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Modeling of the adsorptive removal of arsenic: A statistical approach

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ABSTRACT

Arsenic in drinking water has been recognized as a serious community health problem because of its toxic nature and therefore, its removal is highly essential. A series of adsorption experiments (batch and column) were performed utilizing iron impregnated sugarcane carbon (Fe–SCC), a composite adsorbent, to remove arsenic from aqueous systems. Under optimized batch conditions, the Fe–SCC could remove up to 94.5% of arsenic from contaminated water. The artificial neural network (ANN) model was developed from batch experimental data sets which provided reasonable predictive performance ($R^2 = 0.964$; 0.963) of arsenic adsorption. In batch operation, the adsorbent dose had the most significant impact on the adsorption process. For column operation, central composite design (CCD) in response surface methodology (RSM) was applied to investigate the influence on the breakthrough time for optimization and evaluation of interacting effects of different operating variables. The perturbation plot depicted that the breakthrough time is more sensitive to initial concentration and adsorbent dose than flow rate. The optimized result obtained from bar plot revealed that the Fe–SCC was an effective and economically feasible adsorbent; whereas more than 93% desorption efficiency showed the reusability of the adsorbent. The high arsenic adsorptive removal ability and regeneration efficiency of this adsorbent suggest its applicability in industrial/household systems and data generated would help in further upscaling of the adsorption process.

Introduction

Arsenic's history in applied science has been overshadowed by its notoriety, and the drinking water containing arsenic is a challenging environmental issue [1–5]. Exposure to arsenic through drinking water sourced from groundwater has emerged as a major concern on a global scale [1,2,6]. Groundwater enriched with arsenic in the form of arsenate [As(V)] and arsenite [As(III)] poses a serious health hazards in several developing countries [2,7,8]. As high as, the WHO provisional guideline of 10 μg/L of arsenic in drinking water is now recognized as a worldwide problem in many countries, especially in the Southeast Asia, including India, Bangladesh, and China [1]. A largest segment of population currently is at risk in the Bengal Basin area of Bangladesh and West Bengal in India [9,10]; however, it is remarkable that these two countries have retained the earlier WHO guideline of 50 μg/L as their standard of arsenic in drinking water [11,12]. About 70 million people are suffering from arsenic problem alone in these regions; this is perhaps the largest poisoning in world's history [13,14]. Today, in West Bengal, the arsenic contamination in groundwater, and eventually in drinking water, has been reported in the range from 50 to 3600 μg/L and the arsenic species in contaminated drinking water were found to be arsenate and arsenite in 1:1 ratio [8,15].

Development of effective technologies to remove arsenic from water drew great attention over the last two decades. Several physiochemical techniques, such as adsorption, ion exchange, lime softening, membrane filtration, coagulation and precipitation have been applied to remove arsenic from aqueous system. Among these, adsorption technology is mainly used because it is very simple and cost effective [7,8,16–18]. Besides, it is also popular due to availability of a wide range of adsorbents.

Among all types of conventional and non-conventional adsorbents, commercially available activated carbon has been extensively used for arsenic removal because of its extended surface area, micro/mesoporous structure and significant adsorption capacity. However, owing to the high cost and difficult procurement of activated carbon, efforts are being directed to develop cheaper but effective adsorbents from a variety of agricultural/industrial waste materials [2,7,8,19]. Considering the surface carbon chemistry, only physically active char carbon prepared from these agricultural/industrial waste materials is likely to provide good substitute for activated carbon. Carbonized sugarcane bagasse, i.e., sugarcane carbon (SCC) is an alternative

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Abbreviations: Fe–SCC, iron impregnated sugarcane carbon; ANN, artificial neural network; ANOVA, analysis of variance; CCD, central composite design; D–R, Dubinin–Radushkevich; RSM, response surface methodology; SDDC, silver diethyl dithiocarbamate; SEM, scanning electron microscopy; 2FI, two factor interactions.

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adsorbent to fulfill such a purpose. Only a few studies on SCC, as an adsorbent, have been conducted [16,19] and no research has been reported on the modified SCC that may have higher arsenic removal efficiency.

Thus, the purpose of this study is to develop a modified SCC, by impregnated with iron (Fe–SCC), and to investigate the application of Fe–SCC for the removal of arsenic from aqueous system. The present study deals with a series of adsorption experiments (batch and column) to assess the potentiality of Fe–SCC for removal of arsenic from contaminated water. For sensitivity analysis and optimization abilities, the adsorption experiments have been statistically modeled using artificial neural network (ANN) and central composite design (CCD). The models have also been applied to study the individuals as well as the combined effect of different variables influencing the adsorption process. In addition adsorption–desorption studies were carried out in order to regenerate and reuse the adsorbent. As a whole a complete study for the economic, easy and eco-friendly solution of catastrophic arsenic pollution has been done, that can be implemented in the developing countries. Results obtained from this study are presented and discussed.

Materials and methods

Reagents and apparatus

Chemicals of AR grade were procured from M/S, Merck India Ltd., and used as such. All reagents and standards were prepared using double distilled water. Sodium arsenate hydrate ($Na_2HAsO_4 \cdot 7H_2O$) and sodium arsenite ($NaAsO_2$) were used for the preparation of As(V) and As(III) solutions, respectively. The required arsenic concentrations to perform the whole experiments were prepared by mixing the As(V) and As(III) solutions in 1:1 ratio. The pH of arsenic solution was adjusted by the addition of 0.1 M HCl and NaOH solutions whenever necessary. All glassware were cleaned by being soaked in 15% HNO_3 and rinsed with double distilled water before use.

Instruments and software

The shaking in batch experiments was conducted in a temperature controlled magnetic stirrer (Spinot, Cat No. 6030). A UV–visible spectrophotometer (Systronics, Vis double beam Spectro 1203) with a 1-cm quartz cell was used for quantitative determination of arsenic in solution. pH was measured by a digital pH meter (Eutech, pH 700 Meter) with an accuracy of ±0.01 unit. A high precision electrical balance (Denver, SI-234) was used for weighing. A peristaltic pump (Mrclab, Model No. PP-X-10) was used for providing constant arsenic solution of fixed-bed column. An adsorbent muffle furnace (PTC1, Paragon made) was used for preparing SCC. Surface morphology of the adsorbent was studied by a Hitachi, S-530 (Make: Eiko Engineering, Ltd., Japan) scanning electron microscope.

SPSS-17 and Design-Expert (7.0.3) software were used for the data analysis and fitting the values in various models.

Adsorbent preparation and characterization

Sugarcane carbon (SCC) was first prepared by the carbonization of raw sugarcane bagasse that was collected from a sugarcane juice stalls in the premises of Golapbug campus of Burdwan University, Burdwan, West Bengal, India. The carbonization by a physical activation method of sugarcane bagasse was done following the method of Amin [19].

The SCC with a monoparticle size of 250 μm was first rinsed with double distilled water to remove dirties, and then washed by 0.001 M HCl solution to remove all salts precipitated in its pores. Then, the SCC was repeatedly washed with the double distilled water to remove all traces of the acid. Subsequently, the washed SCC was oven-dried at 85 °C for 24 h to volatilize the organic impurities, and activated by 1.0 M HNO_3 for 5 h at the room temperature.

Table 1
Physical properties of SCC and Fe–SCC.

Parameters	Unit	SCC	Fe–SCC
BET-surface area	m^2/g	856	803
pH_{ZPC}		5.68	7.56
Ash content	wt%	10.8	8.1
Iodine no.	mg/g	927	788
Fe-content	% (w/w)	0.43	8.4
Pore volume	cm^3/g	0.82	0.63

For the preparation of iron impregnated sugarcane carbon (Fe–SCC), a mixture of $FeCl_3/FeSO_4$ (molar ratio 2:1) and 5 mol NaOH was kept at 70 °C and pH 9.5 for 10 min with the gentle stirring of 60 rpm, and then the solution was impregnated into the activated SCC. The obtained materials were dried in an oven at 100 °C for 3 h. Finally, the dried Fe–SCC was stored in a vacuum desiccator for future use [20].

The physical properties (i.e., pH_{ZPC}, surface area, iodine no., etc.) of the virgin SCC and the Fe–SCC determined by standard procedures [8,16,18,20], are shown in Table 1.

Analytical determination

Estimation of arsenic was done spectrophotometrically by silver diethyl dithiocarbamate (SDDC) method [8,12,15,21,22] with minimum detectable amount of 1 μg [21]. Each sample was analyzed thrice and the results were found reproducible within ±3% error limit. Calibration was carried out daily with a freshly prepared arsenic standard, before analysis. Experiment done with control adsorbent indicated no release of arsenic by the adsorbent. Blank experiments were also conducted to ensure that no adsorption was taking place on the walls of the apparatus used.

Experimental setup

In the batch adsorption experiments, the effect of different parameters (i.e., pH, contact time, initial arsenic concentration, dose of adsorbent, agitation speed and temperature) on adsorption of arsenic was studied. The 100 mL solution of arsenic was taken in each Erlenmeyer flask of volume 250 mL separately. After pH adjustment, a known quantity of dried Fe–SCC adsorbent was added and the arsenic bearing suspensions was kept under magnetic stirring until the equilibrium was reached. After stirring, the suspension was allowed to settle down and filtered using Whatman-42 grade. The filtrate was collected and subjected for arsenic estimation following SDDC method. The arsenic concentrations before and after adsorption were recorded, and then the percent value for arsenic adsorption (removal) by the adsorbent was computed by using the following equation:

$$\text{percent adsorption (removal)} = \left[\frac{C_i - C_e}{C_i}\right] \times 100 \tag{1}$$

where C_i and C_e are the initial and final arsenic concentration in the solution.

The arsenic uptake loading capacity (q_e = μg/g) of Fe–SCC for different concentrations of arsenic at equilibrium was also determined as

$$q_e = \left(\frac{C_i - C_e}{M}\right) \times V \tag{2}$$