- 2 shows that increasing the sorbent dose from 0.01 to 5.0 g/l increased the uptake from 0.91 to 22.51% with PAC and 8.75 to 70.21% with PAC+SDS. It can be explained from the fact that on increasing sorbent dose availability of binding sites on sorbent surface increases to a greater extent.

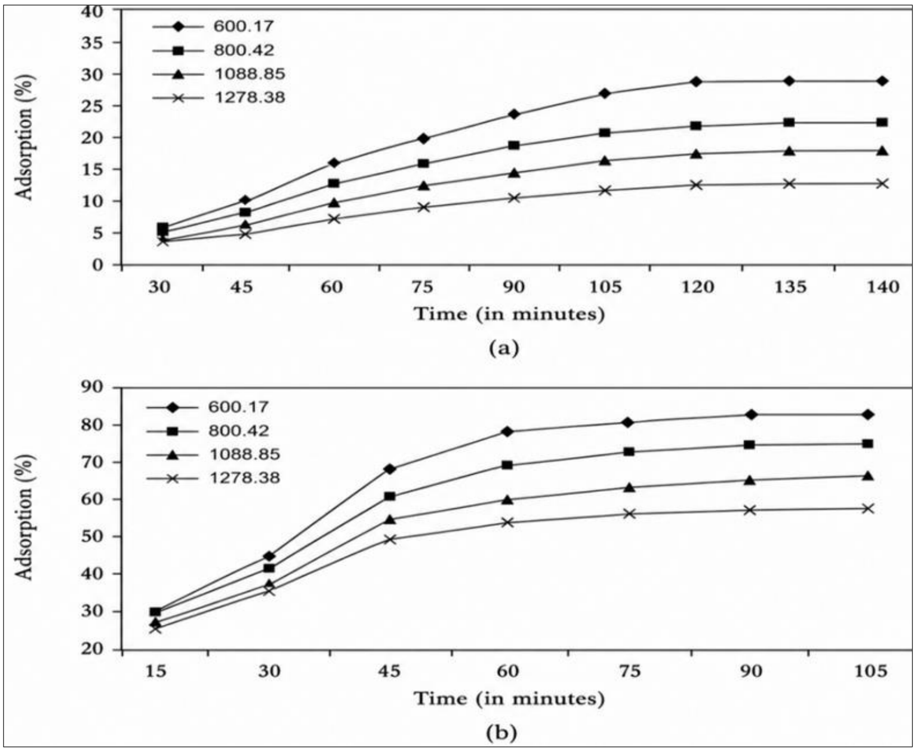

Fig 1: Water softening efficiency at different concentrations with time (a) in absence of micelle, and (b) in presence of micelle at pH 5 and 25°C

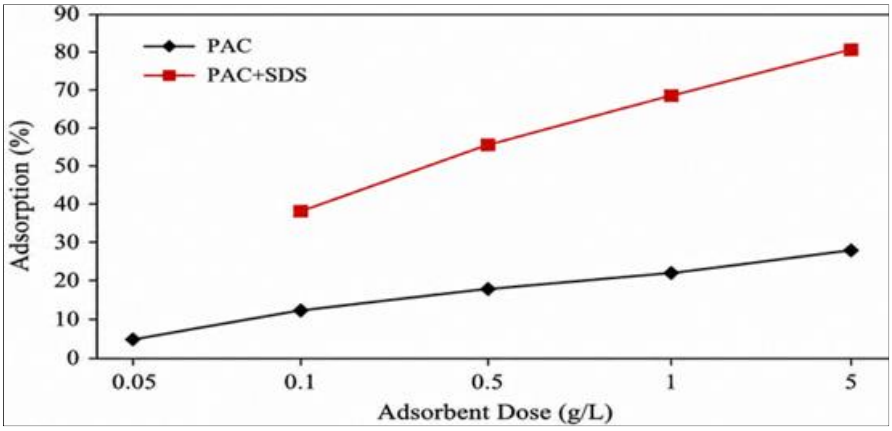

Fig 2: Effect of PAC dose on hardness (600 mg/l) in presence and absence of micellar (3 g/l SDS solution) media at pH 5 and 25°C

Conclusion

The removals of total hardness from the different sources of water in Agra city (India) by Pseudoactivated carbon (PAC) and micellar solution were investigated as a potential remediation method for contaminated aquifers. Batch experiments were used to elucidate potential benefits and effects of agitation time, sorbent dose and hardness on hardness removal using Pseudoactivated carbon (PAC) in presence and absence of micellar solution. The extent of hardness removal on PAC increases with decreasing hardness. The maximum water softening by Pseudoactivated carbon (PAC) in the absence of micelle was 27.81% in batch studies for 600 mg/l hard water. The removal with micellar solution was 81.1 %. Equilibrium was attained within 2.00 hours with PAC and 1.25 hours with PAC + SDS. The maximum removal was found 27.8 % with 5 g/l PAC at pH 5, 25°C for 600 mg/l hardness. With PAC + SDS the removal was enhanced to 81.1 % with 10 ml of 3 g/l SDS and 5 g/l of PAC for the same. The present paper shows the possibility of using agrowastes particularly wheat husk abundantly available in our country to produce cheaper activated carbons. The data thus generated may be used for designing treatment plants for industrial effluents having low levels of heavy metals and hold a promise for commercial exploitation.

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