STUDIES ON ADSORBENTS FOR PERCHLORATE REMOVAL FROM WATER

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by

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ABSTRACT

Perchlorate is widely used as an oxidizer in solid rocket propellants, explosives, and missiles. It is also in various commercial products like air bag inflators, matches, safety flares, fireworks, and pharmaceuticals. It has been detected in public drinking water systems, foods, natural waters, and humans themselves in trace amounts. Perchlorate presence in water is of increasing concern because of its toxicity. It inhibits the iodine uptake by the thyroid gland, affecting/altering the production of thyroid hormones and subsequently causing malfunction of the metabolic processes resulting in neurological damage, and anemia. Since its health effects, USEPA set an interim health advisory level of perchlorate at 15 $\mu g.L^{-1}$ in 2009 and has declared a decision to regulate perchlorate under the Safe Drinking Water Act in 2011 (US Environmental Protection Agency 2011). Due to its characteristics of high mobility, high stability, non-volatility, and non-reactive nature, perchlorate is commonly viewed as a persistent water pollutant, and hence effective removal of perchlorate from water is very important. Several methods are applied for perchlorate treatment such as adsorption, ion exchange, membrane technology, bioremediation, chemical treatment methods including catalytical and photocatalytic reduction, and electrochemical techniques. Compared with other treatment technologies, the adsorption process is attractive due to its advantages of high treatment efficiency, easy operation, and low cost. A series of adsorbents have been investigated for the removal of perchlorate.

N-doped activated carbon with a hierarchical pore structure having very high perchlorate adsorption capacity is synthesized from polypyrrole using Pluronic 123 as a template followed by KOH activation. The synthesized porous carbon samples are characterized by FTIR, Raman, XRD, SEM, and surface area analysis. The N_2 adsorption-desorption isotherm of the N-doped activated carbon shows a combination of micro and mesopores, with a high BET surface area of 1720 $m^2.g^{-1}$ and a total pore volume of 0.869 $cm^3.g^{-1}$. Systematic batch experiment studies are

conducted to understand the effect of pH, contact time, and other interfering anions on the perchlorate adsorption. The equilibrium adsorption data are well described by the Non-linear Freundlich adsorption model. The adsorption kinetic data is fitted by the pseudo-first-order model with R^2 >0.99. The adsorption mechanism is established as an electrostatic interaction of positively charged N-doped carbon with perchlorate ions. The spent adsorbent could be regenerated by treatment with 2 M NaCl solution and the regenerated adsorbent retains the perchlorate adsorption capacity of the virgin sample over a large number of adsorption-desorption cycles. The maximum adsorption capacity of 587 $mg.g^{-1}$ is obtained for polypyrrole-based N-doped activated carbon prepared in the presence of the pore template and KOH activated at 650

A novel and green method is followed for the synthesis of highly mesoporous nano-hydroxyapatite (nHA) and its magnetic composite aerogels (SPIONS@nHA) utilizing wasted 'eggshells'. The perchlorate removal efficiency of the materials is investigated and the factors that influence the perchlorate adsorption capacity are explored and optimized. The magnetic composite of nHA shows an excellent separation in the presence of an external magnetic field from contaminated water after adsorption. Very fast removal kinetics is observed and the experimental maximum adsorption capacity for nHA and SPIONS@nHA are 148.4 and 305.8 $mg.g^{-1}$, respectively. Other commonly existing ions exhibited no remarkable effect on the adsorption performance, and the adsorption process is found to follow pseudo-second-order and intra-particle diffusion kinetic models. The regeneration performance of spent magnetic adsorbent shows greater than 90% recovery on the adsorption capacity even after the fifth adsorption-desorption cycle, revealing the stability, reusability, and economic efficiency of the adsorbent. XPS analysis and zeta potential measurements show that the main driving force behind the adsorption of perchlorate is ion exchange and ion-pair formation/electrostatic interaction.

A green preparation process is espoused for the conversion of the biowaste-watermelon rind into super hydrophilic hierarchical porous carbon by a self-activation strategy, without involving any activating agents, templates, and corrosive chemicals. A simple, but highly proficient synthetic procedure: freeze-drying followed by pyrolysis is preferred for the synthesis of the hierarchical porous carbon (WRPC-X), X-stands for carbonization temperature. The hetero elements naturally present in the biowaste act as an in-situ activating agent during carbonization. The perchlorate adsorption capacity of the materials is explored for the first time and the factors that influence the perchlorate adsorption capacity were investigated and optimized. The resultant porous carbons show a comparatively high surface area, large pore volume, and a desired pore size distribution, which facilitate good perchlorate adsorption. The effect of functionalization (N-doping and magnetic functionalization) on the perchlorate removal efficiency is also studied in detail. The magnetic functionalization could provide additional active sites to enhance the interaction of WRPC-Mag with the perchlorate and increase the adsorption capability. The synthesized materials: WRPC-600, WRPC-N2, and WRPC-Mag show a perchlorate adsorption efficiency of 787 $mg.g^{-1}$, 1008 $mg.g^{-1,}$ and 1496 $mg.g^{-1}$ respectively, which are the highest values reported to date. Magnetic functionalization offers excellent separation of the spent adsorbent from contaminated water after adsorption in the presence of an external magnetic field. The super hydrophilic nature of the porous carbons proffered a very good surface wettability and better adsorbate-adsorbent interaction. Zeta potential measurements and XPS analysis show that the main driving force behind the adsorption of perchlorate is electrostatic interaction. The regeneration performance of the three spent adsorbents proved greater than 92% recovery on the perchlorate adsorption capacity even after the fifth cycle, revealing the high stability, reusability, and economic effectiveness of the adsorbents.

A series of zeolitic imidazolate frameworks (ZIFs) are synthesized at room temperature and thoroughly characterized. The perchlorate removal efficiency of the materials is investigated and the factors affecting the perchlorate adsorption

capacity are explored and optimized. Among the different ZIF materials, ZIF-L shows the highest adsorption capacity towards perchlorate followed by ZIF-8, ZIF-67, ZIF-7, and ZIF-11. Water contact angle measurements, XPS analysis, and zeta potential measurements are conducted to establish the adsorption mechanism of perchlorate onto ZIF-L. Comparatively faster removal kinetics was exhibited by ZIF-L compared to other adsorbents. The maximum adsorption capacity exhibited by ZIF-L of 1636 $mg.g^{-1}$ at pH 5 at room temperature, which is higher than that of other reported metal-organic frameworks towards perchlorate. The higher correlation coefficient for the pseudo-second-order kinetic model implied that the rate-limiting step of perchlorate adsorption by ZIF-L is chemisorption. The adsorption mechanism can be explained by a two-step process. The first step is the protonation of nitrogen groups in the imidazolium ring in acidic pH, followed by electrostatic interaction between the protonated nitrogen atoms and negatively charged perchlorate anions. Perchlorate-loaded adsorbent can be easily regenerated at room temperature and ZIF-L preserves more than 88% of its initial adsorption capacity during five consecutive adsorption-desorption cycles revealing the stability, reusability, and economic efficiency of the adsorbent.

The findings of the present study are expected to append innovative acquaintance in the field of sustainable, renewable, inexpensive, and proficient adsorption technologies for the removal of perchlorate ions from water.